Molecular Dynamics simulations of reactive and diffusive processes in different zeolite structures
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Chapter 1

Introduction

The effect of the confinement of the species sorbed in the interior of zeolite micropores, characterized by "molecular" dimensions, is a fascinating and extremely complex issue. The applications of these systems in various fields of chemistry, as separation and catalysis, can barely be rationalized on the basis of simple steric, thermodynamic or kinetic considerations. Indeed, the efficiency of a zeolite structure in favoring a given process often stems from a complicated balance between various effects, each one showing unusual (and not easily predictable) features. For example, the different speed characterizing the motion of molecules with different shapes and dimensions is crucial both in catalytic and separation processes, because it controls the approach of each species to the active sites, where they can be sorbed and/or transformed. However it is very difficult to obtain a general rule which, on the basis of structural and dynamic properties of the zeolite and guest species, allows to predict the behavior of the system in given experimental conditions. The study of diffusion in the cavities is definitely one of the main problems in this research field. The improvements of experimental methods and the big, continuous growth in the available computing power allowed a better interpretation of experimental data and also highlighted new phenomena deserving further studies, as the correlation effects. In particular, there is an evident need for theoretical models allowing to schematically capture the main features of the diffusive motion in the cavities: with this purpose we will show a new statistical model that extends and improves the random-walk model for the molecular diffusion in the channel system of silicalite. The basic idea of the new model is to describe the molecular propagation as a sequence of pairs of displacements between intersection sites, instead of a series of single uncorrelated jumps as in the random-walk model. This improves the description of the molecular motion, because it avoids the random-walk assumption that the directions of two subsequent jumps are independent, which, as we will show, is often incorrect. The analysis of the Molecular Dynamics trajectory gives the probabilities and mean times for each possible pair of jumps; these data could be employed in upcoming kinetic Monte Carlo simulations, which have recently been adapted to the study of diffusive processes in zeolites occurring on very long time scales.

Albeit the diffusion to and from active sites is a key step also in reactive processes, additional effects as well have considerable influence on the catalytic activity of a zeolite structure. Actually the detailed knowledge of even simple reactive processes is still far from the level reached in the study of diffusion, due to the greater experimental and
theoretical difficulties inherent to the analysis of reactive systems imbedded in such a complex “solvents”. Even with the large computing resources today available, dynamical \textit{ab initio} simulations are out of reach, especially for space and time scales large enough to include the main phenomena characterizing the reactive event. Nevertheless, working with suitable empirical force fields, one can carry out classical Molecular Dynamics simulations that allow to illuminate accurately the action of different zeolite structures over simple reactive processes. The main purpose is to understand if and how a particular zeolite structure can favor a reaction, by comparing the rate and the probability with which the process occurs in different structures. Indeed we believe that the main effects highlighted in this way have general validity and could be extended also to more complex reactive processes. We have previously shown that the model we use to represent the zeolite lattice adequately reproduces the energy exchanges with the sorbed molecules. The thermal effect of the zeolitic environment over the internal and external modes of the sorbed reactive species is one of the key elements of the catalytic action, both in the reactants activation and in the excited products stabilization. Using a potential able to adequately represent such effect, we can simulate, with the above-mentioned purposes, simple reactive processes, as halogen dissociation–recombination reactions and the transfer of a light particle between two heavier species. The first ones are representative of reactions not requiring thermal activation, like many radical reactions, while the second ones have been chosen as a prototype of activated processes, with a low energy barrier. These two kinds of reactions have been examined in two common zeolites, showing deep structural differences, so as to enclose a wide enough range of properties and effects of zeolitic systems. The comparison with the data obtained in a liquid inert solvent allows to further illuminate the peculiarities of zeolite “solid solvents”. Note that in the most part of reactions catalyzed by zeolites the active sites (usually hydroxyl protons) are directly involved in the chemical process. In this thesis we do not address such step, but we are interested in the general action of the zeolite which drives the reactive process over rather large time and space scales. The results of this kind of study are not limited to a better understanding of the mechanism of catalytic processes in which the zeolite is used as an inert substrate, offering to the reactive system a reaction path often different from that experienced in solution. Indeed, it is plausible that the energetic and structural effects that a zeolite shows in such situation may persist also when the same structure possesses acid sites directly involved in the reaction. Since in this case it is very difficult to account for the multifarious effects simultaneously present, accurate information may be gained by putting together separate results of long-range simulations, having general, explorative character, with detailed dynamical studies of the active sites, over much shorter scales. Various research groups work today on studies of the second kind, obtaining interesting data, yet affected by the vast computing resources required. We concentrated on more general simulations, relying on the fact that the obtained results may be a valid support to the other studies in the understanding of the overall activity of zeolites.
Chapter 2

Zeolites: structure and properties

The term “zeolite” comes from the Greek ζεύλα-boil and λιθίσ-stone, due to the fact that on heating the first minerals of such class (as many zeolites do) lose copious amounts of steam. This fact alone might partially explain the large applicability of zeolites in material science. The zeolite crystals contain water, and as the water is driven off by heating, there is no noticeable collapse of its framework structure. This leads to a highly crystalline, microporous adsorbent with an internal structure which can be easily tailored to adsorb any number of different species. Zeolites\(^1,2\) are microporous aluminosilicates of synthetic or natural origin. They have crystal structures that are constructed from TO\(_4\) tetrahedra (where T stands for Si or Al at the tetrahedron center), each apical oxygen atom of which is shared with an adjacent tetrahedron. Thus the metal (Si plus Al) to oxygen ratio is 2; the Si:Al ratio may change, but it is always > 1. The individual TO\(_4\) tetrahedra in the zeolite structures are generally close to regular, but the shared oxygen linkage can accommodate a wide range of T-O-T bond angles from \(\sim 125^\circ\) to \(\sim 180^\circ\). The tetrahedra can therefore be combined in various ways to form a variety of different structures. The main feature of these structures is the microporosity, i.e. the presence of internal voids that in different zeolites vary in shape, size and dimensionality; however the effective pore size is always of the same order of molecular diameter. The strict regularity of the crystalline lattice, with microporosity that is an intrinsic characteristic of the structure, distinguishes zeolites from other microporous materials such as silica gel and carbon molecular sieves, allowing high selectivities to be achieved in both catalysis and sorption processes. Further, in marked contrast to most other catalytic systems in which activity is restricted to external surfaces, in zeolites all atoms comprising the extended three-dimensional structure are within a few angstroms of the internal surface and can influence or contribute to processes occurring there. It may be estimated that more than some 98% of the total surface area is internal.

Compositionally, we can write a general formula for the aluminosilicate zeolites as:

\[
M^{m+}_{x/m} [Si_{1-x}Al_xO_2] \cdot nH_2O
\]

where \(M^{m+}\) represents a metallic ion. The aluminosilicate framework takes in a negative charge for each aluminum atom present in T-positions. A corresponding number of extraframework cations (metals, protons or organic cations) is required for charge compensation. A zeolite's chemical characteristics depends on the framework compos-
ition: higher Si:Al ratios lead to hydrophobic properties and higher affinity for organic molecules, compared to zeolites with higher aluminum contents, which determine hydrophilic sorptive characteristics. The Si:Al ratio and the zeolite composition depend on the synthesis conditions and can be still adjusted by post-synthesis modification. Thus a zeolite is usually classified rather with its framework structure than with its chemical composition. In every structure it is possible to observe the organization of the basic tetrahedral units into larger secondary units, as rings, fused rings or more complex groups, whose interconnection gives rise to the three-dimensional zeolite structure. Two common secondary units are the sodalite and the pentasilic units, depicted in Fig. 2.1.

![Fig. 2.1: (left): sodalite unit; (right): pentasil unit](image)

The aperture dimensions which control entry to the internal pore volume are determined primarily by the number of T-atoms and bridging oxygens in the rings defining them. Effective aperture sizes range from ~4 Å for 8-ring structures (such as those of LTA-type zeolites), through ~5.5 Å for 10-rings (MFI zeolites), to ~7.4 Å for 1-ring (FAU zeolites). The fundamental feature is the strictly defined, very narrow distribution of pore sizes in each zeolite, contrasting to the broad distributions shown by other porous materials such as alumina and silica gel. This makes sure that only molecules of a certain size or smaller can penetrate within a specific zeolite and adsorb there. Moreover, the pore size of a zeolite can be fine-tuned replacing by ionic exchange the extraframework cations: they are usually located near the pore apertures, and tend to partially block them. For instance, the mean free aperture dimension of NaA zeolite, which is about 4 Å, is reduced to about 3 Å when the Na$^+$ ion is exchanged with the larger potassium cation, while the partial exchange with Ca$^{2+}$ ions removes Na$^+$ cations from the blocking sites, permitting the full aperture size of 5 Å to be realized.

### 2.1 Applications

#### 2.1.1 Ionic exchange

The cations located in the cavities can be partially or completely exchanged with other cations through ionic exchange; the process is usually very fast. The ionic ex-
change properties of zeolites are exploited mainly to modify the properties of a structure, as seen before for zeolites A. They are also widely used in low phosphate detergents, where they exchange Ca$^{2+}$ and Mg$^{2+}$ ions out of the washing water. Subsequently, under neutral or mildly acidic conditions in the environment the zeolite dissolves to form relatively benign silicate or aluminate species. Another application is in the radioactive wastewater treatment. In this field, natural and relatively low cost clinoptilolite and mordenite zeolites are utilized for extracting radioactive cesium and strontium isotopes from contaminated water. One exploits the high stability of zeolites to high doses of radiations and their selectivity, which allows to trap isotopes present at very low concentrations in presence of other harmless, more concentrated ions such as Na$^+$. 

2.1.2 Separation

Zeolites have been given the term “molecular sieves” because of their ability to discriminate between molecules on the basis of their shape and dimensions. This property is exploited in separation as well as in catalytic processes. Zeolite NaA can adsorb H$_2$O, CO$_2$ and NH$_3$ and has been used for removing CO$_2$ from natural gas; zeolite KA admits water and ammonia, but larger molecules such as alcohols or alkanes are “sieved out”, so that it is used for intensive drying of gas streams. The CaA zeolite can adsorb n-alkanes, but excludes branched isomers, opening the way to its commercial use for extracting n-alkanes (precursors to detergents) from various hydrocarbons streams. These three systems show the potentiality of fine-tuning and optimizing a zeolite structure for a specific application. Another kind of separation exploit the differing affinities for differing molecules that can all enter into the zeolite. The different affinity leads to different equilibrium compositions of the sorbed and contacting phases. The high electric field gradient present in low Si:Al ratio zeolites leads to the fact that nitrogen is sorbed more strongly than oxygen, because of its high quadrupole moment. Therefore the zeolite in contact with air will leave a gas enriched in oxygen. The selectivity of zeolites is also exploited in a chromatographic type separation: the mixture is introduced into a column of the zeolite sorbent and the first component to emerge is the least strongly sorbed one. This allows the separation of mixtures of Cs aromatic isomers.$^3$

2.1.3 Catalysis

Catalysis is the main application of zeolites. From a commercial point of view a high selectivity is usually more appreciated than a high catalytic activity. A common characteristic of many catalysts is that they can differentiate between chemical classes of compounds but not between specific molecular structures. For example, a catalyst capable of hydrogenating an olefinic bond will operate on a double bond in nearly any structure (with the exception of a few cases of very severely shielded positions). This stands in marked contrast to the enzyme catalysts that discriminate between molecules possessing very slight structural differences. However, some of the zeolites have made it possible to create catalyst systems of high structural selectivity. Compared to other heterogeneous catalysts, zeolites show unusual kinds of selectivity, often associated
with higher thermal stability. In contrast to solid catalysts in which reactions occur at the surface without particular steric constraints, in a zeolite the reactive process occurs within the pores, with all the steric constraints due to the geometry of the cavities. Brønsted acid mechanisms are most important in zeolite catalysis, as bridging hydroxyl groups (Si-OH-Al) are the commonest type of acid sites. They may be considered as protonated oxygens, the protons being present to compensate the negative charge introduced by aluminum. The catalytic process conventionally involves a step in which the acidic hydroxyl group protonates insaturated organic molecules, or basic groups such as OH or NH₂. The fate of the protonated species strongly depends on other acid-base properties of the zeolite, including Lewis acidity and basicity of the framework oxygens. In other catalytic processes zeolites are utilized as polyfunctional catalysts (where hydrogenation/dehydrogenation functions such as Pt, Pd transition metals are introduced in addiction to the acid sites), oxidation catalysts (with Cu²⁺ or Fe³⁺ ions⁴ or with titanium or other atoms incorporated in framework T-positions⁵), basic catalysts, and finally as inert substrates where one exploits their selectivity, without any more direct chemical involvement.

The main catalytic application of zeolites is in petroleum refinery: catalytic cracking (conversion of residues of petroleum into low molecular weight olefins and gasolines through Y-type zeolites), selectoforming (ZSM-5 is used to increase the octane number of gasoline by transforming linear paraffins in olefinic gas), hydroisomerization (Pt-mordenite and Pt-ZSM-5 zeolites are used to transform linear paraffins to branched isomers; Pt has the role of transforming the paraffins into olefins that the acid sites rearrange into isomers). In the fuel production the methanol to gasoline (MTG) process⁶ with H-ZSM-5 is the most known reaction. In environmental catalysis the nitrogen oxides NOₓ present in gas emissions are reduced to N₂ with hydrocarbons in Cu exchanged mordenite and ZSM-5 in the presence of molecular oxygen.⁷

The previous classification refers to the basic reaction mechanism; another fundamental point concerns the way in which products are controlled by the geometry of the zeolite structure. In a schematic representation of the catalytic event the reactants enter the pores of the zeolite and move constrained by the force field of the pore system. Then they may be sorbed at an active site and eventually converted to products that finally are desorbed and transported away from active sites. Each of these steps is strongly influenced by the composition and constitution of the framework structure and also by the geometric properties of the void space that make up the porous volume within the crystal. This property, that is the ability to control the chemical processes on the basis of geometric constraints alone, is known as shape-selectivity; three types of shape selectivity have been evidenced, as schematically shown in Fig. 2.2.

- Reactants shape selectivity: in a mixture, certain molecules that are too big to enter in the pores cannot reach the active sites located within the cavities and cannot react, as in the cracking of linear paraffins from a mixture with branched alkanes (Fig. 2.2a) in small pore zeolites, or in the dehydration of primary alcohols in a mixture with secondary and tertiary ones.

- Products shape selectivity: over all the possible reaction products, only less bulky molecules that can quickly diffuse away from the active sites to the external environment are formed, while the formation of bulky products is hindered: after
being formed reversibly, they are not able to exit from the internal cavities, and therefore they transform into molecules with higher diffusivity. The alkylation
of toluene to xylene in medium-pore zeolites (ZSM-5), favoring the para isomer, falls into this class (Fig. 2.2b).

- Transition state selectivity: it favors the formation of products whose reaction
path involves a transition state and/or an intermediate sterically compatible with
the porous system. For example, in the transalkylation of dimethylbenzene the
1,3,5-trimethylbenzene is disfavored by the large dimensions of the reaction in-
termediate (Fig. 2.2c). This kind of selectivity is mainly observed for bimolecular
reactions involving a rather large intermediate.

To resume, we can conclude that the popularity of zeolites in catalysis results from
the combination of shape-selective properties with the rather uniform distribution of
active sites within the cavities.

2.2 Modelling of dynamical and reactive processes in zeo-
lites

For the most part of the catalytic processes mentioned, a detailed knowledge not
only of the exact reaction mechanism, but also of the main aspects of the influence
exerted by the structure on the reactive species is still lacking. For instance, among
the reaction catalyzed by zeolites, the MTG process is one of the most known. Al-
though this process is utilized on a vast scale since many years, its mechanism is far
from being unveiled, and even the nature of the initial interaction of the methanol with
the hydroxyl proton is still unclear, in spite of many previous theoretical and experi-
mental studies.8−11 Nevertheless, a rationalization of the main effects due to the steric
and energetic interactions with different zeolite structures might be very useful. When
setting up a new catalytic or adsorption process a key step is to modify the pore shape
and size, as well as the position and properties of active sites, in order to obtain the
best selectivity. As this corresponds to “try” different framework topologies, one can
realize the need and the importance of knowing in advance the connection between the
microporous structure and the behavior of specific molecules in zeolites. If we could
predict the efficiency of some zeolites in given experimental conditions, their choice
and optimization for a specific purpose would be made easier. At the same time, a
detailed knowledge of the behavior of the molecules sorbed within the pores in vari-
ous conditions is interesting in itself, according to the more general purpose of gaining
information on the motion of molecules confined in restricted geometries.12 However,
as stated above, the theory of adsorption and transport, and to a greater extent of
reactivity in zeolites is still incomplete, and their use is often based on empirical prin-
ciples: one tries to determine the connection between zeolite structure and properties
by synthesizing, characterizing and testing a large number of different samples13 in
different operating conditions. Today the availability of fast and powerful computers
allows advanced theoretical and modelling studies.14 In the study of diffusion, Mo-
olecular Dynamics (MD) simulations have proven to be very useful to gain accurate
information on the molecular adsorption and the diffusion at equilibrium,15,16 which
(a) Reactants shape-selectivity

(b) Products shape-selectivity

(c) Transition state selectivity

Fig. 2.2: The three classes of shape-selectivity
as we pointed out are fundamental in determining the shape-selective properties. The force fields usually adopted in MD cannot perform equally well in describing the very chemical details of the catalytic reaction; as a first hypothesis, one could develop new potential functions able to describe events as bond breaking and formation, but this would imply an enormous amount of work to parametrize every studied reaction. The catalytic reaction is often studied through quantum mechanics (QM). For gas-phase reactions, the standard ab initio methods can give structures, vibrational frequencies and relative energies of reactants and intermediates, i.e. the main “ingredients” to calculate the transition-state rate constant. However, in heterogeneous catalysis the application of QM methods is complicated by the virtually infinite dimensions (on a molecular scale) of the solid. In some cases the translational symmetry of the system can be exploited,\textsuperscript{17,18} but the random, symmetry-breaking distribution of active sites and the considerable dimensions of the zeolite unit cells represent big obstacles. Full periodic calculations of this kind are still limited to systems like sodalite or chabazite, with only 36 atoms per unit cell.\textsuperscript{11,19,30} Another common method limits the system treated by quantum mechanics to a small cluster of atoms, representing the active site and the reactive species; in other words, one cuts out from the whole lattice all the atoms that are thought not to be important in order to describe the active site. Hydrogen atoms are placed at an appropriate bond length in the direction of the first missing atoms, so as to saturate the dangling bonds.\textsuperscript{20,21} This approach is very common, because it makes computationally tractable problems that would otherwise be too cumbersome, but has serious drawbacks. The effect of the surrounding structure is thus taken into account only in a very rough way, as the site-sorbate interaction is ruled by local factors only. Rather different results may arise when going from a cluster with 3 T-atoms to a 5-T;\textsuperscript{22} the convergence of macroscopic properties may often require prohibitive cluster sizes. Interesting data may nonetheless stem through the combination of ab initio data for an isolated active site with theoretical predictions (based on classical molecular mechanics potentials) of the stability (and therefore the relative probability) of zeolite structures with the aluminum and the neighbor active site in different crystallographic positions. The paper of Kramer \textit{et al.}\textsuperscript{23} is an excellent example of this idea.

In any case, there is a lack of extended studies of reactive processes, concerning in particular the direct interaction framework-reactive species, and factors such as energetic exchanges, activation and relaxation of reactant and products. Actually the ab initio studies mentioned above provide static properties: their conclusions are based on minimized ($T = 0K$) structures and energies of reactants, products and possible intermediates, sorbed close to the active site. A static representation is limited: suffices here to say that at a nonzero temperature the sorbed molecules move and explore conformations and regions energetically unfavorable. The standard QM methods can only give an estimate of the properties of the system at a nonzero temperature, which are accessible through a statistical analysis of dynamical trajectories at the given temperature. It might appear easy to carry out a dynamical ab initio trajectory, where the potential gradient and forces computed through full quantum calculations are utilized to integrate the classical equation of motions. However the gradient calculation involves enormous computing resources: for example, the integration of a reactive trajectory for six atoms over 500 integration steps (0.25 ps) required 7 hours on a powerful workstation (SGI/MIPS R10000).\textsuperscript{24} By now, such direct dynamical methods are limited to
traditional studies of gas-phase trajectories,\textsuperscript{24} where reactants collisions with different energies and orientations are studied, or to mechanistic studies of trajectories started from the transition state, still in gas phase.\textsuperscript{25}

The Car-Parrinello (CP) method\textsuperscript{26} allows \textit{ab initio} MD simulations of the nuclei-electrons extended system. It combines the density functional (DF) method\textsuperscript{27} for the treatment of the quantum system of the electrons with the MD method. At every time step the forces acting between bonded and non bonded atoms are computed by quantum mechanics, and they are used to update the nuclear positions according to the classical mechanics laws.\textsuperscript{*} In practice, the evolution of the system does not depend on potentials determined \textit{a priori}, as for the classical Molecular Dynamics, but the energies and forces that control the nuclear motion are determined “on the fly”, on the basis of the instantaneous electronic distribution. Compared to the other dynamical \textit{ab initio} methods, the CP method takes advantage of approximations that make it more efficient in terms of CPU time, allowing the inclusion of the solvent in the simulations. Nevertheless, the present hardware resources also limit the dimensions of the systems modelled with the CP method to a few tenths of atoms, which often are not enough for an adequate representation of the effects of the structure on the reaction path. Thus at present the CP method is not applicable to complex systems such as zeolites, with the exception of those with small crystallographic cells (e.g., the sodalite cell, which is a valid prototype to develop simulation methods for more complex zeolitic systems).

Indeed the CP studies carried out on sodalite\textsuperscript{28–33} highlighted some interesting effects, related to the protonation of methanol and water and to the behavior of the proton solvated by rare gases, but the very short duration of the trajectories limits the possibility to obtain quantitative and comprehensive data concerning the dynamical processes in the cavities. One can obtain accurate data, for instance related to the charge transfer as well as to the vibrational frequencies of the system, but longer range phenomena such as slow oscillations of diffusive motions are out of reach. Probably in the future more powerful hardware technologies will allow the application of the CP method to more realistic space and time scales; in any way, such scales are presently accessible only through the classical MD, whose accuracy on the other way is poorer than that of QM-based methods. However, if the empirical force field is well constructed, the classical methods too can give reliable results, in particular if the main interest is on the general action of a zeolite structure: these kind of data could be completed by CP simulations focused on different, local effects occurring over shorter time scales. Moreover, the MD simulations based on empirical potentials allow to develop and improve computational techniques and algorithms related to particular problems (as in the study of “rare events”, see par. 5.1.2), which could be exploited in the future, when CP or similar methods will extensively be applied also to zeolites.

Hybrid QM/MM methods have recently been developed; basically, the system is divided into two subsystems: a small complex containing the chemically interesting atoms and the bulk environment. The first is described in detail through QM, while the latter is described using classical potentials. Using these combined potentials one is able to include the influence of the surroundings on the quantum system properties.

\textsuperscript{*}Note that quantum effects are considered only in the electronic dynamics and not in the nuclear one, and this could be inaccurate for some light species such as the proton, for which quantum effects are not negligible.
Compared to ab initio MD simulations the hybrid methods are less costly; the price to be paid is of course a simplified representation of the bulk environment. The QM/MM methods have been applied to study reactive processes in solution, with systems of several hundredth of atoms. To our knowledge, dynamical simulations of this kind have not been carried out in zeolites yet. In a very recent work the reactivity of several zeolite structures is compared by calculating the static properties of a reactive QM cluster embedded in a large (~1000 atoms) zeolitic substrate, described through classical potentials.

These points show that, at present, a suitable way to face the study of reactive processes in zeolites over meaningful space and time scales is to devise an effective potential describing the formation and the breaking of bonds within a reactive system, and to insert it in a zeolite structure, following its dynamical evolution through classical techniques. In this thesis we will proceed along this way; the reactive processes we will deal with are rather simple, because in this case the development of the force field representing them is easier, and at the same time we are more interested in the comparison between the activity of different topologies, rather than in the specific process considered. The discussion about the limits of the classical Molecular Dynamics in the description of phenomena having a deep quantum nature, like the vibrational relaxation and the chemical reactions themselves, will be continued in the following chapters. As J. B. Anderson pointed out, "Classical mechanics has been found to be a very good approximation to quantum mechanics for many chemical reactions and a surprisingly good approximation even for reactions involving light hydrogen atoms. For reactions of heavier atoms no exact potential energy surfaces are available at present. For these the errors introduced by the use of classical mechanics cannot be directly evaluated, but it is likely that the errors in the potential energy surfaces lead to uncertainties greater than those due to the use of classical mechanics. Thus, one can argue that the errors of classical mechanics are not so serious in themselves and not as serious as other errors”.

2.3 Silicalite and ZK4

In this thesis we will focus on two very common zeolite structures: silicalite and ZK4. Both are completely siliceous forms; their importance stems from the fact that they are isostructural with the more important aluminated forms ZSM-5 (for silicalite) and LTA (for ZK4), which as we saw before are widely used on an industrial scale. The simulation of dealuminated forms has the primary advantage that they do not contain counterions, so that long-range coulombic interactions are absent, allowing much shorter calculations times. Moreover, most zeolites contain only a little amount of Al$^{3+}$ ions, for which there are no conclusive data about the existence of preferential positions in the framework T-sites. When an aluminated structure is represented, one configuration out of the many possible structural arrangements has to be arbitrarily chosen, and this choice could affect the validity of results. In the siliceous zeolites the adsorbent-adsorbate interactions are governed by the dispersion forces: the choice of a structure without counterions entails a substantial uniformity of the electrostatic potential inside the porous system, which excludes possible effects of the electric field on the geometry of the sorbed species and on their energy. When counterions are present,
the electric field within the cavities is no longer negligible and its effect, principally with polar sorbates, must be taken into account.\textsuperscript{38}

The considered structures are rather different, and thus well-representative of a broad range of zeolite properties. Silicalite, according to crystallographic data based on X-rays diffraction studies,\textsuperscript{39} crystallizes in the orthorombic system, space group $Pnm\alpha$. It belongs to the class of pentasil zeolites, whose framework is made from the interconnection of pentasil units (Fig. 2.1). The unit cell dimensions are $a = 20.022\ \text{Å}$; $b = 19.899\ \text{Å}$; $c = 13.383\ \text{Å}$; the cell contains 96 silicon and 192 oxygen atoms. The porous structure is characterized by cylindrical channels delimited by 10-T rings. There are two channel types: straight channels with elliptic section (diameters $5.7 \times 5.2\ \text{Å}$), directed along $b$, orthogonally intersected by sinusoidal (or zigzag) channels with circular section (diameter $5.4\ \text{Å}$), pointing on average along $a$. The channel intersections are elongated cavities of $\sim 9\ \text{Å}$ diameter.

The ZK4 structure results from the interconnection of sodalite units (Fig. 2.1) through oxygens bridging the 4-T rings. This leads to a structure with large spherical cages ($\alpha$ cages) with diameter $11.4\ \text{Å}$, accessible through rather narrow windows (diameter $4.2\ \text{Å}$). The $\alpha$ cages are arranged on a cubic lattice (each cage is connected to 6 cavities occupying the vertices of an octahedron). The ZK4 cell has been represented (according to structural data for the NaA zeolite\textsuperscript{40}) in the $Fm\overline{3}c$ space group, with edge $a=24.555\ \text{Å}$; it includes 192 silicon and 384 oxygen atoms.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{zeolite_structure.png}
\caption{Structure of silicalite, pointing along the straight channels ($y$ direction)}
\end{figure}
Fig. 2.4: Structure of silicalite, pointing along the sinusoidal channels (z direction)

Fig. 2.5: Structure of ZK4, showing the central $\alpha$-cage
Chapter 3

Molecular Dynamics simulations

3.1 The role of computer simulations

Before the advent of high-speed computers, scientific research in the physical sciences field was based on the interplay between “experiment” and “theory”. In the experiment one obtains numerical results from direct measurements, and then tries to extract from them useful, general information concerning the system. To this purpose, a theory is developed starting from a model of the system, usually in the form of a set of mathematical equations. The model is then validated by its ability to describe the system behavior in a few selected cases, simple enough to allow an exact solution to be computed from the equations. In this way one obtains some macroscopic properties according to the model, and the comparison with the corresponding experimental data allows to assess the validity of the theory. For instance, starting from the ideal gas model, the kinetic theory of gases leads to the equation of state $PV = Nk_BT$, which allows to explain the experimental behavior of ideal gases. In more complex (and more interesting) cases, such as system characterized by a large amount of degrees of freedom and significant intermolecular interactions, one has to resort to approximations to make the problem solvable, and often accurate solutions are out of reach, so that the validity of the model could hardly be verified. Numerical simulations\textsuperscript{41-43} introduce a new element acting as a bridge between experiment and theory. The starting point is still a theoretical model, but the calculations needed to get the properties predicted by the model are carried out by the machine (by means of various numerical techniques and algorithms). The simulation provides essentially exact results for problems otherwise intractable by numerical methods, allowing to improve the model until it reproduces the experimental data. For instance, molecular dynamics simulations allow to evaluate the melting temperature of a material, represented by a certain model. This important test for the model was not available in the past, i.e., without computers. After devising and building a suitable model, simulations can provide essential “microscopic” information, useful to understand a certain experiment, and also macroscopic data, as transport coefficients, equations of state, etc. The latter are particularly important to study conditions not accessible experimentally, or which would imply very expensive experiments, as extremely high temperatures and pressures. Numerical simulations have then a dual role: (i) they represent a (difficult) test for theoretical models, allow-
ing to build new models and more accurate theories; (ii) they are a powerful means to get detailed information not accessible experimentally.

### 3.2 The Molecular Dynamics method

In order to perform MD simulations of a system, a set of $N$ particles contained in a cell of volume $V$ is chosen. In a particular instant $t$ the collection of $3N$ coordinates $\{r_i(t)\}$ and of $3N$ momenta $\{p_i(t)\}$ of all particles is a point in the $6N$-dimensional phase space formed by all the microstates $\Gamma = \{r_i, p_i; i = 1, \ldots, N\}$ accessible to the system. When the system evolves in time, starting from any initial point, it generates a trajectory in phase space. The object of Molecular Dynamics (MD) is to determine this trajectory by numerically integrating the classical equations of motion over successive time intervals. Such trajectory may not appear particularly relevant by itself; its importance arises from the statistical mechanics concept that a physical property can be calculated by averaging over many configurations distributed according to a certain statistical ensemble: the MD trajectory provides such ensemble of configurations. In practice, as shown below, a measurement of a physical quantity by simulation is simply obtained as an arithmetic average of the various instantaneous values assumed by that quantity during the MD run.

#### 3.2.1 Equations of motion and integration algorithms

The classical equations of motion can be expressed in hamiltonian, lagrangian or (more frequently) newtonian form. The latter are:

$$m_i \ddot{r}_i = f_i = -\nabla r_i V(r_1, \ldots, r_N) \quad i = 1, \ldots, N$$ (3.1)

where $m_i$, $r_i$ and $f_i$ are respectively the mass, the position of $i$-th atom and the force on it. $V$ is the potential energy of the system when the $N$ atoms are arranged in the specific configuration $\{r_1, \ldots, r_N\}$. The potential function is the fundamental input to the simulation: the construction of a model essentially entails setting up the interaction potential that controls the dynamic evolution of the system.

The total potential energy is given by:

$$V = \sum_i v_1(r_i) + \sum_i \sum_{j>i} v_2(r_i, r_j) + \sum_i \sum_{j>i} \sum_{k>j} v_3(r_i, r_j, r_k) + \ldots$$ (3.2)

where the $\sum_i \sum_{j>i}$ notation indicates a summation over all distinct pairs $i$ and $j$ without counting any pair twice (i.e. as $ij$ and $ji$). The first term in eq. 3.2 represents the effect of an external field; the remaining terms represent particle interactions. The second term $v_2$, the pair potential, is the most important. While the contribution of four-body and higher terms are expected to be small in comparison with $v_1$ and $v_2$, the $v_3$ term, involving triplets of molecules, is undoubtedly significant at densities typical of condensed phases. However it is only rarely included in computer simulations because the calculation of quantities connected to three-body interactions is very time-consuming on a computer. Fortunately, the pairwise approximation gives a remarkably good description of the system because the average three-body effects can be partially included.
by defining an “effective” pair potential, which can be determined by theoretical calculations and experimental data.\textsuperscript{47}

Therefore, if the external field is zero, we have:

\[ V = \sum_i \sum_{j \neq i} v_2(r_{ij}) \]  

(3.3)

where \( r_{ij} = |\mathbf{r}_j - \mathbf{r}_i| \): indeed, the pair potential depends only on the magnitude of the pair separation \( r_{ij} \).

The Newton’s equations then become:

\[ m_i \ddot{\mathbf{r}}_i = -\sum_{j \neq i} \frac{1}{r_{ij}} \frac{\partial v_2(r_{ij})}{\partial r_{ij}} \mathbf{r}_{ij} \quad i = 1, \ldots, N \]  

(3.4)

The term inside the sum is the force exerted on the \( i \)-th particle by the \( j \)-th particle; the sum then gives the resulting total force on the \( i \)-th particle. Eqs. 3.4 are a system of \( 3N \) second-order differential equations, that can be approximately solved by finite difference numerical methods.\textsuperscript{48} The general idea is as follows: given the molecular positions, velocities, and other dynamic information at time \( t \), we attempt to obtain the positions, velocities etc., at a later time \( t + \delta t \), and in a series of consecutive instants \( t + 2\delta t \), \( t + 3\delta t \) etc., generating a discrete trajectory in the phase space by successive iterations. The time interval \( \delta t \) is named time step, and its value must be carefully chosen: larger \( \delta t \)'s allow a given period of simulation time to be covered in less integration steps, i.e. less CPU time. However, the larger \( \delta t \), the less accurately will our solution follow the correct classical trajectory. The integration methods are indeed affected by two types of errors:

- **Truncation errors**: finite difference methods are based on a Taylor expansion truncated at some term, thus reducing the accuracy of the solution with respect to the true one.

- **Round-off errors**, related to the finite number of digits used in computer arithmetics.

Both errors can be reduced by decreasing \( \delta t \). One has to find an appropriate compromise between accuracy of results and saving of CPU time. The stability of the MD trajectory for a certain \( \delta t \) is verified by observing the evolution of a constant of the motion for the statistical ensemble adopted, as the total energy \( E \) in the microcanonical ensemble. If the trajectory is stable \( E \) should not depart significantly from its initial value. The RMS fluctuation of the total energy \( \sigma(E) = \langle (\delta E)^2 \rangle^{1/2} \), where \( \delta E = E(t) - E(0) \), averaged over the whole trajectory, should stay below 0.1%. \( \delta t \) is usually system-dependent: to adequately represent the system it should be significantly smaller than the times characterizing the fastest motions in the system, which usually are the highest frequency vibrations. Typical \( \delta t \) values for simulations of zeolites range between 0.5 and 20 fs; values of about one femtosecond are necessary to describe the lattice vibrations, but if framework flexibility is not allowed (rigid lattice), a one-order of magnitude increase in the time step is possible. The overall length of the generated trajectory depends on the time scale of the studied process: accurate statistical averages require an extensive sampling of the event. For example, the study of diffusion
of species that move very slowly in the zeolite cavities (due to steric and/or kinetic
reasons) may require trajectories of many nanoseconds to give accurate results.

Different finite difference algorithms are available to integrate the equation of mo-
tions; in all cases a Taylor expansion in $t$ is performed to obtain positions, velocities
etc. at $t + \delta t$. The difference between the various algorithms essentially lies in the
different order where the Taylor series is truncated. Clearly, an expansion to a higher
order leads to better accuracy and stability of the trajectory, thus allowing longer time
steps, but at the same time it entails more intensive and CPU-demanding calculations
per time step.

### 3.2.2 The Verlet algorithm

One of the most widely used methods of integrating the equations of motion is that
developed by Verlet.\textsuperscript{49,50} Given the positions $r(t)$, accelerations $a(t)$, and the positions
$r(t - \delta t)$ from the previous step, the equation for advancing the positions to the next
step reads as follows:

$$
r(t + \delta t) = 2r(t) - r(t - \delta t) + \delta t^2 a(t) \tag{3.5}
$$

Eq. 3.5 is the result of adding the Taylor expansions about $r(t)$:

$$
r(t + \delta t) = r(t) + \delta t \, v(t) + \frac{1}{2} \delta t^2 a(t) + \frac{1}{6} r'''(t) \delta t^3 + O(\delta t^4) \tag{3.6}
$$

$$
r(t - \delta t) = r(t) - \delta t \, v(t) + \frac{1}{2} \delta t^2 a(t) - \frac{1}{6} r'''(t) \delta t^3 + O(\delta t^4) \tag{3.7}
$$

The velocities are not needed for updating the positions, but they are useful for esti-
mat ing the kinetic energy and other dynamic information. They may be obtained by
subtracting Eqs. 3.6 and 3.7, giving:

$$
\mathbf{v}(t) = \frac{r(t + \delta t) - r(t - \delta t)}{2\delta t} \tag{3.8}
$$

The acceleration $a(t)$ at time $t$ is directly computed by the corresponding instantane-
ous force, which in turn is obtained from the positions $r(t)$ according to eq. 3.4. Whereas
$\delta t^2$ is except for errors of order $\delta t^4$ the velocities from eq. 3.8 are subject to
errors of order $\delta t^2$, so that the Verlet algorithm does not handle velocities with the same
accuracy as positions. Some numerical inaccuracy also arises because in eq. 3.5 a small
term of order $\delta t^2$ is added to the difference between two larger terms of order $\delta t^0$. To
overcome these difficulty, some variants of the Verlet algorithm have been developed,
which give rise to exactly the same trajectory. In our simulations we will adopt the
modified version known as “velocity form”\textsuperscript{51} of the Verlet algorithm. The quantities
$z(t)$, representing mean velocities in the interval $\delta t$, are introduced; starting from initial
positions and mean velocities at time $t$, the coordinates at time $t + \delta t$ are given by:

$$
r(t + \delta t) = r(t) + z(t) \delta t \tag{3.9}
$$
Next, forces and accelerations at $t + \delta t$ are updated, giving the new mean velocities $\mathbf{z}(t + \delta t)$ according to:

$$\mathbf{z}(t + \delta t) = \mathbf{z}(t) + \mathbf{a}(t + \delta t)\delta t$$  \hfill (3.10)

The instantaneous velocities are finally obtained by:

$$\mathbf{v}(t + \delta t) = \frac{1}{2}\{\mathbf{z}(t + \delta t) + \mathbf{z}(t)\}$$  \hfill (3.11)

This version of the Verlet algorithm is one of the most widely used both because of its easy implementation and numerical accuracy.

### 3.2.3 Initial conditions

At the beginning of the MD run, the initial positions and velocities must be specified. Unlike liquids, where the detailed structure is unknown, in the case of zeolites there are enough structural and crystallographic data, usually obtained from diffraction studies, providing the equilibrium positions of the framework atoms, and in some cases also the sites occupied by the sorbed molecules. In general, experimental coordinates will not match exactly the minimum of the potential energy resulting from the adopted model, and two possible strategies can be chosen:

- Starting from coordinates as close to the possible to the potential energy minimum, the velocities assigned to the particles are sampled from the Boltzmann distribution corresponding to the selected temperature. With this procedure the system gets a small linear momentum, leading to an unwanted overall translational motion, and care must be taken to remove it, by subtracting the appropriate component from the velocity of each particle.

- Starting with zero velocities from coordinates that are close to their equilibrium value*, velocities are rescaled until the temperature reaches and maintains the selected value.

Both procedures require some time before the system stabilizes at the target temperature; this phase is called “equilibration run”. Relevant quantities should not be collected during this stage, but only after the equilibration has ended. In the simulations carried out we adopted the second strategy, which is easier to apply and at the same time ensures (due to the linear momentum conservation law) that the overall linear momentum is zero.

### 3.2.4 Periodic boundary conditions

The critical parameter influencing the duration of a simulation is the number of particles: indeed the more time-consuming section of any MD computer program is where particle interactions are calculated. The time taken to evaluate the forces is proportional to $N^2$; this limits the number of particles included in the simulated system to

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*If we started with zero velocities from the equilibrium positions, the system would remain stuck in this configuration, because there would be no net force on each atom.
values between 100 and 10000 atoms for standard single-processor workstations. In the case of zeolites this correspond to 1-10 crystallographic cells. A major problem arising from this small sample is that the fraction of molecules which lie on the surface would be much greater than the corresponding fraction in a real system. The surface atoms have less neighbor particles and experience quite different forces with respect to the internal atoms. The simulated system would be governed by surface effects, and it would show properties different from those of the bulk system: everything would be surface. However, the bulk system is the actual objective of the study. In order to overcome surface effects the so-called “periodic boundary conditions” (PBC) are applied. The particles are enclosed in a (usually cubic) box, which is replicated throughout space to form an infinite lattice. The upper face of each cube matches the lower face of another cube, and so on. Therefore, for each molecule moving in the central cube, there will be infinite periodic images in the other cubes, moving in exactly the same way. Note that only the “real” particle (not its images) is represented in the program. When a molecule crosses the face of a cube one of its images will enter through the opposite face. In this way there are no walls at the boundaries, and no surface molecules; the number density \( N/V \) is conserved. When solid systems are simulated, one exploits the translational symmetry by using one or more adjacent unit cells as simulation box. Apparently, the number of pairs of interacting particles increases enormously when PBC are applied, because of the additional particles in the surrounding cubes. However, the interactions are usually short-ranged, so that this is not true. The “minimum image convention” (MIC) simplifies things further. It is based on the finite range of interaction forces: when two particles are separated by a distance larger than a cutoff distance \( R_c \), they do not interact. If the size of the box is larger than \( 2R_c \) along the three cartesian directions, it can be shown that a particle \( i \) in the box can interact with at most one among all the periodic images of another \( j \) particle in the box. The MIC thus entails selecting the closest among all the possible images of \( j \), and discarding the others.\(^1\) In fact only the closest is a candidate to interact, all the others certainly do not. Now, if \( r_{ij} < R_c \) their interaction force is determined, otherwise this contact also is ignored. The MIC is illustrated in Fig. 3.1: an useful picture is to imagine each particle in turn at the center of a cell equal to the simulation box. The central particle will only interact with the \( N-1 \) particles – or images – found within this cell, and in particular with those found inside the sphere with radius \( R_c \) centered on the particle.

### 3.2.5 Limitations

First, it is important to ask if the properties of a small system represented with PBC, and the macroscopic system which it models are the same. There is not a general answer; the equivalence can only be checked \textit{a posteriori}, for example by carrying out simulations with a larger number of molecules (and a corresponding increase in the box volume, so as to maintain a constant density). Despite this remark, the common experience in simulation work is that PBC have little effect on the equilibrium properties of the system away from phase transitions and where the interactions are short-ranged.

\(^1\) This is equivalent to rescale each component of the distance vector between \( i \) and \( j \) note again that only one particle \( i \) and one particle \( j \) are actually present in the computer program. While their coordinates are usually left free to evolve, their distances are processed according to the MIC.
3.2 The Molecular Dynamics method

![Molecular Dynamics Diagram](image)

**Fig. 3.1:** Minimum image convention in two dimensions. The central box contains six molecules, as the dashed box built around the central dark molecule. Only three out of the six molecules are within the cutoff circle.

Another problem is connected with the use of classical mechanics and Newton’s laws to determine the evolution of the system, while it is well known that on the atomistic level systems obey quantum mechanics laws. Quantum mechanics calculations are much more intensive and require much longer CPU times, so that at present they are not suitable for studying complex systems as liquids and solids. A simple test of the validity of the classic approach is possible by calculating the de Broglie thermal wavelength, defined as:

\[
\Lambda = \left( \frac{\hbar^2}{2\pi mk_B T} \right)^{1/2}
\]  

(3.12)

where \( k_B \) and \( h \) are the Boltzmann and Planck constants, \( m \) is the mass of the particle and \( T \) the temperature. \( \Lambda \) is the de Broglie wavelength \( h/mv \) of a particle with kinetic energy of \( \sim k_B T \). If \( a \) is the average distance of nearest neighbors \( (a \sim \rho^{-1/3}, \text{ with } \rho = N/V, \text{ particle number density}) \), then the classical treatment is justified when \( \Lambda \ll a \), that is when two neighbor molecules are usually found at distances considerably greater than \( \Lambda \). This condition is more likely to be respected for larger masses and higher temperatures, and lower densities. For liquids at the boiling point, \( \Lambda/a \sim 1.1 \) for He, 0.8 for H\(_2\), 0.25 for Ne, 0.1 for Li and Ar and decreases further for heavier species, or in gas phase. Therefore at ordinary temperatures quantum effects can be neglected for the most part of atomic and molecular species, but can be significant for light species such as H\(_2\), He and Ne at high densities. For very low \( T \), quantum effects cannot be neglected for any system, and the classical approximation is inadequate. Clearly the condition \( \Lambda \ll a \) does not apply at all for electrons, whose deep quantum nature is undoubted.
3.3 Statistical Mechanics

3.3.1 Average properties

MD simulations provide a great amount of data at the microscopic level, such as positions and velocities of all the particles. Statistical mechanics allows converting this extremely detailed (and thus very complex) information into macroscopic equilibrium properties of the system under study. $\Gamma$ is a generic point in phase space, that is a microstate composed by all the position and velocity vectors of the $N$ particles for a given configuration. Let us focus on the determination of the system property $A$, for example the potential energy, and suppose that $A(\Gamma)$ is the value of $A$ when the system is in the microstate $\Gamma$. The system evolves in time, so that $\Gamma$, and hence $A(\Gamma)$ will change. It is reasonable to assume that the experimentally observable “macroscopic” property $A_{\text{obs}}$ is really the time average of $A(\Gamma)$ taken over a long time interval:

$$A_{\text{obs}} = \langle A(\Gamma(t)) \rangle = \lim_{t_{\text{obs}} \to \infty} \frac{1}{t_{\text{obs}}} \int_{0}^{t_{\text{obs}}} A(\Gamma(t)) dt$$  \hspace{1cm} (3.13)

We clearly cannot hope to extend the integration of eq. 3.13 to infinite time, but might be satisfied to average over a long finite time $t_{\text{obs}}$. This is exactly what we do in a MD simulation. The equations of motion are solved on a step-by-step basis, so that the integral 3.13 becomes a finite sum over the total number of time steps $\tau_{\text{obs}} = t_{\text{obs}}/\delta t$:

$$A_{\text{obs}} = \langle A(\Gamma(t)) \rangle = \frac{1}{\tau_{\text{obs}}} \sum_{\tau=1}^{\tau_{\text{obs}}} A(\Gamma(\tau))$$  \hspace{1cm} (3.14)

MD simulations usually describe a system where the particle number $N$, the volume $V$ of the simulation cell and the total energy $E$ are always constant. Therefore we work in the microcanonical ($NVE$ statistical ensemble. An equilibrium thermodynamic state is completely specified by three macroscopic parameters such as $N$, $V$ and $E$. When they are fixed, the region (hypersurface) of the phase space accessible to the system is also defined. The enormous number of points in this region corresponds to the ensemble of microstates associated with that equilibrium state. The fundamental postulate of statistical mechanics is that for an isolated system with fixed energy and dimensions (specified by the parameters $N$, $V$ and $E$) all microstates are equally likely at equilibrium. Therefore during a measurement (lasting $t_{\text{obs}}$) the system will explore all the phase space points that are compatible with the selected parameters $N$, $V$ and $E$: this is the “quasi-ergodic” hypothesis. In other words, if the simulation is performed for a sufficiently long time and we exclude the possibility that the system may get trapped for a long time in the same region of phase space, then during the simulation the system will explore a relevant region of phase space, giving accurate average values. As an example, we report the expression for computing the average temperature. According to the equipartition principle the temperature $T$ of an $N$-

---

$^1$Regions of phase space showing high-energy barriers could represent “bottlenecks” through which the trajectory will pass only rarely. The adequate sampling of these regions requires special techniques or much longer simulations.
particle system is proportional to its kinetic energy:

$$
\langle K \rangle = \left\langle \sum_{i=1}^{N} \frac{p_i^2}{2m_i} \right\rangle = \frac{3}{2} N k_B T \tag{3.15}
$$

where $p_i$ and $m_i$ are the momentum vector and the mass of particle $i$. Hence, through eq. 3.14:

$$
T = \frac{2}{3 N k_B} \frac{1}{\tau_{\text{obs}}} \sum_{j=1}^{N} \sum_{i=1}^{N} \frac{p_i^2(j)}{2m_i} \tag{3.16}
$$

The calculation of time averages as for MD is different from the statistical mechanics approach, where the time average is replaced by an ensemble average. The statistical ensemble may be considered as a set of points $\Gamma$ of phase space. Each microstate has associated a certain probability $\rho(\Gamma)$ depending on the macroscopic parameters ($NVT$, $NPT$ etc.) which identify the ensemble. In practice the average properties are obtained from a “snapshot” of the ensemble of microstates and not from the time evolution of a single element of the ensemble. This corresponds to replacing the time average in eq. 3.13 by an average taken over all the members of the ensemble, “frozen” at a particular time:\footnote{The basic assumption is that, during the experimental measurement, the system passes through all the available microstates, visiting several times and more often states with a high associated probability. Therefore the measured (time-averaged) property and its value computed according to eq. 3.17 will match}

$$
A_{\text{obs}} = \langle A(\Gamma) \rangle_{\text{ens}} = \sum_{\Gamma} \rho_{\text{ens}}(\Gamma) A(\Gamma) \tag{3.17}
$$

where $\rho_{\text{ens}}$ is the ensemble-dependent probability function. The statistical approach to the calculation of an average quantity requires the evaluation of $\rho_{\text{ens}}$ for the specific ensemble and the sum over all microstates $\Gamma$. But the calculation of this sum is not feasible for a many-particle system: there are too many microstates, whose most part have very low probabilities. The best procedure would be to include only the high-probability states in the sum, neglecting those with a lower weight. The idea of generating a chain of states in the phase space, distributed according to the probability $\rho_{\text{ens}}(\Gamma)$, so as to obtain average properties as arithmetical averages, is exploited in the Monte Carlo methods.\footnote{\ref{13,53}}

### 3.3.2 Radial distribution functions

The radial distribution function $g(r)$ gives the number of atoms separated by the distance $r$, compared with the number at the same distance expected for a completely uniform distribution (as that of an ideal gas) at the same density. The presence of intermolecular attractive forces leads to maxima in the $g(r)$ function, corresponding to the most likely distances between two atoms. In the case of the subsystem composed by the molecule adsorbed in a zeolite, the $g(r)$ functions related to the distance between the atoms of the crystalline lattice and the sorbed molecules provide important information
on the adsorption sites inside the cavities and on the intensity of the local guest-host interactions. An MD simulation produces a series of configurations, each one with a certain distribution of interatomic distances. For each configuration one calculates the number $n(r)$ of pairs of atoms whose distance is in the interval $(r, r + \delta r)$, and this calculation is repeated for all microstates in the trajectory, giving the average number of distances $\bar{n}(r)$ comprised in that interval according to eq. 3.14. This procedure is repeated for several different values of $r$, compiling a histogram where $\delta r$ is the width of each bin. The histogram is then normalized according to the definition of $g(r)$ given above: as $\bar{n}(r)$ is also the number of atoms found on average within the spherical shell of width $\delta r$, positioned at distance $r$ from another atom at the center, the normalization factor is the corresponding number of atoms that would be situated in the same volume for an uniform distribution:

$$g(r) = \frac{\bar{n}(r)}{\frac{4}{3}\pi \rho \{(r + \delta r)^3 - r^3\}}$$

(3.18)

The term within curly braces in the denominator, multiplied by $\frac{4}{3}\pi$, is the volume of the spherical shell, and $\rho = N/V$ is the particle number density.

### 3.4 Diffusion

#### 3.4.1 Fick’s and Einstein’s equations

Diffusion is the tendency of matter to migrate, in absence of stirring, in such a way as to eliminate spatial variations in composition, thereby approaching a uniform equilibrium state. This behavior is simply a manifestation of the tendency towards maximum entropy or maximum randomness. Diffusion obeys Fick’s laws:

$$J = -D \frac{\partial c}{\partial x}$$

(3.19)

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

(3.20)

In eq. 3.19, $J$ is the flux, or number of molecules crossing the unit area in the unit time and $D$ is the diffusion coefficient: it is proportional to the concentration gradient. This law can be deduced from the kinetic theory of gases but it applies to the diffusion of molecules in condensed phases too: the diffusion coefficients is inversely proportional to the viscosity of the medium. The Fick’s second law, eq. 3.20 relates the rate of change of concentration of particles at a point in an inhomogenous region to the spatial variation of the concentration at that point: it concerns the spreading of inhomogeneities with time. Eq. 3.20 shows that the rate of change of concentration is proportional to the local curvature of the concentration with respect to distance. If the concentration changes sharply from point to point then the concentration changes rapidly with time; conversely, if the curvature is zero, then the concentration at any point is constant because the inflow of particles is exactly balanced by the outflow. Diffusion is a very slow process, which is why solutions are usually stirred, to assist mixing by convection.
3.4 Diffusion

It is possible to apply Fick’s laws to the random (brownian) motion of a fluid of identical particles at equilibrium. In order to do so one group of particles must be considered to be distinguishable from the other particles, that is they must be regarded as “labelled”. This labelling does not produce any effect on the interaction of the marked particles with the other; the motion of marked particles through non-marked, otherwise identical particles is named auto-diffusion or self-diffusion. It is easy to show by differentiation that a general solution of eq. 3.20 is:

\[
\frac{c(x, t)}{M} = \frac{e^{-\frac{x^2}{4\pi D t}}}{\sqrt{4\pi Dt}}
\]  

(3.21)

or, in three dimensions:

\[
\frac{c(r, t)}{M} = \frac{e^{-\frac{r^2}{4\pi D t}}}{(4\pi Dt)^{3/2}}
\]  

(3.22)

\(M\) in the previous equations is the total quantity of diffusing substance, so that eq. 3.22 gives the probability of finding at position \(r\) a particle which was located at the origin at time zero. This quantity is termed propagator and, as it is a Gaussian function, it is completely defined by the time dependence of its mean square half width, or mean square displacement (representing the width at time \(t\) of the concentration profile, centered on its mean value \(\langle r \rangle = 0\):

\[
\langle x^2(t) \rangle = \int_{-\infty}^{+\infty} x^2 \frac{e^{-\frac{x^2}{4\pi D t}}}{\sqrt{4\pi Dt}} \, dx = 2Dt
\]  

(3.23)

\[
\langle r^2(t) \rangle = \int_{-\infty}^{+\infty} r^2 \frac{e^{-\frac{r^2}{4\pi D t}}}{(4\pi Dt)^{3/2}} \, dr = 6Dt
\]  

(3.24)

These equations show that the diffusing species, initially positioned at the origin, will spread more and more with time. They are known as Einstein’s equations, and provide a direct correlation between the diffusivity, as defined by Fick’s laws, and the most observable quantitative feature of Brownian motion. We can follow the diffusion of a single kind of particles at equilibrium (self-diffusion) either by tagging a certain fraction of the diffusants or by determining the mean square displacement (MSD) of a large number of individual diffusants. In the first case \(D\) is given by \(J^* = -D \frac{\partial c}{\partial x}\), where the asterisk denotes the marked particles, while in the latter case eqs. 3.23, 3.24 are directly applied. The self-diffusion coefficient concerns an equilibrium system and will match the diffusion coefficient (named transport diffusivity) measured in the presence of a real concentration gradient only at infinite dilution, that is when the interactions between the diffusants are negligible. In such case the molecular flux in the non-equilibrium system and the flux of marked particles in the equilibrated system will be equal. However in the general case the flux of marked particles is slowed down by the presence of non-marked particles and the self-diffusion coefficient will be lower than the transport diffusivity.

\footnote{As \(\langle r(t) \rangle = 0\) at any time, the spreading of particles released at the origin at \(t=0\) is better described by the RMS distance \(\langle r^2(t) \rangle\)}
3.4.2 Calculating the diffusion coefficient by MD simulations

Although the diffusion coefficient is a macroscopic quantity, the MSD bears a precise microscopic interpretation: it is the mean square distance covered by a “marked” molecule in a certain time. The MSD can be calculated from an MD trajectory through the following expression:

\[
\langle r^2(t) \rangle = \frac{1}{N_0 N} \sum_{i=1}^{N} \sum_{t_o=1}^{N_o} |r_i(t_o + t) - r_i(t_o)|^2
\]

(3.25)

where the average is over \( N \) molecules and all the \( N_o \) time origins spaced by \( t \) existing in the trajectory, in such a way to get the best possible sampling of the mean square distance covered by a molecule in that interval. Note that in the computation of the right of eq. 3.25 it is important not to switch attention from one periodic image to another, which is why it is sometimes useful to have available a set of particle coordinates which have not been subjected to PBC during the simulation. It should be remarked that the Einstein’s diffusive regime takes only place after a (short) fraction of time: the MSD curves we calculated show indeed a short-time region where the Einstein’s equations are not applicable. In this region the influence of the molecular interactions is still not established and the molecules move freely (with constant velocity). After a few picoseconds the motion achieves the true diffusive behavior of eq. 3.22. From now on, the MSD shows a linear trend whose slope gives the diffusion coefficients according to eqs. 3.23, 3.24. In practice the following expression is applied:

\[
D = \lim_{t \to \infty} \frac{\langle r^2(t) \rangle}{2dt}
\]

(3.26)

where \( d \) represents the corresponding dimensionality.

3.4.3 Diffusion in zeolites

In porous systems with large openings (pore diameter in the micrometer range) the pore dimensions are larger than the mean free path of the gaseous species adsorbed and the diffusivities are equal to the ordinary gaseous diffusion coefficients reduced by the corresponding fraction of accessible void space. At smaller sizes of the pores (pore size \( < \) molecular mean free path) we are in the situation where the diffusive properties are considerably influenced by the attractive and repulsive interactions with the cavity walls.\(^{55,56}\) This can lead to several interesting phenomena like supradiffusivity,\(^{57}\) whenever the dimensions of diffusants and the internal curvature of the cavities lead to the cancellation of the radial forces acting on the molecule, which “floats” inside the channels without any friction. Diffusion in zeolites shows particular and often unusual aspects: it is not easy to predict \emph{a priori} if in a certain microporous structure two seemingly similar species may move with different velocities. Weiss\(^{58}\) coined the term “configurational diffusion” to describe the molecular migration in zeolites: due to the small difference between the pore and molecule diameters, different configurations (conformations) assumed by the diffusants will have different diffusivities and their weight on the effective diffusion coefficients will be much more marked than in the homogeneous phase. Among the others, this is on the basis of the different diffusion coefficient
3.4 Diffusion

of cis- and trans-butene in the CaA zeolite and of the periodic trend (resonant diffusion) of the diffusion coefficient of linear paraffins in erionite\textsuperscript{69} and silicalite.\textsuperscript{60-62} These phenomena cannot be understood or predicted only on the basis of static parameters such as lengths and diameters. The rotational and vibrational motions and in general the exploration of the configurational space of each molecule must be taken into account, and in this area the MD simulation turn out to be essential. Note again that the reactant and product selectivity of zeolites (not the transition-state selectivity) are strictly connected to the diffusive properties of sorbed molecules. The experimental measurements of such diffusive properties is often a difficult task and simulations are a further important tool in this field. The calculation of diffusion coefficient by MD is based on expressions (3.21, 3.22) assuming the isotropy and homogeneity of the diffusing fluid. Zeolites does not present an homogeneous environment (and often neither an isotropic one) to the diffusing species; however the experimental measurements of \(D\) are carried out over randomly oriented crystallites, so that the obtained values are actually averages of the diffusion coefficient over different orientations. This ensures that the diffusion coefficients calculated by MD for molecules diffusing in zeolites are directly comparable with experimental data obtained by NMR. The MD simulations also allow a direct evaluation of monodimensional MSDs along the cartesian axes. This is particularly useful in order to compute the components of the diffusion coefficient (eq. 3.26 with \(d=1\)) and to study the diffusive anisotropy in non-cubic zeolites, as will be shown in the following. If the considered directions are orthogonal the total diffusion coefficient must match the average of its three components:

\[
D = \frac{D_x + D_y + D_z}{3}
\] (3.27)

In order to obtain an accurate estimate of the true diffusion coefficient the minimum path length that must be covered by a sorbed molecule should be on the order of the crystallographic cell \(L\). The condition \(\langle r^2(\tau) \rangle > L\) ensures that during \(\tau\) the molecule really diffuses and it is not subject to a localized motion, scarcely relevant for the long-range diffusive properties of the sorbed system. This roughly defines the minimum duration \(\tau\) of a MD simulation, which could reach the second in the case of very long and bulky sorbates. The time scale typical of MD simulations is currently on the order of several nanoseconds: hence they are succesfully applicable to study the diffusion of, among the others, short and medium chain n-alkanes \((C_1 - C_{14})\).\textsuperscript{63}

The experimental techniques for studying diffusion in zeolites may be divided into two groups\textsuperscript{55} macroscopic methods (such as uptake rate measurements) and microscopic methods, such as Pulsed Field Gradient Nuclear Magnetic Resonance (PFG-NMR) and Quasi-Elastic Neutron Scattering (QENS).\textsuperscript{64} The main difference between the two groups is the time scale of the measurement, which is on the order of the second for macroscopic methods and of the millisecond or less for microscopic ones. This leads to considerable difference between the estimated diffusion coefficients, those calculated by macroscopic methods being two orders of magnitude lower. This is probably due to phenomena occurring at long times, connected for example to the intercrystalline mobility of sorbates, which does not affect the microscopic measurements. It is therefore not surprising that the \(D\) values provided by the MD simulations are in much better agreement with the microscopic techniques. In practice MD and microscopic methods
measure the true intracrystalline diffusivity, which is definitely more important in determining the properties of zeolitic systems. The discrepancy between microscopic and simulation values with respect to macroscopic methods is also connected to the fact that the first work on an equilibrium system, while the latter measurements are taken in a non-equilibrium situation. Appropriate correction formulas\textsuperscript{65} have been developed to take into account this point, but considerable discrepancies still persist for many systems and an experimental method allowing to bridge the gap between the two groups of techniques is still sought.

3.4.4 Determining the statistical error

The error in the diffusion coefficient calculated by MD can be assessed through a basic statistical procedure.\textsuperscript{66} The trajectory is cut into \( m \) blocks of equal length and for each block the corresponding MSD and diffusion coefficient are separately evaluated. The error in the overall diffusion coefficient (whose value is roughly equal to the averages of the \( m \) diffusion coefficients of each block) is then obtained by the standard expression:

\[
\delta D\% = \sqrt{\frac{1}{m(m-1)} \sum_{i=1}^{m} (D_i - \bar{D})^2} \cdot \frac{100}{\bar{D}}
\]  

(3.28)

where \( D_i \) is the diffusion coefficient of the \( i \)-th block and \( \bar{D} \) the average value.

3.4.5 Diffusion as a random walk

We saw before that the diffusion arises from the random thermal motion (brownian motion) of the molecules. Many of the important features of diffusion can be understood and interpreted, both qualitatively and quantitatively by considering the process as a random walk in which the particles move by a sequence of steps of equal size \( l \), taken at constant frequency \( \tau^{-1} \) and with equal probability in any direction. We can make the discussion simpler by considering a one-dimensional system in which steps of \( \pm l \) are taken with equal probability along a straight line (the \( z \) axis); the total distance covered after \( n \) steps is then \( nl \). Nevertheless the particle will not presumably be found at such distance from the origin (i.e., the point where it was released at \( t=0 \)) because the directions of successive steps can be different. This should be taken into account in order to obtain the effective distance from the origin at time \( t \). Let us consider the propagation of a great number of random walkers; the best description of their chaotic movement is provided by the propagator \( P(r,t) \): it is a probability density, where \( P(r,t)dr \) represents the probability of finding at time \( t \) a random walker in the volume element \( dr \), at a distance \( r \) from the starting point. In the model of stochastic movement in one dimension the determination of this function is a simple task requiring only elementary probability theory,\textsuperscript{67} which gives:

\[
P(x,t) = \frac{e^{-\frac{x^2}{2Dt}}}{\sqrt{4\pi Dt}}
\]  

(3.29)

This equation is identical with the distribution of labelled molecules diffusing from a source into unlabelled but otherwise identical surroundings (eq. 3.21) calculated
from Fick’s second law. The generalization to a three-dimensional isotropic system is straightforward. Since movement in the three principal directions is assumed to be uncorrelated, the three-dimensional propagator may be written as the product of the three monodimensional propagators:

\[ P(r, t) = P(x, t)P(y, t)P(z, t) = \frac{e^{-r^2/(4Dt)}}{(4\pi Dt)^{3/2}} \]  

(3.30)

which is identical to eq. 3.22. This equivalence shows that for an isotropic and homogeneous fluid the diffusion can indeed be interpreted as resulting from a large number of steps in random directions.

### 3.5 Time correlation functions

Time correlation functions represent another powerful statistical tool linking the MD trajectory to measurable properties. The time correlation function of two variables \( A \) and \( B \) is:

\[ C_{AB}(t) = \langle A(0)B(t) \rangle \]  

(3.31)

\( C_{AB}(t) \) is the average of the product of \( A \) and \( B \) evaluated at two different times spaced by \( t \); accurate results are obtained by including in the average as many independent instances of these quantities as possible. Values of \( C_{AB}(t) \) close to 1 indicate a high degree of correlation. For identical functions, the autocorrelation function \( C_{AA}(t) \) gives a clear picture of the dynamic behavior of \( A(t) \), with an absolute maximum at \( t=0 \) and additional maxima (minima) at times where \( A \) takes values identical (opposed) to those assumed an interval \( t \) before. A suitable expression to evaluate \( C_{AA}(t) \) from an MD trajectory is:

\[ C_{AA}(t) = \frac{1}{N_o N} \sum_{i=1}^{N} \sum_{t_o}^{N_o} A_i(t_o + t) A_i(t_o) \]  

(3.32)

where \( N \) is the number of molecules and \( N_o \) the number of independent time intervals \( t \) present in the trajectory. To ensure statistical accuracy the time origins included in the average should differ by several time steps (according to the correlation time of \( A \)). Note that \( N_o \) depends on \( t \) and decreases linearly with time; therefore the statistical accuracy of \( C_{AA}(t) \) gets worse at long times. The great importance of time autocorrelation functions in simulations arises from three aspects:

- they give a clear picture of certain dynamical aspects
- their Fourier transforms may often be related to experimental spectra
- their time integrals are directly related to macroscopic transport coefficients

For example the diffusion coefficient is proportional to the (center of mass) velocity autocorrelation function (VACF) according to:

\[ D = \frac{1}{3} \int_0^{\infty} \langle \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \rangle dt \]  

(3.33)
where \( \mathbf{v}_i(t) \) is the center of mass velocity of molecule \( i \); usually, a VACF is calculated for each of the \( N \) molecules and the total VACF is averaged over all VACF's. Nevertheless in the calculation of the diffusion coefficient eq. 3.26 is often preferred because the integration in eq. 3.33 cannot be extended to infinite times, and this source of error is not present with the other method.

The Fourier transform of the autocorrelation function of the total velocity of the system (vector sum of the velocity vectors of single atoms) allow extracting the frequencies of all vibrational motions in the considered system (or subsystem).\(^6\) The power spectrum calculated in this way can reproduce with good accuracy the frequencies of experimental vibrational spectra, but not the band intensities. It is thus possible to test the efficacy of a force field in modelling the vibrational motions of polyatomic molecules and crystalline solids. The vibrational spectra of silicalite and ZK4, as reproduced by the harmonic model described in section 3.6.2, are shown in Fig. 3.2. The

![Vibrational spectra](image)

**Fig. 3.2:** Vibrational spectra of silicalite and ZK4, as reproduced by the harmonic potential adopted for the zeolite lattice

highest frequency bands in Fig. 3.2 are attributed to the stretching modes (symmetric and antisymmetric) of the O-T-O bonds within \( \text{TO}_4 \) tetrahedra. The vibrations of 4- and 6-rings, as well as the O-T-O bending modes give rise to the bands at about 500 cm\(^{-1}\). The lowest frequency bands (\( \sim 300 \text{ cm}^{-1} \)) arise from the “pore breathing”, i.e. the collective motions of atoms that form the cavities, which give rise to periodic fluctuations in the diameter of the pores.

The autocorrelation of the end-to-end \( \mathbf{u}(t) \) versor, aligned to the bond axis, provides useful information on the rotational motion of the molecule:

\[
U(t) = \langle \mathbf{u}(t) \cdot \mathbf{u}(0) \rangle
\]  

(3.34)
$U(t)$ equals 1 at $t=0$, and decays to zero as the molecule rotates about its principal axis. The faster the rotational motion, the faster the decay. The behavior of $U(t)$ is strongly influenced by the density: in gas phase, due to the quasi-free molecular rotations, $\dot{U}(t)$ can reverse its direction with no significant hindering by the other molecules, and $U(t)$ shows large oscillations about zero, with gradually decreasing amplitude. In a liquid and in zeolite channels the rotation is considerably hindered by frequent collisions with the surrounding environment and the inversion of $\dot{U}(t)$ is often incomplete: $U(t)$ directly decays to zero without assuming negative values. The decay is faster for smaller molecules with greater rotational freedom within the cavities. In the silicalite channels, as we will see, larger molecules tend to stay aligned along the channel axis for rather long times, so that $U(t)$ decays much more slowly.

### 3.6 Interaction potentials

The potential energy of the simulated systems may be separated into four contributions:

$$U_{\text{tot}} = U_{\text{zeo}} + U_{z-s} + U_{\text{int}} + U_{s-s}$$

(3.35)

where:

- $U_{\text{zeo}}$ = potential energy of the zeolite framework (or the solvent)
- $U_{z-s}$ = potential energy of the zeolite (solvent)-sorbed molecules interactions
- $U_{\text{int}}$ = internal potential energy of sorbed molecules
- $U_{s-s}$ = intermolecular potential energy of the sorbate-sorbate interactions

For the systems we will consider, the first three terms are always present, while the last term is only present when more than one sorbed species is considered.

### 3.6.1 Rigid vs. flexible models for the zeolite framework

In our simulations the choice of the potential that controls the interaction between the atoms making up the crystalline lattice is crucial, because it affects the extent of energy exchanges and coupling with the sorbed molecules and the fluctuations of the cavity dimensions. These effects should be carefully reproduced if a realistic representation of any chemical phenomenon within zeolites is sought. In spite of that, many previous simulations of zeolitic systems does not include this interaction: the zeolite lattice is kept rigid, with the atoms held fixed at the crystallographic positions. With a rigid framework model the calculation of forces is easier, and longer simulations can be carried out, allowing to study the diffusion of slowly moving adsorbates. However, the rigid framework approximation is a very crude one, which cannot be adequate for simulating reactive processes, where the guest-host energy transfer is essential. On the other hand, the importance of a flexible framework model in the simulation of diffusive processes within zeolites is still debated. The framework oscillations can play a crucial role in the diffusion of species whose size is on the order of the diameter of channels or when cations are sited in such a way as to partially obstruct internal windows.
and passages. It has been shown that while the total system (oscillating framework + sorbed molecules) is microcanonical, a part of it (the sorbed molecules) behaves like a canonical (NVT) ensemble by continuously exchanging energy with the heat reservoir of the zeolite framework. The sorbed molecules thus "see" the motion of the framework like a heat bath. This can have important consequences, among the others, on the kinetic energy fluctuations of the sorbed molecules, which in a microcanonical ensemble are lower than in the canonical one. In a rigid framework the sorbed molecules make up a microcanonical ensemble and their energy distribution is thus narrower compared with the flexible framework. However the kinetic energy distribution in the rigid framework approaches that of a canonical ensemble with increasing particle number. Due to the energy exchanges between the guest molecules, the kinetic energy distribution for a bulk system of 20 molecules already converges to that typical of a canonical ensemble. In any case, in ref. 74 it was shown that the thermal equilibration of the sorbed subsystem is faster in a vibrating framework than what observed in a rigid framework where the only source of thermal equilibration are the interactions between the sorbed species themselves. The difference is even larger for low loadings. In the vibrating framework case collisions are less elastic and energetic because the lattice flexibility makes the cavity walls softer and more able to absorb the impact with the sorbed molecules; lattice vibrations also enhance the number of binary collisions while multiple collisions are inhibited.

Thus there are enough indications supporting the use of a flexible framework model to accurately model any kind of physical process in zeolites. In particular cases (high concentration of sorbed species, whose size is considerably smaller than the channel diameters) it is possible to study the diffusion in zeolite with a rigid framework model. In any case, when more powerful and faster computing resources are available, the benefit of a rigid model in terms of the shorter CPU time required could be insignificant, and in the long run the greater reliability of the flexible model should prevail.

### 3.6.2 The harmonic potential for the zeolite framework

The problem of designing an analytical potential suitable for MD simulation is not trivial. The potential should preserve the topology of the lattice, and in particular the directionality of T-O bonds which make up the single TO$_4$ tetrahedra, in turn interconnected via different patterns. This purpose can be attained by introducing some terms depending on the $\angle$O-T-O and $\angle$T-O-T angles but they are generally three-body interactions which leads to an increase in the computer time required (see section 3.2.1 on page 16). This problem may be solved by a simpler approach: first the total potential energy of the zeolite framework (considered as a sum of pair interactions) is expanded in power series:

\[
U_{zo} = \sum_{i<j} \left\{ U(r_{o,ij}) + \sum_{k=2}^{\infty} \frac{(r_{ij} - r_{o,ij})^k C_k}{k!} \right\}
\] (3.36)

The problem of designing an analytical potential suitable for MD simulation is not trivial. The potential should preserve the topology of the lattice, and in particular the directionality of T-O bonds which make up the single TO$_4$ tetrahedra, in turn interconnected via different patterns. This purpose can be attained by introducing some terms depending on the $\angle$O-T-O and $\angle$T-O-T angles but they are generally three-body interactions which leads to an increase in the computer time required (see section 3.2.1 on page 16). This problem may be solved by a simpler approach: first the total potential energy of the zeolite framework (considered as a sum of pair interactions) is expanded in power series:

\[
U_{zo} = \sum_{i<j} \left\{ U(r_{o,ij}) + \sum_{k=2}^{\infty} \frac{(r_{ij} - r_{o,ij})^k C_k}{k!} \right\}
\] (3.36)
where $U(r_{o,ij})$ is the pair potential for the $i, j$ interaction evaluated at the equilibrium distance $r_{o,ij}$; the $C_k$ coefficients are given by:

$$ C_k = \left( \frac{\partial^k U(r_{ij})}{\partial r_{ij}^k} \right)_{r_{ij} = r_{o,ij}} $$

(3.37)

The term within curly braces in eq. 3.36 does not include the term with $k = 1$ because the gradient is zero at the equilibrium geometry. According to the harmonic crystal approximation\(^{77}\) the constant term $U_{0,ij}$ is neglected because it does not affect the dynamics of the system and the expansion is truncated at the second order. The pair potential is therefore given by:

$$ U(r) = \frac{1}{2} K (r - r_o)^2 $$

(3.38)

The potential thus assumes that the Si-O and O-O interactions are represented by quadratic functions of the displacement from a given equilibrium bond distance. No other possible contacts are included; the initial topology of the framework bonds is retained during the simulation and only first neighbours are considered as interacting atoms. The interactions between nonbonded T and O atoms are not included, but they are implicitly accounted for by using effective pair potential directly obtained from experimental data. The directional character of Si-O bonds is ensured by the O-O potential functions which do not correspond to chemical bonds but take the place of a potential depending on the angle between bond and make the calculations simpler, yet preserving the angles between bonds. In practice this harmonic picture the framework of a zeolite is considered as a three-dimensional network of springs connecting the first neighbors oxygen atoms between themselves, and each silicon atoms to the four oxygens with which it is really bonded. All atoms oscillates harmonically about its equilibrium position: while this approximation allows to reproduce correctly the vibrational dynamics and equilibrium properties of the framework, it cannot be used to simulate dynamical events involving large interatomic distance variations such as melting. Its major advantages stem from the finite range of the interatomic forces, which together with the fixed (constant) connectivity allow to include only a small predetermined list of contacts in the calculation of forces, with a big saving of computer time. The model has been previously applied to anydrous natrolite,\(^{78}\) zeolite $A^{79}$ and silicalite,\(^{80}\) and it has been shown to effectively reproduce the main structural and dynamical properties of the framework. Moreover, it has been recently shown that the harmonic model reliably models the energy exchanges with the sorbed molecules, enhancing the rate of vibrational relaxation of diatomic molecules with bonds oscillating at frequencies close to those of the normal modes of the framework.\(^{81,82}\) The presence of similar resonance effects is expected on the basis of simple mechanics rules concerning coupled oscillators\(^{\ddagger}\), but it is essential to verify that even a simplified model as ours can adequately

\(^{\ddagger}\) The transfer of energy from a vibrationally excited molecule is a quantum phenomenon, being more probable when the energy level gaps of the molecule are close to those of the framework. For harmonic oscillators, the energy level gaps are proportional to the classical frequency, and the quantum energy transfer corresponds to the classical resonance between oscillators, where the maximum energy transfer rate occurs when the frequencies of the oscillators are the same. The dependence of the energy
reproduce them.

The parameters of the harmonic pair interactions are shown in Tab. 3.1. The \( K \) values and the equilibrium distance have been fitted starting from spectroscopic and structural data, respectively.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>( K ) (kJ mol(^{-1})A(^{-2}))</th>
<th>( r_o ) (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O</td>
<td>2.092</td>
<td>1.605</td>
</tr>
<tr>
<td>O-(Si)-O</td>
<td>0.431</td>
<td>2.618</td>
</tr>
</tbody>
</table>

### 3.6.3 Other potentials

Because of the high symmetry of the zeolite frameworks, the average electric field generated by the framework itself is very small or negligible, so that the electric field acting upon an adsorbed molecule is close to the local one generated by the cations. In our simulations only dealuminated zeolites are considered, and no charge-balancing cations are present. Moreover, we only considered nonpolar sorbed species or, in the case of quadrupolar molecules, infinite dilution conditions. Therefore polarization effects due to the electric field generated by the framework and by the other guest molecules are absent, and the dominant intermolecular interactions are weak van der Waals forces. The pair potential most widely used in microscopic simulations where such interactions are dominant, such as liquid argon, is the 12-6 Lennard-Jones (LJ) potential:

\[
V(r) = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]
\]  

(3.39)

This pair potential has a long-range attractive tail of the form \(-1/r^6\), a negative well of depth \( \epsilon \) with a minimum for \( r = 2^{1/6}\sigma \) and a steeply rising repulsive wall at distances less than \( \sigma \). It should be remarked that the pair potentials used in condensed phase simulations are **effective** potentials with parameters adapted to represent the many-body interactions, not directly included in the force field. For instance, the \( \epsilon \) and \( \sigma \) values of the pair LJ potential for liquid argon are different the corresponding values of the isolated dimer. In MD simulations of zeolites the interaction between the silicon atoms and the sorbed species is usually neglected: the radius of Si is much shorter than the radius of O, due to the partial ionicity of the Si-O bond; one therefore assumes that silicon atoms are well-shielded by the oxygen atoms, and their contribution to the guest-host interaction can be neglected. The \( \epsilon \) and \( \sigma \) parameters for the interactions between unlike atoms can be approximated using the mixing rules:

\[
\begin{align*}
\sigma_{AB} &= \frac{1}{2} \left[ \sigma_{AA} + \sigma_{BB} \right] \\
\epsilon_{AB} &= \left[ \epsilon_{AA} \epsilon_{BB} \right]^{1/2}
\end{align*}
\]

(3.40)

transfer rate on frequency is not so different in quantum and in classical mechanics, so that, even if oscillators in real systems often are not exactly harmonic, from the above considerations it appears that a **classical** model which adequately reproduces resonance effects can be used to model vibrational energy exchanges and all the associated events.
3.6 Interaction potentials

where $\sigma_{AA}$ and $\epsilon_{AA}$ are the self-interaction parameters between identical atoms, which
in the case of zeolitic oxygens are $^{85} \sigma_{OO} = 2.529$ Å and $\epsilon_{OO} = 1.51$ kJ mol$^{-1}$.

In the simulations of polyatomic molecules several atoms are frequently grouped
and considered as a single interaction site: for example we represent the two methyl
groups of ethane as two interaction sites centered on the positions occupied by the
carbon atom. In this way a smaller number of interaction sites (two instead of eight)
are considered, saving lots of computer time. Moreover, by not explicitly including
the hydrogen atoms in the dynamics a larger time step can be adopted, because the
high-frequency oscillations of C-H bonds need not to be accounted for. The LJ interaction
parameters are usually extracted from previous simulations, adapting them to the
specific system considered. For example, the CH$_3$(ethane) $-$ O(zeolite) LJ interaction has
been modeled through the LJ parameters previously optimized in order to reproduce
some experimental properties of methane sorbed in silicalite in MD simulation where
the CH$_4$ was represented as a single spherical interaction site.$^{70,71,86}$ Analogously the
parameters we use for the interactions of Cl, Br and I with the oxygen atoms are the
same as those used to model the pair interactions between Ar-O, Kr-O and Xe-O in
zeolites. This is possible because the number of electrons and the mass of halogen atoms
are close to those of the rare gases which follow them in the periodic table, and many
simulation studies of rare gases in zeolites are available, providing adequate interaction
parameters.$^{87,88}$ The cutoff radius of the LJ interaction sphere has been fixed to 10 Å
in all cases.

The $U_{s-s}$ term in eq. 3.35 represent possible interactions between sites belonging to
different adsorbed molecules. The interaction between two different ethane molecules
is the sum of the interactions between all possible pairs of sites in the two molecules.
Therefore the potential energy of interaction between two molecule $i$ and $j$ is given by:

$$U_{ij} = \sum_{a=1}^{2} \sum_{b=1}^{2} u(r_{ab})$$

(3.41)

where $r_{ab} = |r_{ia} - r_{jb}|$ is the distance from site $a$ in the molecule $i$ to site $b$ in the
molecule $j$; $u(r_{ab})$ is the LJ pair potential between these sites.

The internal potential energy $U_{int}$ of the diatomic molecules we will consider (ethane
and halogens) corresponds to the chemical bond, which is always modeled by means of the
Morse potential related to the electronic ground state of the molecule:

$$U(r) = D_v \left\{1 - e^{-\beta(r-r_0)} \right\}^2$$

(3.42)

where:

$$\beta = \sqrt{\frac{\mu}{2D_v}} \quad \omega = 2\pi c \nu$$

(3.43)

In eq. 3.43 $\mu$ is the reduced mass and $\omega$ is the stretching frequency of the bond,
expressed in Hz; $D_v$ is the bond dissociation energy and $r_0$ is the equilibrium bond
length. The expressions of the internal potential for the other molecules considered
will be discussed in the following.
Chapter 4

Dissociation-recombination reactions in zeolites

4.1 Main interests and objectives

The dissociation-recombination process may be shortly described as follows: first, the adsorption of UV-visible radiation induces the excitation of the molecule above the dissociation limit. In gas-phase the dissociation is almost immediate and in a few picoseconds the two photodissociated fragment may depart by hundredths of Å from one another. In a dense gas or in a liquid solvent this picture drastically changes: the dissociating atoms may be caged in by the surrounding molecules and be induced to recombine before they can separate from one another. Such recombination is possible by the removal of the relative kinetic energy of the dissociating atoms by collisions with solvent molecules. This event is termed geminate recombination to highlight that it is the recombination between two fragments coming from the same initial molecule. The time scale of this process has represented a central problem in the liquid-phase reaction dynamics.\(^9\) When the dissociated radicals succeed in escaping the solvent cage they can collide with fragments coming from different molecules (nongeminate recombination), or they can re-encounter each other after having covered considerable distances.

However the basic distinction usually made is between primary recombination of two radicals that never completely escaped the original cage and secondary recombination, in which the photofragments have been separated by (at least) a solvent molecule before recombining. In the first case the recombination is fast, as the distance between the radicals never exceeds the diameter of the solvent cage. The secondary recombination is slower (some tenths of picoseconds) and more complicated, being affected by the relative diffusion of the radicals in the solvent. In the following we shall solely consider primary recombination processes. The last stage of the recombination process is the vibrational relaxation of the formed molecule: the recombination originates a vibrationally excited species and if the solvent is not able to remove the excess energy the radicals will dissociate again.

Our interest in the recombination of two dissociated radicals in zeolites arises from two basic factors:

- The photodissociation-recombination of iodine has been extensively studied in
the last 60 years,\textsuperscript{90} both experimentally\textsuperscript{91-105} and by theoretical methods.\textsuperscript{106-113} Thorough studies have been performed in a wide range of densities from gases to liquids\textsuperscript{114,115} and recently in solid matrices\textsuperscript{116} and clusters\textsuperscript{117-119} too. The vibrational relaxation of the iodine molecule formed through geminate recombinations in various solvents has been the subject of many studies aimed at interpreting the nature of the solvent-solute interactions that bring about the energy dissipation.\textsuperscript{99,104,109,120} This great interest stems from the fact that a process easy to analyze both through spectroscopic and simulation methods may provide a big amount of data concerning the effect of the solvent on the reaction dynamics, on the mechanism of energy transfer and its dependency on basic parameters such as solvent density and structure. Moreover, the study of this process at the microscopic level allowed to test the validity of various theories and reaction models.\textsuperscript{93,121,122}

- The photochemistry of compounds adsorbed in zeolites, exploiting many of their specific properties (see below), results in a particularly suitable starting point to obtain comparative information on the influence of a certain structure on the catalytic activity, related in particular to the guest-host energy exchange and on the effect of the topology of the cavities on the dynamics and the probability of reaction.

It should be remarked that this work is not addressed to study the detailed features of the dissociation-recombination of iodine or the other diatomic species considered. We are mostly interested in observing and comparing the dynamics of such process in different structures, in order to understand and illuminate new aspects of the catalytic activity of zeolites. This class of reactions is used here mainly as a “probe” to explore the diverse dynamical response of two zeolites, without considering the exact reaction dynamics. By observing how and to what extent a certain structure is able to limit and adsorb the separation of the excited radicals following their dissociation we can obtain important indications on the action of that structure. Clearly the nature of these indications will be rather general, i.e. we expect that our simulations will give a reliable reproduction of phenomena connected to the overall action of a zeolite but we cannot hope that they also exactly model the reaction dynamics of the specific recombination process. Indeed, in order to make the calculations feasible in a reasonable time, a simplified model for the reaction has been adopted, which does not consider the participation of excited electronic states in the dissociation-recombination process; the curve-crossing dynamics should be included in the simulations in order to achieve a more detailed description of the exact reactive dynamics. It is well known that the iodine geminate recombination results from multiple crossings of excited bound or dissociative electronic surfaces, which vary according to the wavelength used to dissociate the molecule.\textsuperscript{123} Recently, methods for incorporating nonadiabatic electronic transitions in molecular dynamics simulations have been developed,\textsuperscript{124} but they are computer resources demanding, and we preferred to model the recombination as occurring on a single electronic surface. This strong simplification allows of performing a large enough number of trajectories of suitable time length (which are required to reach the main purpose of our study) in a reasonable calculation time. However, usually MD simulations effectively reproduce energy transfer and solvent caging effects,
and even with a simplified model reasonable predictions on the time scales for geminate recombination should arise. In fact the recombination times for iodine in a liquid solvent estimated with our model are in good agreement with experimental and theoretical data.

Finally, note that the dissociation-recombination of iodine, after becoming a prototype for investigating such kind of processes in various environments, has recently been studied in the nanocavities of cycloextrins. In such work the comparison between the dynamics in water and tetrahydrofuran “classical” solvents has been exploited to highlight effects of the confinement such as the reduced degrees of freedom and modified coupling to the solvent “heat reservoir”. This consolidated our interest to exploit these processes to address the more general effects of a confined geometry on the reaction dynamics.

### 4.1.1 Zeolite photochemistry

In solution, the properties of the solvent, such as polarity and viscosity, determine the photochemical behavior of the system to a great extent and likewise any intrazeolite photochemistry is heavily influenced by the zeolite environment. The confinement within the cavities of zeolites determines the fate of the reactants and radicals formed upon irradiation by restricting their relative mobilities. For example, while in solution the intermediate radicals readily diffuse apart to form all possible coupling products in statistical ratios, in many cases the zeolite could severely inhibit the radicals movement (hindering their out-of-cage diffusion, which would lead to random radical coupling); therefore it is possible to selectively obtain only the geminate cage recombination products. Moreover, the mobility restrictions and size-selectivity of zeolites can considerably differ from each other and lead to different product distribution after the photochemical excitation. The protective power of the zeolite cavities may stabilize transient species that would have much shorter lifetimes when generated in solution thus allowing new reaction pathways involving these transients. Finally, the zeolite active sites can in some cases directly and actively cooperate in the success of a photochemical reaction. All these effects are rather complex; however they are undoubtedly also in many reactive processes (other than photochemical). A broad range of zeolite properties is exploited and illuminated in the photochemical processes: their study, even from a general point of view as in our case, allows highlighting various basic properties of the zeolite activity.

### 4.2 Simulations in silicalite and CCl₄

We initially focused on the iodine dissociation-recombination in silicalite and in a liquid solvent modeling CCl₄. The most part of both experimental and theoretical studies of the iodine recombination process has been conducted in CCl₄ and liquid xenon as solvents. In our model each CCl₄ molecule is represented as a LJ sphere; the absence of an internal structure implies that the liquid solvent we consider is more similar to liquid xenon, in particular when aspects connected to the energy exchanges are investigated. As noted above, we are mainly interested in the comparison between two reaction environments with deep differences both structural and related to the
mechanism of energy exchange with the solute. Indeed, the deactivation of the vibrationally “hot” molecule occurs on two different collisional pathways: inside the zeolite, the excess vibrational energy of the molecule can be transferred to the vibrational internal modes of the framework, while the adopted structureless model for the liquid solvent allows for (solute) vibrational to (solvent) translational energy transfers only. The relative importance of V-V or V-T transfer mechanisms in the deactivation of the excited oscillator has been the subject of several studies in the past;\textsuperscript{90} intuitively, it may be argued that the coupling between the vibrational modes could probably lead to a faster relaxation of the excited molecule inside the zeolite. However, previous works\textsuperscript{109,112} showed that in liquid solvents the V-T deactivation mechanism may be competitive with V-V energy transfer. In particular, V-T transfer seems to dominate when the excited molecule moves in the upper half of the Morse well. The V-V mechanism should only prevail after the lower half of the well has been reached. The present study of the recombination process in the two environments, with the choice of a structureless model of CCl\textsubscript{4}, entails a direct comparison of the effectiveness of the two energy-transfer mechanisms: in each environment a different relaxation mechanism is active. Other effects, like the different masses and density of the two media could also play an important role in the relaxation phenomenon, and they will be thoroughly examined.

4.2.1 Method

In both liquid and silicate cases, a total of 200 MD trajectories were analyzed. Each trajectory started with the dissociation of a stable iodine molecule in an equilibrated environment. In a real experiment the adsorption of light with $\lambda = 5300$ Å can produce almost instantaneously (< 1 ps) two dissociated iodine radicals. Therefore, at the beginning of each simulation, dissociation was induced by attributing to each iodine atom a kinetic energy corresponding to $0.5 h\nu$ (equal to 112.9 kJ mol\textsuperscript{-1}) along the axis of the molecule. After the initial dissociation, each trajectory was followed for a maximum of 60 ps. The methods followed to generate distinct and uncorrelated trajectories in either environments will be described below. Recombination was considered to have occurred when the I-I distance fell below an empirical \textit{inner cutoff} $R_{ic}$, provided that no further dissociation was observed. By direct inspection of the trajectories, a value of 4.30 Å has been assigned to the inner cutoff: indeed, once the dissociated atoms came closer than this distance, successful stabilization of the formed molecule was found to be very probable. In some cases collision-induced recrossings of the critical distance were observed: this occurs when the molecule is not quickly stabilized by the solvent. The possibility of a later read dissociation was accounted for by fixing a secondary cutoff $R_{sc}$ at 4.8 Å, which is the “external bound” for the reaction. If, after colliding, the two atoms were not able to dissipate the excess vibrational energy and their distance again exceeded 4.8 Å, a \textit{redissociation} event was accounted for. Note that after the redissociation the two atoms may definitely separate or collide again, up to the eventual final recombination. We will term the first event a complex dissociation and the latter a complex recombination, where “complex” means that they are preceded by several ineffective collisions between the two radicals. In order to shorten the calculations, an outer cutoff at 13 Å was also included: when the distance between the two dissociated fragments
reached this value, a later encounter was rather unlikely on the examined timescale (60 ps) and the trajectory was terminated. To sum up, the possible events accounted for have been divided in two major groups: reactive (i.e., ending in the stabilization of the recombined molecule), and non-reactive (i.e., ending with the two radicals separated). Within these two groups, we adopted the following abbreviations:

- **RS**: simple recombinations. A single, definitive crossing of the internal cutoff was observed.
- **RC**: complex recombinations. The final recombination is preceded by several crossings of the $R_{ic}$ and $R_{sc}$ distances.
- **DS**: simple dissociations. The two dissociated radicals directly separate, without any previous encounter.
- **DC**: complex dissociations. The final dissociation is preceded by several ineffective collisions.

### 4.2.2 Interaction potentials and generation of reactive trajectories

The radicals always interacted via a Morse potential describing the $X$ electronic ground state of the iodine molecule,\cite{140} with parameters $r_e = 2.666$ Å, $D_e = 148.703$ kJ mol$^{-1}$ and $\beta = 1.867$ Å$^{-1}$. The iodine and oxygen atoms of the zeolite structure interacted via a LJ potential whose parameters are the same as Xe-O,\cite{87} reported in Tab. 4.1. From these values, using the zeolite oxygen LJ parameters (sec. 3.6.3), the combining rules (eq. 3.40) give $\sigma_{I-O} = 4.02$ Å and $\epsilon_{I-O} = 1.998$ kJ mol$^{-1}$. The latter parameters were used to obtain the I-CCl$_4$ parameters reported in Tab. 4.1 (the source of the LJ parameters for pure tetrachloromethane is ref. 141).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$\sigma$ (Å)</th>
<th>$\epsilon$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-O</td>
<td>3.2745</td>
<td>1.737</td>
</tr>
<tr>
<td>I-CCl$_4$</td>
<td>4.645</td>
<td>2.489</td>
</tr>
<tr>
<td>CCl$_4$-CCl$_4$</td>
<td>5.27</td>
<td>3.101</td>
</tr>
</tbody>
</table>

Table 4.1: Intermolecular potential (LJ) parameters for iodine

The liquid solvent was modeled by 256 particles enclosed in a cubic simulation box, with a side of 34.487 Å, reproducing the liquid density of the tetrachloromethane at 300 K. At the beginning of each trajectory, a diatomic molecule was created in the liquid equilibrated configuration by substituting two randomly-chosen nearest neighbor tetrachloromethane molecules with two iodine atoms. Then the two atoms were approached along the axis of the molecule at the equilibrium bond length and the system was equilibrated for 1000 time steps (each time step being equal to 10 fs). After this initial equilibration, dissociation was induced and the trajectory followed for further 60 ps (or until the outer cutoff was reached). The next trajectories always started from the same equilibrated configuration, each time replacing a random pair of molecules different from those chosen in the previous trajectories.

The simulation box in the silicalite case consisted of $2 \times 2 \times 2$ crystallographic cells,
resulting in 2304 framework atoms (768 Si and 1536 O). The box volume was 42696.2 Å³, which is close to the volume of the simulation box in the liquid case (41017.2 Å³). The time step (1 fs) was shorter than in the liquid case, in order to accurately describe the fast vibrational motions of the framework atoms (Fig. 3.2). In the zeolite case, the initial relaxed system was created by introducing a stable iodine molecule in a channel of the silicate framework and then equilibrating the configuration for 200 ps. In each trajectory the molecule was allowed to diffuse for a 10 ps interval, at the end of which all information useful for the next trajectory was recorded; then dissociation was induced and the dynamical evolution of the system was followed. The next trajectory was started from the previously stored configuration and the same procedure was repeated, so that the initial iodine molecule moved inside the channels of the silicalite, independently of any dissociation, exploring a great part of the available void space. In this way it has been possible to carry out the dissociation and to follow the dynamics in different regions of the silicalite starting with completely equilibrated configurations.

4.3 Analysis of reactive trajectories

4.3.1 Recombination probabilities and rates

Tab. 4.2 shows the percentages of reactive events observed during the 200 trajectories in both solvents. The average time between the initial dissociation and the first encounter and that between the dissociation and the final recombination are also reported. The latter time is larger due to the contribution of complex recombinations, which require several collisions before the final recombination.

<table>
<thead>
<tr>
<th></th>
<th>CCl₄</th>
<th>silicalite</th>
</tr>
</thead>
<tbody>
<tr>
<td>RS</td>
<td>59.5%</td>
<td>26.5%</td>
</tr>
<tr>
<td>RC</td>
<td>19%</td>
<td>8.5%</td>
</tr>
<tr>
<td>DS</td>
<td>19.5%</td>
<td>60%</td>
</tr>
<tr>
<td>DC</td>
<td>2%</td>
<td>5%</td>
</tr>
<tr>
<td>t_C(ps)²</td>
<td>2.2±0.4</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td>t_R(ps)²</td>
<td>2.6±0.4</td>
<td>4.0±0.8</td>
</tr>
</tbody>
</table>

²Average first-collision time
³Average recombination time

The liquid solvent shows a greater efficiency in promoting recombination: in almost 80% of the trajectories the two iodine atoms recombine, and the small difference between the mean times of first collision and recombination denotes a considerable efficiency of collisions in leading immediately to recombination. In silicalite the encounter between atoms after the initial dissociation is less probable and, when it occurs, it appears to lead to the reaction less effectively than in the liquid phase. Indeed the time between the first collision and the final recombination is considerably larger than in CCl₄; moreover, if we analyze only the trajectories showing at least one encounter, in silicalite the fraction of ineffective (dissociative) encounters is much larger than in
the liquid solvent: the DC/[RS + RC + DC] ratio is 12.5% in silicalite and 2.5% in the liquid. The different structural organization of the two media is obviously involved in these differences. In dense solvents the dissociating atoms may be trapped in a cage of surrounding molecules, increasing the primary recombination yield*. In silicalite the adsorbed molecule does not suffer any liquid-like caging and explores, driven by the surface oxygen atoms force field, channels and cavities with a relevant free volume available. In such a situation the dissociation will cause, in most cases, the iodine atoms to depart more easily away from each other, leading to a lower recombination probability; moreover, the higher fraction of ineffective encounters and the considerable time between the first encounter and the final recombination seem to denote that the stabilization of the newly formed molecule is slower in silicalite. The average recombination times in CCl₄ is 2.6 ps; due to the previously mentioned limitations of the model (in particular, the absence of internal degrees of freedom for CCl₄ and the exclusion of excited state dynamics) a meaningful comparison could rather be made with previous works regarding the iodine dissociation-recombination in liquid xenon, whose mass and size are similar to CCl₄. The MD simulations of ref. 112, which consider only a single repulsive surface coupled to the ground state, lead to geminate recombination times of 2.5–4 picoseconds at the various densities considered. This is in agreement with previous simulations on similar systems,¹⁰⁶–¹⁰⁸,¹¹²,¹¹⁴ as well as with our results. Moreover, the agreement with experimental results⁹⁹,¹⁰¹ is connected to the observation that the curve-crossing process (i.e., the jump from a repulsive unbound surface or an excited bound to the ground state, preceding the recombination) is very fast in the system here considered. For this reason MD simulations could adequately predict recombination times without explicitly including surface-hopping models, as in the present study: the relevant processes over the recombination time scales occur after the rapid jump to the ground state. The inclusion of all electronically excited states in the simulation (the most relevant are about ten⁹⁰) could probably slow down the recombination: the occasional trapping of the molecule in an excited bound electronic state may slow the recombination rate down by a factor of five.¹²³ The present simulation data should therefore be considered as lower bounds to the values of geminate recombination times.

The distributions of the observed recombination times are shown in Fig. 4.1 for both liquid and zeolitic cases. It is interesting to notice the similarity of the curves obtained in the two phases. A high probability of recombination in the first 2 ps after the initial dissociation and then a regular decrease to very small values are observed, the two cases differing only in the rate of occurrence of such a decrease, which is slower in silicalite. This feature agrees with the previous observations: several collisions are often needed to form the molecular species in silicalite.

4.3.2 Relaxation processes: energies

In order to better understand the previous data, further investigations on the energy relaxation processes of the excited species formed by dissociation and by recombination

---

* At the same time, the cage hinders the encounter of atoms which have escaped from it. This last effect leads to a time scale of tens of picoseconds for secondary recombination, but actually none of the observed reactive trajectories shows such a behavior: i.e., all the recombinations observed in the liquid involve atoms which never completely escaped from the first solvent cage
have been carried out. In the first case, while in the zeolite the dissociated species retain a great part of their high initial kinetic energy, in the liquid the two dissociating atoms spend a part of it in deforming the surrounding solvent cage. This is shown in Figs. 4.2(a) and 4.2(b), where the kinetic energy of the two atoms, in the first 2 ps after the dissociation, has been reported for tetrachloromethane and silicalite cases respectively. A greater decrease of the kinetic energy curve is recorded in the liquid case. On the contrary, when the atoms have recombinated the silicalite appears to be more efficient in the dissipation of the excess vibrational energy of the molecule. This is shown in Figs. 4.3(a) and 4.3(b), reporting the vibrational energy of the molecule relaxing in CCl₄ and silicalite respectively, averaged over all the trajectories which lead to simple recombinations\(^1\). Note that the initial energies are similar in Figs. 4.3(a) and 4.3(b), but if we included in the average all the reactive events, the initial vibrational energy in silicalite would be considerably higher: -1.2 kJ mol\(^{-1}\) in silicalite vs. -8.8 kJ mol\(^{-1}\) in the liquid). Larger fluctuations are recorded in the molecular vibrational energy for the liquid case. We further discuss this point below.

### 4.4 Relaxation processes: solvent-solute collisions

The role of iodine-solvent collisions was also investigated. The collisions of the zeolite oxygen atoms or the CCl₄ molecules with the dissociated radicals, as well as with the atoms of the diatomic molecule, have been recorded in the first picosecond following:

\(^1\)The other (complex) recombinations could not have been included in the average because they would have complicated the interpretations of results, due to the multifarious encounter-separation cycles (at varying times) between the first encounter and the final recombination.
4.4 Relaxation processes: solvent-solute collisions

**Fig. 4.2:** Kinetic energy of the iodine atoms in the first 2 ps following the dissociation

**Fig. 4.3:** Vibrational energy of the iodine molecule in the first 50 ps following the recombination
a) the initial dissociation; b) the eventual recombination (if any). A collision was accounted for whenever the distance between two atoms fell below the corresponding LJ parameter \( \sigma \), i.e. when the interaction energy became positive. The frequency, duration (i.e., the time interval when the distance remained less than \( \sigma \)) and total energy loss were averaged over all guest-host collisions, and are reported in Tab. 4.3. Note that there the I-solvent \( \Delta E \) refers to the average kinetic energy lost by the two radicals in the collisions after the initial dissociation, while the I\(_2\)-solvent \( \Delta E \) represents the total internal energy lost by the formed molecule in the collisions after the recombination.

<table>
<thead>
<tr>
<th></th>
<th>I-CCl(_4)</th>
<th>I(_2)-CCl(_4)</th>
<th>I-O(_{zeo})</th>
<th>I(<em>2)-O(</em>{zeo})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency (ps(^{-1}))</td>
<td>9.6±0.4</td>
<td>6.4±0.5</td>
<td>13.1±0.6</td>
<td>9.1±0.8</td>
</tr>
<tr>
<td>( \Delta E ) per collision (kJ mol(^{-1}))</td>
<td>10.7±1.7</td>
<td>0.9±1.1</td>
<td>20.0±1.2</td>
<td>5.0±1.0</td>
</tr>
<tr>
<td>Duration (fs)</td>
<td>176.1±2.3</td>
<td>131.0±5.0</td>
<td>96.0±3.0</td>
<td>67.0±4.0</td>
</tr>
</tbody>
</table>

When a single, highly energetic, atom is considered (first and third column in Tab. 4.3), tetrachloromethane shows the better dissipative process. It is characterized by a lower number of collisions in the unit time, but also by a greater efficiency in the energy transfer process for the single collisions, together with a longer duration of the single collisions. Conversely, after the recombination the opposite happens. Now (columns 2 and 4 of Tab. 4.3) a greater efficiency in the excess energy dissipation pertains to the silicate framework, again with a lower duration of collisions but with a difference of almost one order of magnitude in the energy lost by the oscillator per collision. The liquid solvent seems to better absorb the dissociation of the two atoms: the kinetic energy relaxation of the dissociated radicals is favored by the similarity of the colliding masses; the radicals dissipate of their high kinetic energy through a direct transfer to translational solvent motion, and this mechanism seems to be very effective in the liquid. After the reaction the energy transfer process between the silicate framework and the vibrationally excited molecule appears more efficient, notwithstanding the short duration of the collisions. It is well known that resonance between vibrational levels can significantly enhance the rate of energy transfer.\(^{81,82,109}\) The vibrational relaxation of a molecule is enhanced by the presence of solvent vibrational levels whose separation is comparable to that of the solute vibrational levels. This point resembles the classical picture of two coupled oscillators, whose best energy exchange is achieved when their fundamental frequencies match. In practice the efficiency of any vibrational energy transfer is roughly determined by the power spectrum of the solvent: the transition rate from one vibrational level to another is proportional to the magnitude of the power spectrum of the solvent at the transition frequency. Near the dissociation limit, the frequency of the “hot” molecule is significantly lower than its resonant ground state value (\( \omega \sim \omega_0/4 \), where \( \omega_0 = 214\text{cm}^{-1} \) is the equilibrium frequency\(^{109}\)). In principle this should favor the vibrational relaxation in the liquid: the power spectrum of the structureless CCl\(_4\) (Fig. 4.4) only presents “translational” frequencies below 100 cm\(^{-1}\), while in the vibrational spectrum of silicalite (Fig. 3.2) the lowest-frequency band is above 250 cm\(^{-1}\).

Therefore the V-T transfer in the liquid should be more efficient of the V-V transfer in silicalite. The fast vibrational relaxation of iodine just after the recombination
4.4 Relaxation processes: solvent-solute collisions

Fig. 4.4: Tetrachloromethane power spectrum (Fourier transform of the VACF at 300 K)

in chlorinated solvents (CCl₄, CHCl₃, CH₂Cl₂) was previously explained on similar grounds:⁹⁰,⁹⁹,¹⁰⁹ the small gap between the vibrational levels at the top of the Morse curve favor the V-T transfer, but later the vibrational gap increases and the V-V transfer dominates over the V-T one. These experimental data involve solvents with an internal structure, which simultaneously allow both transfer routes. Nevertheless their conclusions should cover our simulations too, where the two mechanisms act separately. Our results show that the V-V transfer in the zeolite is always (i.e., at any time after the recombination) more efficient, contradicting what could be expected on the basis of the frequency overlap alone. Clearly in a detailed explanation of this phenomenon other effects than just the frequency overlap should be considered. The flexible network of strongly bonded oxygen atoms is able to absorb and redistribute within the lattice the impact of the colliding diatomic molecule with greater ease, compared with the compact distribution of heavy spherical atoms of the liquid. A collision with the liquid spheres will return a larger fraction of the vibrational energy to the molecule; the diatomic molecule-CCl₄ is more elastic, as highlighted by the large fluctuations in Fig. 4.3(a). If a flexible model for tetrachloromethane was used, leading to other possible energy-exchange channels with the molecule, the collisions would be probably “softer” (and the energy fluctuations smaller), as in the zeolite case. The model we adopted is more akin to a monoatomic solvent, as already discussed; the first conclusion is that the zeolite is more efficient in the stabilization of the molecule formed by recombination, compared to a structureless liquid solvent.
4.4.1 Interconversion between internal energy modes

The energy relaxation channels have been further analyzed in terms of energy exchange between the oscillator internal modes. The total energy of the molecule was separated into translational, rotational and vibrational parts according to the following expressions:

\[
E_{\text{TOT}} = \frac{1}{2}(v_1^2 + v_2^2) + V(R)
\]  
\[E_{\text{TRASL}} = \frac{1}{4}(v_1 + v_2)^2 \]
\[E_{\text{VIB}} = \frac{1}{4}m \left[ \left( v_1 \cdot \frac{R}{R} \right) - \left( v_1 \cdot \frac{R}{R} \right)^2 \right] + V(R) \]
\[E_{\text{ROT}} = E_{\text{TOT}} - E_{\text{TRASL}} - E_{\text{VIB}} \]

where \( m \) is the mass of an iodine atom, \( v_i \) is the velocity vector of \( i \)-th atom and \( V(R) \) is the Morse potential energy.

In Fig. 4.5 the mean energies of the oscillator internal modes are reported in the first 10 ps after the recombination event while Fig. 4.6 shows in more detail the trend obtained in the first picosecond. This enlargement highlight the continuous transformation of vibrational into rotational energy, and vice versa, which follows the oscillation of the molecule and is more marked for the liquid where the vibrational energy fluctuations are greater. The energy flux between translational and rotational modes is larger in the zeolite and already in the first picosecond following recombination (Fig. 4.6(b)) an appreciable V-R and then R-T flux is evident. After that (Fig. 4.5(b)) the vibrational energy seems to decrease almost independently with respect to the rotational and translational motions. In the liquid solvent a stronger link between the vibrational and rotational motions is always present, while the translational energy is less involved in the overall relaxation. The excess vibrational energy can be directly (i.e., without previously passing through rotational or translational modes) transferred to the zeolitic environment through the efficient V-V coupling. In the liquid case this mechanism is inactive, and the vibrational energy needs to be converted in rotational energy so that the solvent translational modes are able to accept it. Indeed Fig. 4.5(a) shows that a stronger link between the vibrational and rotational motions is always present in the liquid.

4.5 Outline of the main effects of the solvent topology

Let us summarize the main points highlighted up to now, concerning the correlation between the solvent topology and the recombination dynamics. Due to the worse energy dissipation mechanism soon after the dissociation, in silicalite the radicals collide with a higher kinetic energy than in the liquid. The direct result is a greater initial
**Fig. 4.5:** Mean energies of rotational (dashed curve), translational (continuous curve) and vibrational (lower curve) modes in the first 10 ps after recombination in tetra-chloromethane.

**Fig. 4.6:** Enlargement of Fig. 4.5 showing in greater detail the first picosecond
energy of the formed molecule, which results less stable than the molecule formed in the liquid solvents, notwithstanding the greater efficiency characterizing the single collisions of the molecule with the silicalite lattice. According to the latter effect, silicalite might be a better “solvent” for the recombination process, but the lack of a suitable cage leads to a lower percentage of recombinations, due both to the worse energy dissipation of dissociated atoms and because it is often unable to prevent a consistent departure of the dissociating radicals. The silicalite structure is rather “open”, i.e. the channels diameter is always large enough to let the iodine diffuse easily, and no narrow passages are present. At this point further investigations in a ZK4 zeolite, with its three-dimensional network of cages, will be very useful to confirm these comments and illuminate new aspects.

4.6 Simulations of Cl₂, Br₂ and I₂ recombination in silicalite and ZK4

The previous simulations illustrated what kind of information can be obtained by comparing two systems (a crystal and a liquid) where the dissociation-recombination process is simulated by means of a simplified reaction model. There it has emerged the need of further simulations in a different zeolitic structure, both to confirm the hypotheses made in the analysis of the previous results, and to gain new data on the basis properties of zeolite structures and how they can affect the mechanism of radical reactions. With the same purpose we shall extend our study to the dissociation-recombination of bromine and chlorine, so as to cover a large spectrum of relative dimensions and other properties both of the reactive species and of zeolite cavities hosting them.

The intramolecular interaction is always modeled by the ground-state Morse potential, and the LJ potential controls the intermolecular interaction with the zeolite oxygen atoms. The Morse curves for the three studied molecules are represented in Fig. 4.7; the corresponding parameters are reported in the following (INSERISCI RIF.), together with the LJ parameters (INSERISCI RIF.). The simulation box for both zeolites is made of 2x2x2 crystallographic cells, corresponding to 4608 atoms (1536 Si and 3072 O) for ZK4 and 2304 for silicalite. In this study as well as in the previous one the adsorbent systems were chosen to be considerably large, so as to avoid spurious recombinations due to the application of the periodic boundary conditions (PBC): if the distance between the two atoms exceeded L/2 (L being the side of the simulation box), the scaling implicit in the PBC would bring them close again, thus altering the recombination dynamics. By adopting large enough values of L, together with the “outer cutoff” distance of 13 Å (< L/2) beyond which the trajectories are ended (vide supra), such possibility is completely ruled out: trajectories always end before the distance between the two atoms may reach L/2. Moreover, the inclusion of a larger portion of the silicate framework in the simulation undoubtedly leads to a more realistic description of the overall action exerted by the host on the guest species.

For each system 200 trajectories lasting 60 ps are carried out as for the iodine-silicalite system. The energy needed to induce the dissociation is obviously different for the three molecules, as the corresponding Morse well depths are different (see Fig. 4.7).
In order to achieve a comparable description of the dissociative event in the three cases, the excess kinetic energy (given by $E_{\text{diss}} - D_c$, where $E_{\text{diss}}$ is the kinetic energy furnished to break the bond, and $D_c$ is the Morse dissociation energy) was kept equal to the value previously adopted for the iodine, i.e., 77 kJ mol$^{-1}$. In this way the two atoms, after having escaped from their Morse well, should have similar kinetic energies in all cases, and their subsequent dynamics should be driven only by the topology and the energetics of the environment. The $R_{ic}$ and $R_{sc}$ values too have to be adapted to the corresponding Morse curve. Since $V_{\text{Morse}}(R_{ic}) = -5.5k_BT$, and $V_{\text{Morse}}(R_{ic}) = -2.2k_BT$ at $T = 300K$ for iodine, we chose the cutoff values for chlorine and bromine in such a way to respect the same relations, thus obtaining: $R_{ic} = 3.73$ Å, $R_{sc} = 4.18$ Å for chlorine, and $R_{ic} = 3.97$ Å, $R_{sc} = 4.44$ Å for bromine. It should be remarked that these values are not crucial for the interpretation of results, as the ultimate fate of a trajectory (reactive or non-reactive) is absolutely independent on them, but they are very useful in the distinction of different recombination routes. For example, we are able to distinguish a simple reaction from a complex one on the basis of the observed number of crossings of the cutoffs, as explained before.

### 4.6.1 Recombination probabilities

Tab. 4.4 reports the results of the 200 trajectories for each system, with the same labels as before. In order to make the comparison easier we report again the iodine-silicalite data. A new class of simple recombinations, labeled RS', has been introduced, representing trajectories in which the two atoms never separate by more than $R_{ic}$, so that the molecule actually fails to dissociate, probably because at the dissociation time
it is placed in an unfavorable position, or in a very confining site. Indeed, such events are present almost exclusively in the more confining silicalite. The label N stands for trajectories in which none of the other events has been recorded: i.e., in the 60 ps following the initial dissociation the two radicals do not recombine nor reach the outer cutoff (actually, very few trajectories fall into this category; this fact shows the adequacy and completeness of the classification criteria adopted).

Table 4.4: Analysis of halogen recombination trajectories in silicalite and ZK4

<table>
<thead>
<tr>
<th></th>
<th>Silicalite</th>
<th>ZK4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TOT RS RC RS'</td>
<td>TOT RS RC RS'</td>
</tr>
<tr>
<td>reactive</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>40.5 27 9 4.5</td>
<td>46.5 22.5 23.5 0.5</td>
</tr>
<tr>
<td>Br₂</td>
<td>33 21 10 2</td>
<td>51 24 27 0</td>
</tr>
<tr>
<td>I₂</td>
<td>35 22 8.5 4.5</td>
<td>64 26 37.5 0.5</td>
</tr>
<tr>
<td>dissociative</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>59.5 52 7.5 0</td>
<td>53.5 35.5 18 0</td>
</tr>
<tr>
<td>Br₂</td>
<td>67 64 3 0</td>
<td>49 33 16 0</td>
</tr>
<tr>
<td>I₂</td>
<td>65 59.5 5.5 0.5</td>
<td>36 22 14 0</td>
</tr>
</tbody>
</table>

Tab. 4.4 shows a considerable influence of the host topology on the fate of the dissociated atoms, and on the probability of recombination: in the iodine case, ZK4 leads to a 29% increase of reactive trajectories compared to silicalite, while the increase is 18% for bromine and only 6% for chlorine. This trend is mostly brought about by steric effects: the narrow windows of ZK4 hinder the passage of a large iodine atom, thus often preventing the definitive separation of radicals, which are kept in the same cage. This phenomenon is somewhat similar to the cage-effect in the liquid, albeit the latter entails much larger restrictions to the relative motion of the two atoms. The structure of silicalite, on the other hand, does not show comparable narrow passages, and the definitive dissociation of radicals is easier. The pseudo-caging in ZK4 is obviously less effective for the smaller Br and Cl atoms, whose escape through the windows is consequently easier. The considerable difference between the DS in the two zeolites confirms this point: in silicalite they are more frequent by 38% for I₂, 31% for Br₂ and 17% for Cl₂. It is interesting to note that Br and Cl atoms show a similar ability to escape from the ZK4 α-cage (i.e., similar percentages of DS events in ZK4), while in silicalite the chlorine unexpectedly gives rise to the least percentage of DC’s (also lower than iodine), in spite of its low weight and dimensions, which should favor the separation of the radicals. Obviously other effects than simple steric considerations come into play in this case: after the dissociation, an ineffective dissipation of the excess kinetic energy of radicals may assist their definitive separation (up to the outer cutoff distance), especially in the less-confining structure of silicalite. Therefore the behavior observed in silicalite could be due to the better dissipation of the excess energy of chlorine atoms (whose mass is closer to that of the framework oxygens, compared to the Br and I masses), which prevents a larger number of DS events to be recorded, and at the same time leads to an higher number of reactive trajectories. In other words, in ZK4 the steric effects have a greater influence on the dynamics, through the cage-like action discussed before, and lead to the order I₂ > Br₂ > Cl₂ for the recombination.
yield, essentially reflecting the different ability of the radicals in leaving the original cage. In silicalite, steric effects are less important, and chlorine shows the highest recombination percentage, because of the less probable separation of Cl atoms, which quickly dissipate their excess kinetic energy; the enhanced rotational freedom of Cl$_2$ in the silicalite channels, compared to Br$_2$ and I$_2$, may also be involved in this point (see section INSERSCI RIF.). We also note that, with the present model, both the dissociation energy and the equilibrium bond length of the Morse oscillator may have some influence on the reaction dynamics. Indeed, they determine the range of the attractive force between the two atoms, which increases going from chlorine to iodine. Therefore, in principle, the iodine recombination could be favored by the longer range of the attractive force between the two radicals. However, our results show that the action of the environment plays the dominant role in the recombination dynamics by means of both steric and energetic effects.

4.6.2 Collisions

We gathered in Tab. 4.5 all the data concerning the radical-zeolite collisions (after dissociation) and the molecule-zeolite (after recombination) collisions. The dissipation rate reported there is simply the product of $\Delta E$ by the collision frequency: it is a useful parameter to collect the main features of the collisions.

| Table 4.5: Parameters of halogen-zeolite collisions |
|-----------------|-----------------|-----------------|-----------------|
|                 | Silicalite after | ZK4 after       |
|                 | dissociation    | recombination   | dissociation    | recombination   |
|                 | Frequency (ps$^{-1}$) |                | Frequency (ps$^{-1}$) |                |
| Cl$_2$          | 19.7 ± 0.8      | 15.0 ± 1.1      | 13.9 ± 0.5      | 6.3 ± 0.7       |
| Br$_2$          | 16.8 ± 1.4      | 11.0 ± 1.0      | 12.7 ± 0.5      | 9.2 ± 0.8       |
| I$_2$           | 13.1 ± 0.6      | 9.1 ± 0.8       | 14.0 ± 0.5      | 7.7 ± 0.7       |
|                 | Duration (fs)   |                | Duration (fs)   |                |
| Cl$_2$          | 81.7 ± 1.7      | 66.0 ± 3.0      | 90.0 ± 1.8      | 65.0 ± 4.0      |
| Br$_2$          | 103.2 ± 2.4     | 71.0 ± 6.0      | 113.0 ± 3.0     | 80.0 ± 6.0      |
| I$_2$           | 96.0 ± 3.0      | 67.0 ± 4.0      | 121.0 ± 3.0     | 81.0 ± 6.0      |
|                 | $\Delta E$ per collision (kJ mol$^{-1}$) |                | $\Delta E$ per collision (kJ mol$^{-1}$) |                |
| Cl$_2$          | 26.2 ± 1.3      | 7.5 ± 1.2       | 25.0 ± 2.0      | 15.2 ± 2.3      |
| Br$_2$          | 26.3 ± 2.0      | 5.6 ± 1.5       | 21.6 ± 1.8      | 10.6 ± 1.8      |
| I$_2$           | 20.0 ± 1.2      | 5.0 ± 1.0       | 14.9 ± 0.9      | 7.6 ± 1.6       |
|                 | Dissipation rate (kJ mol$^{-1}$ ps$^{-1}$) |                | Dissipation rate (kJ mol$^{-1}$ ps$^{-1}$) |                |
| Cl$_2$          | 516 ± 33        | 112 ± 20        | 346 ± 30        | 96 ± 18         |
| Br$_2$          | 442 ± 49        | 62 ± 17         | 274 ± 25        | 97 ± 19         |
| I$_2$           | 262 ± 20        | 45 ± 10         | 209 ± 15        | 58 ± 12         |

The energy loss per collision immediately after the dissociation is about 26 kJ mol$^{-1}$ in silicalite, both for Cl and Br, but the higher frequency of collisions for chlorine leads to a higher dissipation rate, in agreement with the previous hypothesis we made to
explain the large recombination probability observed for Cl₂ in silicalite. Note that also in ZK4 chlorine shows the better dissipation mechanism after the dissociation, but in this case the steric effects are dominant. The direct observation of kinetic and vibrational energy relaxation (Fig. 4.8) of the dissociated atoms and the recombined molecule illuminates further effects.

![Graphs showing kinetic and vibrational energy over time](image)

**Fig. 4.8:** (left) Total kinetic energy of the radicals in the first two picoseconds following the initial dissociation of the diatomic molecule. (right) Total vibrational energy of the diatomic molecule in the 50 picoseconds following recombination. (a) Cl₂; (b) Br₂; (c) I₂. Dashed lines: silicalite; continuous lines: ZK4.

In the 2 ps following the dissociation the energy relaxation is more effective in silicalite in all cases, in agreement with the dissipation rates of Tab. 4.5. An immediate consequence is that, whenever the two radicals collide, the initial energy of the newly-formed diatomic should be lower in silicalite; we directly verified this hypothesis: the initial vibrational energy was averaged over all encounters, and the mean values obtained for silicalite in all the three cases were 8-10 kJ mol⁻¹ lower than for the encounters in ZK4. As the two radicals collide with a lower initial energy the subsequent stabilization of the molecule will be easier and a higher probability for the “simple” reactions (RS) in silicalite should result, regardless of the effectiveness of the following vibrational relaxation, as the molecule is formed in a more stable state. Indeed, the ratio of simple reactions to total encounter numbers (defined as RS/[RS+RC+DC]) is about 62% for silicalite and 33% for ZK4 (surprisingly, these ratios are practically unchanged for all the three species considered). This emphasizes the dominant effect of the initial energy of the diatomic molecule, and thus of the energy relaxation following dissociation: as long as the encounters occur between two highly excited atoms, the outcome of each encounter is determined mostly by their initial energy (depending on the dissipation rate following dissociation) and to a smaller extent by the relaxation route following the collision.
4.6 Simulations of Cl₂, Br₂ and I₂ recombination in silicalite and ZK4

We previously saw that CCl₄– compared to silicalite – showed a better structural capacity to trap the radicals and a more efficient dissipative mechanism after the dissociation. Both effects determine a high recombination probability in the liquid. Now the two aspects are contrasting: ZK4 offer a better structural capacity to keep the radicals together, but silicalite allows a more efficient stabilization of the excited radicals. On the basis of the results of Tab. 4.4 the first effect appears to be more important: indeed even though in ZK4 the molecule often does not form at the first collision due to the large initial energy, the two atoms are kept in the same cage and can collide several times, each time with a lower initial energy, up to the final recombination. This is confirmed by the large percentage of complex reactions (RC) in ZK4.

4.6.3 Recombination times

For each halogen, Tab. 4.6 shows that the different environment does not seem to affect considerably the rate of first encounter and that of the final recombination: no marked differences do exist between the \( t_C \)'s in silicalite and in ZK4, as well as between the \( t_R \)'s. This could confirm that, for this class of reactions (photodissociation-recombination of neutral fragments in inert solvents, at room temperature) the primary recombination rate is largely independent on the molecular details of the environment, while on the other hand the recombination probability is, to a greater extent, solvent dependent, as pointed out by Schwartz et al.¹⁴² There the authors note that the primary recombination time is controlled essentially by the very first collisions between the radicals and the solvent cage surrounding them, which occur at similar times in several different liquids. The geminate recombination process presents a somewhat “universal” behavior independent on the molecular details of the solvent, and this consideration appears to be valid also for zeolitic “solvents”. The first collision between chlorine atoms is only slightly quicker than for the other two halogens, whereas the final recombination of the I₂ molecule is faster than that of Br₂ and I₂, especially in silicalite. This is in line with the preceding discussion: when the first collision occurs, the two chlorine radicals have already transferred to the zeolite a considerable fraction of their excess initial energy, so that the stabilization of the molecule leading to the final recombination is faster.

<table>
<thead>
<tr>
<th></th>
<th>Silicalite</th>
<th>ZK4</th>
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<tbody>
<tr>
<td></td>
<td>( t_C ) (ps)</td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>1.1 ± 0.2</td>
<td>0.90 ± 0.06</td>
</tr>
<tr>
<td>Br₂</td>
<td>1.8 ± 0.3</td>
<td>1.20 ± 0.07</td>
</tr>
<tr>
<td>I₂</td>
<td>1.6 ± 0.2</td>
<td>1.32 ± 0.07</td>
</tr>
<tr>
<td></td>
<td>( t_R ) (ps)</td>
<td></td>
</tr>
<tr>
<td>Cl₂</td>
<td>1.9 ± 0.4</td>
<td>2.4 ± 0.02</td>
</tr>
<tr>
<td>Br₂</td>
<td>4.3 ± 0.8</td>
<td>3.4 ± 0.3</td>
</tr>
<tr>
<td>I₂</td>
<td>4.0 ± 0.7</td>
<td>4.4 ± 0.4</td>
</tr>
</tbody>
</table>
4.6.4 Vibrational relaxation

So far, we have not taken into account the dynamics following the bond formation. Actually the outcome of a trajectory is mainly determined by steric and energetic effects controlling the possibility and the mechanism of an encounter between the radicals. In other words, the dissociation-recombination process in both zeolites can be interpreted almost independently on the vibrational relaxation following the recombination. However such process is interesting in itself, as it offers a deep picture of the modality of the energy transfer from the diatomics to the zeolite (and symmetrically of the reverse process in which the framework assembles energy into a sorbate). As noted by Harris et al.,90 geminate recombination creates an ensemble of diatomic molecules highly excited vibrationally in their electronic ground state, and this represents an unique opportunity to study the vibrational energy transfer between an anharmonic oscillator and its thermal bath.

The single collisions after recombination are considerably more effective in ZK4, as shown in the larger $\Delta E$ (per collision) values of Tab. 4.5. A better vibrational coupling between molecule and framework in the ZK4 case, compared to silicalite, may be due to the sharp band around 500 cm$^{-1}$ in the IR spectrum of ZK4, which should enhance the guest-host energy transfer, especially in the case of chlorine, whose vibrational frequency falls in that region (the equilibrium frequencies of Cl$_2$, Br$_2$ and I$_2$ are 565, 323 and 214 cm$^{-1}$ respectively). However, in the overall relaxation phenomenon other system-dependent collisional properties have to be considered; in particular, the collision frequency, which is mainly determined by the topology of the environment, may be taken into account by referring to the dissipation rate as defined before. For the radical-oxygen collisions after dissociation, the rate of dissipation follows the order Cl > Br > I in both zeolites, strictly corresponding to the better match between the colliding atomic masses. For the collisions of diatomic molecules, additional resonance and steric effects could take part in the energy exchanges together with the above kinetic effects due to the similarity of colliding masses. While in silicalite the order is again Cl$_2$ > Br$_2$ > I$_2$, in ZK4 we have Cl$_2$ ~ Br$_2$ > I$_2$, mainly due to the low collisional frequency observed for the relatively small chlorine molecule in such rather wide environment. Turning to the comparison between the silicates, Fig. 4.8 shows that, for chlorine, the vibrational relaxation in the two environments occurs in a similar way: the two vibrational energy loss curves are almost superimposed. For bromine and iodine the vibrational energy of the excited molecule decays faster in ZK4. Further insight into the effect of the guest-host vibrational coupling is given by the velocity spectra of the excited molecules reported in Fig. 4.9. They have been obtained by Fourier-transforming the velocity autocorrelation functions of the single atoms of the recombined molecule in the 50 picoseconds following the recombinations. Therefore they could give some hints in the interpretation of the vibrational energy curves of Fig. 4.8 that extend to the same time scale. Note that the translational bands (frequency < 100 cm$^{-1}$) are not shown, as they are not directly involved in the vibrational relaxation; the band shown corresponds to the blue shift of the frequencies of of the excited molecule which progressively relaxes to equilibrium, going from the initially lower frequencies to the final equilibrium value.

On one hand, the bands corresponding to the vibration of the excited chlorine molecule and to the low-frequency modes of both silicates considerably overlap, and
Fig. 4.9: Vibrational spectra of excited diatomic molecules in silicalite and ZK4 (continuous lines). The vibrational spectrum of the host silicate (dash-dotted line) is superimposed to each figure for comparison. (a) Cl₂-silicalite; (b) Cl₂-ZK4; (c) Br₂-silicalite; (d) Br₂-ZK4; (e) I₂-silicalite; (f) I₂-ZK4.

This could explain the comparable relaxation rates for Cl₂ in the two environments (Fig. 4.8). On the other hand, for iodine and bromine the molecular vibration band is shifted to lower frequencies and only a weak superimposition is present with the vibrational spectra of both zeolites, which does not account for the faster relaxation observed in ZK4 (Fig. 4.8). Therefore it seems that, when a considerable overlap between the frequencies of sorbates and the spectrum of silicates is present, then the resonance phenomena between vibrational modes can be very important in determining the dynamical behavior of the system. When the molecule oscillates at frequencies outside the vibrational spectrum of the zeolite other system-dependent effects, which would otherwise be obscured by the dominant influence of resonance phenomena, can play a crucial role, e.g. the collision frequency that is accounted for by the dissipation rates defined above. Note that the dissipation rates and the other collisional parameters reported in Tab. 4.5 only sample the first picosecond following recombination, while the energy curves are representative of 50 ps. Therefore the latter better represent the overall relaxation phenomenon, and we referred to them in discussing the resonance effects.
4.7 Diffuse and dynamic properties of the species involved in the reaction

The equilibrium diffuse properties of all the guest species (both diatomic molecules and single atoms) involved in the recombination process have been examined in the two hosts considered. In this case the studied systems consisted of one molecule (or atom) and 576 framework atoms (192 Si and 384 O), corresponding to two unit cells (superimposed along z) for silicalite, or one unit cell for ZK4. These simulation boxes are clearly smaller than those adopted in the previous recombination simulations, because in the present case the molecule does not dissociate, and the distance between the two atoms cannot in any case approach values near $L/2$. Thus spurious effects connected to the application of the periodic boundary conditions are absent, and smaller systems (allowing longer simulations) should give reliable results. In practice all the six different atomic and molecular species present in the previous simulations have been studied. In each case the system was equilibrated in the microcanonical ensemble at $T = 300$ K for 90 ps, then a production run of 20 ns was carried out. Coordinates and velocities of the diatomic (or of the single atom) were stored every 32 fs for later analysis. The MSD and the corresponding diffusion coefficients have been then obtained through the standard method (Eq. 3.25, Eq. 3.26). The MSD curves are shown in Fig. 4.10; they were linearly fitted in the 50-500 ps range, leading to the diffusion coefficients reported in Tab. 4.7.

![Graph showing MSD vs time for Cl, Br, and I in two systems: silicalite (left) and ZK4 (right).](image)

**Fig. 4.10:** Mean Square Displacement of diatomic molecules (right) and single atoms (right) at 300 K; empty symbols: silicalite; filled symbols: ZK4.

The error bars have been obtained from a block analysis of data (Eq. 3.28) by dividing each trajectory in 20 blocks of 1 ns each. The mean potential energies for the guest-host interaction are reported in Tab. 4.8. It is interesting to remark that the guest-host interaction energy is always 35-40 % larger (more negative) in silicalite for all species, due to the more confining silicalite structure. Indeed, the LJ parameters for the guest-host interactions are the same in the two silicates, so that any difference can
only arise from their different topology: the adsorption sites occupied by the molecules sorbed in silicalite are generally more favorable.

**Table 4.7:** Atomic and molecular diffusion coefficients (/10⁻⁹ m² s⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Silicalite</th>
<th>ZK4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>6.7 ± 0.9</td>
<td>3.9 ± 0.7</td>
</tr>
<tr>
<td>Br₂</td>
<td>2.2 ± 0.4</td>
<td>1.9 ± 0.4</td>
</tr>
<tr>
<td>I₂</td>
<td>1.1 ± 0.1</td>
<td>0.28 ± 0.1</td>
</tr>
<tr>
<td>Cl</td>
<td>13.9 ± 1.4</td>
<td>13.2 ± 2.6</td>
</tr>
<tr>
<td>Br</td>
<td>7.2 ± 2.0</td>
<td>8.2 ± 1.0</td>
</tr>
<tr>
<td>I</td>
<td>3.1 ± 0.6</td>
<td>3.0 ± 0.6</td>
</tr>
</tbody>
</table>

**Table 4.8:** Zeolite-halogen interaction energies (kJ mol⁻¹)

<table>
<thead>
<tr>
<th></th>
<th>Silicalite</th>
<th>ZK4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>-22.6</td>
<td>-14.5</td>
</tr>
<tr>
<td>Br₂</td>
<td>-35.1</td>
<td>-21.9</td>
</tr>
<tr>
<td>I₂</td>
<td>-55.9</td>
<td>-33.9</td>
</tr>
<tr>
<td>Cl</td>
<td>-11.3</td>
<td>-7.4</td>
</tr>
<tr>
<td>Br</td>
<td>-17.4</td>
<td>-11.3</td>
</tr>
<tr>
<td>I</td>
<td>-27.8</td>
<td>-17.3</td>
</tr>
</tbody>
</table>

### 4.7.1 Comparison with experimental data

The results shown in Tab. 4.7 and Tab. 4.8 are useful to test the reliability of the present model to represent the dynamics of halogens sorbed in neutral, all silica zeolites. As the parameter for the Cl, Br and I are the same as Ar, Kr and Xe, the obtained diffusion coefficients and adsorption energies of radicals can be directly compared with corresponding experimental and theoretical data. To our knowledge, no experimental data are currently available on the diffusion of halogen radicals and molecules in silicalite, but a recent work of Kočirčič et al.,¹⁴³ which estimated the lower limit of the diffusion coefficient of iodine in silicalite as 10⁻¹² m² s⁻¹, which is clearly not in contrast with our results. Heinik et al.¹⁴⁣ applied the PFG-NMR technique to study the diffusion of Xe in silicalite, obtaining D ~ 4x10⁻⁹ m² s⁻¹ with a loading of 4 atoms/u.c. Frequency-response measurements¹⁴⁵ gave D ~ 1.1x10⁻⁹ m² s⁻¹ at concentrations lower than 1 Xe atom per unit cell. These values are in reasonable agreement with our value (3.1x10⁻⁹ m² s⁻¹) for the iodine radical at infinite dilution, considering the not negligible error usually involved in the experimental measurements of the diffusion coefficient. The isosteric heat of adsorption in the limit of zero coverage q^0 of Ar in silicalite has been recently estimated as 15.8 kJ mol⁻¹ at room temperature.¹⁴⁶ At low concentration the isosteric heat of adsorption is connected to the mean potential energies of the sorbate-zeolite and sorbate-sorbate interaction < U_{g-h} > and < U_{g-g} > by the expression.¹⁴⁶,¹⁵¹
\[ q_{sl}^0 = -[ < U_{g-h} > + < U_{g-g} > ] + RT \]  

(4.5)

where \( R \) is the gas constant; at infinite dilution the term \( < U_{g-g} > \) is zero. The corresponding adsorption energy is about 2 kJ mol\(^{-1}\) higher than that we obtain for chlorine radical. The isosteric heat of adsorption at 77 K for krypton in silicalite was measured by calorimetry\(^{147}\) as 17.4 kJ mol\(^{-1}\), corresponding to \( < U_{ads} > \sim -16.8 \) kJ mol\(^{-1}\), which compares well with the datum reported in Tab. 4.8 for bromine. The experimental value for the isosteric heat of adsorption of xenon in silicalite\(^{148}\) is 26.6 ± 1 kJ mol\(^{-1}\) at 121 K, whence \( < U_{ads} > = -25.6 \) kJ mol\(^{-1}\), not far from the adsorption energy we calculated for iodine (-27.8 kJ mol\(^{-1}\)). Turning to the comparison with theoretical studies, it must be remarked that all the previous MD simulations of the Xe-silicalite system have been carried out with a fixed framework, which does not allow for the energy exchange between sorbates and zeolite, and for fluctuations in the pore size, which can be of considerable significance, in particular when the size of the diffusants is not much smaller than the channels diameter (see section 3.6.2). Anyway, the agreement with our data is rather good. Pickett et al.\(^{149}\) obtained \( D = 1.86 \times 10^{-9} \) m\(^2\) s\(^{-1}\) and \( < U_{ads} > = -26.9 \) kJ mol\(^{-1}\); again with 4 Xe atoms per unit cell; their \( D \) value is very close to that recently obtained by Jost et al.\(^{150}\) for the same system. Xenon in silicalite at infinite dilution was simulated by June et al.\(^{151}\) by turning off sorbate-sorbate interactions in a large system of 96 sorbates. They obtain \( D \sim 4 \times 10^{-9} \) m\(^2\) s\(^{-1}\), close to our value, along with a value of \( < U_{ads} > = -21 \) kJ mol\(^{-1}\), which is considerably different from all other sorption energy data, included ours. In ref. 87 simulations of Ar and Xe at infinite dilution were carried out with a single diffusant, as in our case. The calculated adsorption energies for Xe (-27.8 kJ mol\(^{-1}\)) and Ar (-11.8 kJ mol\(^{-1}\)) are very close to our data for I and Cl, respectively. Their computed diffusion coefficients at 0 atoms/ue. are seemingly too large, probably due to the too short trajectory length carried out for a single diffusant, which gives rise to a very poor sampling of the diffusive event, but yet adequate for determining the adsorption energy.

No experimental or simulation data are available on the diffusion of rare gases or halogen molecules in ZK4. However, the above comparison with the silicalite data shows that the present model is fairly reliable to study the diffusive process of the halogen species in neutral, all silica zeolites. Such equilibrium properties could also be helpful in the interpretation of the recombination data.

### 4.7.2 Analysis of diffusive properties

The diffusion coefficients obviously decrease going from chlorine to iodine, both for atomic and molecular species; the diatomic molecules move faster in silicalite, excluding bromine, whose diffusion coefficient is almost unchanged in the two silicates. This is rather surprising because, on the basis of purely steric considerations, the passage of diatomic species through the ZK4 windows, which is the crucial step in the cage-to-cage diffusion,\(^{152}\) should slow down the molecules compared to silicalite that does not present such “bottlenecks” for long-range diffusion. Moreover, one would expect that the difference in diffusion coefficients should further increase (in favor of silicalite) for larger diatomics. Actually, this is the case for chlorine and iodine: the latter shows
4.7 Diffusive and dynamic properties of the species involved in the reaction

A much larger decrease in $D$, going from silicalite to ZK4, than chlorine. It could be argued that the peculiar behavior of bromine, which seems not to be slowed down at all in ZK4 compared to silicalite, may be somewhat connected to resonance effects between the breathing motion of the ZK4 windows and the molecular oscillations, which assist the molecule in the window-crossing step. Indeed, in ref. 153 the spectral density of the ZK4 window diameters fluctuations were calculated by means of MD simulations: narrow peaks are present in the 350-400 cm$^{-1}$ region, just above the equilibrium bromine frequency. For chlorine and iodine similar cooperative effects between the windows oscillations and the internal flexibility of the molecules do not significantly assist them in the crossing of the windows. When we turn to the atomic, spherical species, the differences observed before between the diffusion coefficients in the two silicates mostly disappear. The diameters of the atomic species are considerably smaller than the kinetic diameter of corresponding diatomics, and then the passage through the windows is not as complicated and crucial as before. The diffusion of the atomic species in the two environments could have some influence on the recombination dynamics, even if we are not interested in the secondary recombination (of diffusive nature), but only in the primary one. Anyway if a species diffuses faster in a particular environment, the probability that the two atoms definitely separate shortly after the dissociation will increase. In this respect, looking at the percentages of DS events shown in Tab. 4.4, there are considerable differences between silicalite and ZK4, the first allowing an easier separation of atoms than the latter. However, in that case, we are dealing with the diffusion of highly excited atoms, while in the present one, where the diffusive properties of thermalized species are concerned, no differences are seemingly present. Therefore the peculiar features of the photodissociation-recombination process emphasize differences and properties which would not be apparent, or crucial, in an equilibrium simulation.

4.7.3 Translational and rotational dynamics

The center of mass velocity autocorrelation functions (VACF) for the diatomic molecules are reported in Fig. 4.11. The VACF’s in silicalite show a more liquid-like shape, with a sharp negative minimum at $\sim 1$ ps, followed by an oscillatory trend and a more elastic behavior than those in ZK4. The walls of silicalite seem to act more effectively as backscatterers compared to ZK4, which gives rise only to a slight, positive oscillation at $\sim 1$ ps, followed by a broad negative minimum. This minimum extend to larger times for higher masses, ultimately leading to the lower observed diffusion coefficients.

The examination of the VACF components in silicalite (not shown) points out that the deep first minimum mainly results from the $z$-component, as the molecule-wall collisions usually occur perpendicular to the axis of channels (pointing along $z$ and $y$. Moreover, as Fig. 4.11 shows, the backscattering is more effective for iodine, followed by bromine and chlorine: the heavier the molecule, the harder is the impact with the channel walls. This could be explained with a somewhat lower ability of the framework to absorb and redistribute to its interior the impact when the colliding mass is much heavier compared to oxygen. This behavior may also be found in the sharper first oscillation of VACF’s in ZK4, going from Cl$_2$ to I$_2$. This is in agreement with the observed higher collision efficiency ($\Delta E$ per collision in Tab. 4.5) of the lighter diatomic
Fig. 4.11: CM VACF's; continuous lines: silicalite; dash-dotted lines: ZK4

...species.

Fig. 4.12 shows the Fourier transforms of the center of mass VACF's, which are useful tools to analyze the overall translational motion of the molecules. The two environments give rise to very different behaviors. The main peak in ZK4 extends to considerably lower frequencies than the main peak in silicalite. Moreover, the three diatomics show interesting differences. For chlorine in silicalite two peaks are present; the low-frequency band, roughly coinciding with the ZK4 one, is probably connected to the so-called shuttling motion between intersections and channel centers. The second peak arises from the rapid rattling motion normal to the pore axis in silicalite; indeed, it mainly results from the z-component of the spectrum, not shown. Turning to bromine and then to iodine, the low-frequency peak in silicalite disappears, while in ZK4 a weak band around 25 cm⁻¹, absent for Cl₂, appears. In silicalite, for larger and heavier species, the longer-range (low-frequency) shuttling motions are considerably hindered and the main motion is that perpendicular to the walls. On the other hand, the intracage motions in ZK4 are not so heavily hindered for larger guests and the low-frequency peak is always present. Note that in any case the diffusivity in ZK4 depends on the intercage motion and the greater intracage freedom should not affect the diffusion coefficient.

Further information on the rotational dynamics of sorbate-zeolite systems and the rate at which a molecule can change its orientation can be gained following the decorrelation of the unit vector \( \mathbf{\hat{u}}(t) \), parallel to the bond (Eq. 3.34). Fig. 4.13 shows the calculated functions for the three halogen molecules; in ZK4 the molecules have more...
space available to rotate, thus the decorrelation of \( \hat{u}(t) \) is always faster, compared to silicalite. While, on one hand, the two \( U(t) \) curves are rather similar in the chlorine case, the relative differences are much more marked going to bromine and iodine, which experience considerable hindered rotations in silicalite. The channel structure forces the larger molecules to remain roughly aligned with the channel axes, thus keeping their orientation unchanged for longer times. This increased hindering of rotations with increasing molecular dimensions is much less marked in ZK4, which does not force such alignment, thus there the orientational memory remains short-ranged also in the iodine case, where after 10 ps \( U(t) \) already decays to zero. The greater rotational freedom experienced by chlorine in silicalite may have influence on the low probability of a definitive separation of the chlorine atoms after the dissociation, which has been remarked previously (Tab. 4.4). Indeed, if a molecule is roughly aligned to the channel axis at the dissociation time, the two atoms will be pushed in opposite directions along the direction of the channel and their separation will be more likely. But, in the case of chlorine, the molecule may often be placed more or less transversely in the channels, so that after the dissociation the atoms will immediately collide with walls, and their recombination will be more probable, as observed in silicalite.

4.8 Final remarks

A first comment must concern the reliability of these simulations, and thus of the observations drawn here. The basis limitation of classical MD stems from the use of
empirical force fields to determine all the forces acting on the nuclei. In many previous applications this approximation has proven to be adequate to study diffusive and equilibrium properties for many different species sorbed in zeolites. Nevertheless the simulation of complex reactive processes at a first sight appears unfeasible in such a “classical” framework. Indeed, while in equilibrium systems the electronic dynamics can be accounted for in an indirect, implicit fashion by means of effective potentials, with parameters fitted to experimental data, reactive processes give rise to considerable changes in the distribution of the electron density, with the formation and the breaking of bonds in reactants, intermediates and products, often charged, where the solvent can be involved for instance through the solvation and the stabilization of charged intermediates. Clearly an empirical model, where the organization of molecular bonds is fixed and cannot change “on the fly”, cannot provide a description of such processes of reliability comparable to calculations which explicitly account for the electron dynamics. However, at present these \textit{ab initio} MD calculations cannot be applied to follow the dynamics of very large systems for several hundredths of trajectories like those of this study. We are confident that for simple reactive processes such those studied in this thesis an approach based on classical potentials can provide accurate qualitative indications on the activity of different zeolite structures. Here we are concerned with the recombination of neutral species, with a rather large mass, which has been recently\textsuperscript{215} simulated by classical MD. The zeolites studied here do not possess acid sites (protons or cations) which can possibly lead to more complex reaction mechanisms.
Moreover it has been previously shown that the harmonic model of the zeolite’s framework can reliably represent purely quantum phenomena such as energy exchanges and resonance effects with sorbed, vibrationally excited molecules (see ref. 81, 82 and the note at page 33). This fact, as well as the good agreement between the experimental time scales of iodine recombination in CCl₄ and those obtained with the present model, definitely support the previous considerations.

An interesting effect illuminated by this work is the major importance of structural effects that can often counterbalance an ineffective energy dissipation: this is what occurs in ZK4 where, notwithstanding the product molecule may be formed in less stable states due to the slow energy relaxation of the dissociated radicals, the caging imposes repeated encounters between the radicals, which at the same time transfer their excess energy to the environment, and finally recombine with high probability. The lower probability of primary recombination observed in silicalite might be exploited, for instance whenever the reaction between fragments coming from different molecules is sought. In this case the molecular species formed in the primary, geminate recombination would be side (and undesired) products! In ZK4 one would then obtain a larger amount of geminate recombination products, while in silicalite “mixed” products would be obtained to a larger extent. The fine-tuning of the best zeolite structure suitable to host a target photochemical reaction could then proceed through a previous test phase based on MD simulations like the ones performed here. Apart from this direct application, this study was mainly aimed at providing information on the general activity of the considered structures. Among the others, the vibrational relaxation data exploit the fact that the recombination gives rise to molecules in an excited state; in this respect the analysis of power spectra of molecules which progressively relax towards equilibrium provided general information of considerable interest. The analysis of diffusive properties highlighted that some features present in the reactive dynamics are most probably connected to the shift from equilibrium imposed by the dissociation, and thus they cannot be observed in equilibrium simulations. This enforces the basic idea that lead us to choose this class of reactions as representative of some typical effects related to the zeolite activity.
Chapter 5

Activated processes: the exchange reaction

5.1 General purposes

5.1.1 Introduction

The mechanism and rate at which zeolite "solvents" and adsorbed species exchange energy are important in any process occurring inside the cavities, but become crucial in reactive processes where excited species are formed, as they will remain bonded only if the framework is able to adsorb the initial excess vibrational energy from the molecule. The formation of excited products is a phase of the guest-host energetics common to many reactive processes, as the photodissociation-recombination reactions discussed before. A different aspect is the thermal activation preceding the reaction. Radical recombinations are typically non-activated processes and, in order to generate a statistically significant number of reactive trajectories, we only needed to dissociate the molecule in different initial conditions and follow the subsequent dynamic evolution of the radicals. When they collide, the only necessary condition to the success of the reaction is an effective dissipation of their excess energy. Therefore the comparison between several sorbent-sorbate systems highlighted important general aspects concerning the activity of the zeolite structure, both in controlling the separation of the dissociated radicals thus favoring their following encounter, and in extracting their excess energy. We showed the convenience of a classical approach in providing a detailed description, albeit necessarily non-specific, of non-activated processes in zeolites. When an energy barrier is introduced between the reactant and product basins, the general picture drastically changes. First of all, the new additional energy requirement exponentially reduces the reaction probability (according to the Boltzmann factor $e^{-E^\# / k_B T}$), where $E^\#$ is the height of the energy barrier: for example the time required to activate the reactants for the system we are going to study can be longer than 200 ps with a 5 $k_B T$ barrier, and special techniques will be needed to adequately sample the reactive event. Further, now the main purpose of the simulation is shifted to observe how a specific microporous structure can transfer to the reactants the required energy and drive them along the reaction coordinate, finally allowing the barrier crossing. The interest is now on the activation phase preceding the barrier crossing. Once again we found very useful
to start from a simplified reaction model, based on the activated exchange process of a light particle between two heavier centers, as proposed by Allen and Schofield.\textsuperscript{154, 155} This process is very different from the radical encounter not only due to the presence of the barrier, but also because both the breaking and the formation of bonds are now involved. In the previous study the energy needed to dissociate the molecule was provided from the outside (by simulating a high-energy irradiation) and we were only concerned in the eventual “remaking” of the broken chemical bond. Now the action of the environment is more complex, as the overall process is.

5.1.2 Rare events

For activated processes the transitions between stable species become rare events if the height of the reaction barrier is as large as several $k_B T$. Rare events are dynamical processes which occur so infrequently - on the time scale typical of MD simulations - that it is impractical to try to obtain quantitative information about them through straightforward MD trajectory calculations: in most of the trajectories the system would evolve in the phase space region corresponding to stable reactants or products, while the interesting part of the process, that is the transition between the two regions, would be observed so infrequently that no accurate data on the rate and mechanism of reaction could be obtained. In the last 20 years special computational techniques have been developed to face this problem,\textsuperscript{156, 157} allowing to frequently simulate a rare event, not just reactive processes, like for instance diffusive processes over solid surfaces.\textsuperscript{158–160} The “reactive flux" method\textsuperscript{162, 161} involves two distinct series of simulations:

1. several constrained MD simulations are carried out with the reaction coordinate fixed at values ranging from those corresponding to the reactants up to the transition state one; the free energy difference between reactants and transition state is then obtained by integrating the mean constraint force along the reaction path. The transition state theory (TST) kinetic constant is straightforwardly evaluated from this free energy difference. Other similar methods all entail special “biased” techniques to accurately sample the unfavourable phase-space regions near to the transition state.

2. the dynamical correction to $k_{\text{TST}}$, i.e. the transmission coefficient, is then obtained from the plateau value of the reactive flux correlation function. This function describes the effective flux through the transition state, and can be evaluated by averaging over many uncorrelated short trajectories, each one started with the system at the transition state.

The main advantage of this method is that each “dynamical” trajectory of the second phase needs to be followed only for the time needed to reach the plateau, which is much shorter than the chemical relaxation time, independently on the barrier height and on the actual rate of the process. Actually the first phase is often more critical in terms of the CPU time required. In any case the reactive flux method, starting all trajectories from the barrier top, avoids the slow activation of the reactants. For activated processes involving very high barriers, this is the only suitable method because the slow activation of the reactants is not considered.
5.1.3 General objectives

For the reaction studied here we adopted an alternative method (thoroughly described in the following) based on the fluctuation-dissipation theorem,\textsuperscript{152} which allow obtaining accurate kinetic data from the thermal, spontaneous fluctuations always present in an equilibrium system. Its validity is warranted by the not too high energy barriers considered (up to 5 $k_BT$) and by harmonic constraints included to keep the reactants always close to the reaction distance. The constraints imposed on the reaction complex considerably limit the diffusive approach of the reactants and the eventual separation of the products. While this may seem a too serious restriction, it allows us to roughly “isolate” the activation step, which becomes the main aspect of the reaction dynamics, thus simplifying its study. In other words we mostly ignore the environment influence on the relative diffusion of the reactive species (arising by their confinement in the zeolitic host) in order to concentrate on the way in which a particular microporous structure can lead to the barrier passage. The results of the same reaction examined in a liquid solvent provide a further term of comparison to better understand the peculiarities of the microporous structures.

It should be remarked that within the adopted model we considered intermolecular van der Waals forces only: the solvent-solute interactions are weak and short-range. Previous theoretical studies\textsuperscript{163} show that reactions of this kind (e.g. neutral atom exchange in rare gas solvents\textsuperscript{164–166}) are usually characterized by smaller solvent effects compared to exchange reactions in which long-range, strong interactions (both of coulombic and ion-dipole nature, like bimolecular substitutions of alkyl halides by anions in polar solvents\textsuperscript{167–170}) are active. For example, the dynamics of energy flow into the reactants is much more complex for $S_N2$ reactions involving polar and charged species: a larger number of solvent atoms simultaneously take part in the energy transfer to the reactants compared with the Cl + Cl$_2$ model system.\textsuperscript{166,169} A substantial reorganization of the solvent structure always precedes the reaction for the strongly interacting system while such effect is not observed for the weakly coupled case. Moreover the constraints we imposed on the relative diffusion of the reactants could further level off the differences between the silicates and the liquid solvent. Greater differences between the zeolites and the liquid would probably result if the reactants were allowed to separate by releasing the harmonic constraints imposed. Due to caging effects (absent in the silicate pores) the bimolecular encounter in the liquid would be more hindered and less probable, but at the same time, whenever the reactants get trapped in the same solvent cage, the atom transfer should be favored: repeated collisions would occur until the steric and energetic requirements for the barrier crossing will be eventually met.\textsuperscript{171}

It should also be remarked that the two silicate structures considered are all-silica forms and then their cavities do not host charge-compensating protons or metal cations that can act as Brønsted or Lewis acid sites. Many catalytic reactions in zeolites depend on the presence of such sites, which determine large differences between different zeolites, on the basis of the strong interactions between charged reactive intermediates and of the intense, variable electric fields present in the micropores, as well as the possible direct involvement of the protons bonded to the framework oxygens in the reaction mechanism. The simple transfer reaction occurring in the all-silica zeolites considered in this work is considerably easier to model and the perturbation that each framework
structure induces on the reaction system is small. The success of the reaction depends only on the activation of the reactants driven by the topology of the zeolite through collisional energy exchanges. We shall show that structural differences can determine different reaction rates through collisions of different efficiency, and also through the different confinement exerted on the reaction complex. Anyway we do not expect large differences in the reaction rates, as long as only the structure of the surrounding medium is changed while the forces exerted by the environment on the reactants are always kept weak and short-range. We chose to study such kind of reactions on analogous grounds to those that stimulated many previous extensive studies of $X + X_2$ model reactions in rare gas solvents $^{165,168,172}$ the relative simplicity of the interactions and of the model describing them allows to capture and understand in a great detail many general features of such processes, with particular emphasis on the solvent interaction with the reagents $^{166}$. The dynamics of more complex reactions, besides being more difficult to simulate and understand, involves many further effects that may partially obscure the general features of the (crystalline) environment activity in which we are primarily interested. Clearly, aspects connected to charge transfer and solvation of the reaction system, as well as to the influence of the relative diffusion of the reactants are undoubtedly important and deserving of further studies, but in this thesis we shall concentrate on the dynamics of a “constrained” transfer process entailing only short-range solvent-solute interactions. We are confident that several interesting features of each zeolite structure highlighted with this model could be general enough to be, at least partially, extended to more complex reactive processes.

### 5.2 Model and method to study the activated process

#### 5.2.1 Exchange reaction: Allen-Schofield model

We are interested in the transfer of a light particle (labeled $C$) between two heavier, identical, ones, labeled $A$ and $B$:

$$A - C \cdots B \rightleftharpoons A \cdots C - B \quad (5.1)$$

The three particles remain always close to each other during the simulation; thus this process could also approximately represent a unimolecular rearrangement occurring within a tightly bound reaction complex $A - C - B$. The dynamics of the transfer has been followed according to a model proposed by Allen and Schofield$^{154,155}$ with some modifications. The $A$ and $B$ particles have the mass $M$ of xenon and interact with each other and with the zeolitic oxygen atoms via a 12-6 Lennard-Jones potential with xenon-like self-interaction parameters $^{57}$ $\sigma = 4.02$ Å, $\epsilon = 1.998$ kJ mol$^{-1}$; the oxygen self-interaction parameter reported at pag. 35 have been adopted for the interaction $A(B) - O_{veo}$. In all simulations the $m/M$ ratio was fixed to 0.1 ($m$ being the $C$ particle mass). Compared to the original model an additional LJ interaction between the $C$ species and the environment was introduced. It should be remarked that in this process the dominant interaction is between the “solvent” and the two larger bodies that significantly shield the $C$ particle from directly interacting with the surrounding bath. Therefore the choice of the LJ parameters for the $C$ species is not crucial, if the
adopted values are chosen in such a way to model a significantly smaller species than xenon. For this purpose the parameters of fluorine\(^{11}\) \((\sigma = 2.83 \text{ Å}, \epsilon = 0.439 \text{ kJ mol}^{-1}\) have been chosen. The total internal potential of the reaction complex is then:

\[
V_{\text{int}} = V_{LJ}(r_A, r_B) + V_3(r_A, r_B, r_C) + V_R(r_A, r_B)
\]

(5.2)

The first term is the Lennard-Jones interaction between \(A\) and \(B\). The second term is the three body potential which controls the motion of the particles within the reaction complex as proposed by Allen and Schofield:\(^{154}\)

\[
V_3(r_A, r_B, r_C) = \frac{1}{2}m\omega_0^2(u_{\parallel}^2 - u_{\perp}^2/2 + u_{\parallel}/R^2 + R^2/16)
\]

(5.3)

where \(\omega_0\) is roughly the frequency of oscillation of stable species \(A-C\) or \(B-C\), \(r_A\), \(r_B\) and \(r_C\) are the position vectors of the three particles, and \(R = |r_B-r_A|\) is the \(A-B\) distance. The \(u_{\parallel}\) and \(u_{\perp}\) terms determine the motion of the light particle along the \(R\) axis and in any transverse direction, respectively (see Fig. 5.1). In particular, \(u_{\parallel}\) turns out to be a suitable choice for the reaction coordinate. Indeed the motion of the light particle along \(R\) is determined by a symmetric bistable potential (described by the quartic polynomial in \(u_{\parallel}\) shown in Fig. 5.2); each well (at \(u_{\parallel} = \pm R/2\)) corresponds to a stable species with \(C\) bound to one of the two heavy atoms.

\[
\begin{align*}
\vec{R} &= \vec{r}_B - \vec{r}_A \\
\vec{u} &= \vec{r}_C - \vec{r}_{\text{CM, A-B}} \\
\vec{u}_\parallel &= (\vec{u} \cdot \hat{R}) \hat{R} = u_\parallel \hat{R} \\
\vec{u}_\perp &= \vec{u} - \vec{u}_\parallel
\end{align*}
\]

\textbf{Fig. 5.1:} The reaction complex \(A-C-B\) and the various coordinates included in the three-body potential, Eq. 5.3

The two wells are separated by a maximum (at \(u_{\parallel} = 0\)) representing the barrier to transfer, given by:

\[
V_0 = \frac{1}{32}m\omega_0^2R^2
\]

(5.4)

The height of the barrier increases as the reactants move apart, but as strong harmonic forces prevent their definitive separation (see also Eq. 5.5 below), the mean
barrier height is well approximated by putting \( R = \sigma_{A-B} \) in Eq. 5.4. The motion of the light particle in the direction normal to \( \mathbf{R} \) is subject to a harmonic restoring force due to the \( u_\perp \) quadratic term in the three-body potential. The last term in Eq. 5.3 is an attractive term added in order to further control and prevent large separations of the two heavy particles:

\[
V_R = aR^2
\]  

(5.5)

The \( a \) constant was fixed at 1.415 kJ Å\(^{-2}\) mol\(^{-1}\); with this high value the two heavy particles never separate by more than 6 Å, thus we can always consider the system as a “tightly bound” complex. If we allowed greater \( A-B \) separations the transfer probability would clearly decrease as the two heavy particle must get close before exchanging the \( C \) species. Working on a “tightly bound” complex allows a high number of meaningful (reactive) events to be recorded in a shorter simulation time and at the same time it makes more evident the effect of activation of the reactants with respect to their relative diffusion (which is less interesting in the present study, as remarked before).

The MD simulations have been carried out in silicalite and ZK4 at a run temperature of about 300 K, with a 1 fs time step. The simulation boxes consisted of 2 unit cells (superimposed along \( z \)) for silicalite and 1 unit cell for ZK4, both corresponding to a total of 576 framework atoms. We verified that larger cells (up to 2304 atoms) give rise to negligible differences from the present results. Simulations with a liquid solvent, consisting of 256 LJ spheres modeling tetrachloromethane (according to the same potential used in the previous chapter), were carried out in the same conditions.

![Fig. 5.2: The three-body potential projected along the reaction coordinate \( u_\parallel \)](image-url)
5.2 Model and method to study the activated process

5.2.2 Kinetic constants and thermal fluctuations

The Eq. 5.1 reaction represents the passage from a stable region, to the left or right of the barrier in Fig. 5.2, to the other potential minimum (the process can also resemble an isomerization or an unimolecular rearrangement), and can be schematized as \( R \Rightarrow P \). The following rate equations then apply:

\[
\dot{c}_R(t) = -k_f c_R(t) + k_b c_P(t) \tag{5.6}
\]

\[
\dot{c}_P(t) = -k_b c_P(t) + k_f c_R(t) \tag{5.7}
\]

where \( k_f \) and \( k_b \) are the forward and reverse rate constants respectively, while \( c_R(t) \) and \( c_P(t) \) denote the instantaneous concentration of species \( R \) and \( B \). Similar rate laws can be written for the fluctuations from equilibrium concentrations \( \Delta c_R(t) = c_R(t) - c_R^\circ \) and \( \Delta c_P(t) = c_P(t) - c_R^\circ \); if the number of particles is conserved \( \left( \Delta c_A(t) + \Delta c_B(t) = 0 \right) \) one then finds:

\[
\Delta \dot{c}_R(t) = -k_f \Delta c_R(t) - k_b \Delta c_R(t) = -k \Delta c_R(t) \tag{5.8}
\]

where \( k = k_f + k_b \). The solution of rate equation Eq. 5.8 then yields:

\[
\Delta c_R(t) = \Delta c_R(0) \exp(-kt) \tag{5.9}
\]

Eq. 5.9 describes the relaxation of small non-equilibrium perturbations in the concentration of reactants; on the basis of the fluctuation-dissipation theorem\textsuperscript{52} in a system close to equilibrium (linear regime) the decay - in this case exponential - of such externally prepared deviations from equilibrium coincides with the decay of the correlation between spontaneous thermal fluctuations,\textsuperscript{*} which are always present in an equilibrium system:

\[
c(t) = \frac{\langle \delta n(0) \delta n(t) \rangle}{\langle \delta n \rangle^2} = \frac{\Delta c_R(t)}{\Delta c_R(0)} \tag{5.10}
\]

where \( n(t) \) is a dynamical variable strictly connected to \( c_R(t) \) and \( \delta n(t) = n(t) - \bar{n} \). After long times \( \delta n(t) \) becomes uncorrelated from \( \delta n(0) \), so:

\[
\langle \delta n(0) \delta n(t) \rangle \rightarrow \langle \delta n(0) \rangle \langle \delta n(t) \rangle \quad \text{when} \quad t \rightarrow \infty \tag{5.11}
\]

and as \( \delta n(0) = 0 \), \( c(t) \rightarrow 0 \) when \( t \rightarrow \infty \). The loss of correlation with time thus determines the “regression of spontaneous fluctuations”. With \( q = u_\| \) as the reaction

\textsuperscript{*} The basic idea that the relaxation of small perturbations to the equilibrium and that of spontaneous fluctuations are ruled by the same laws has been first expressed as regression hypothesis by Onsager in 1930.
coordinate \((q=0\) on the barrier, while \(q < 0\) corresponds to one species and \(q > 0\) to the other one), the dynamical variable \(n(t) = \theta[q(t)]\) (where \(\theta(x)\) is the Heaviside function):

\[
\theta(x) = \begin{cases} 
1 & x \geq 0 \\
0 & x = 0 
\end{cases}
\]  

(5.12)

may be used to distinguish the two species (each one laying within one side of the bistable potential). Therefore, from Eq. 5.9 and Eq. 5.10, the normalized autocorrelation function of the fluctuations of \(n(t)\) should decay exponentially to zero with a time constant \(\tau_{xxn}\) equal to the inverse of the rate constant \(k\):

\[
c(t) = e^{-t/\tau_{xxn}} \quad \text{when} \quad t > \tau_{mol}
\]  

(5.13)

Eq. 5.13 is only valid after a transient \(\tau_{mol}\) because the rate equations Eq. 5.6-Eq. 5.7 do not apply at very short times but only after a fast “coarse-graining” in time, thus the integrated equation Eq. 5.9 too does not apply and the decay of fluctuations described by \(c(t)\), while still coinciding with the \(\Delta c_R(t)/\Delta c_R(0)\) ratio (Eq. 5.10), is not exponential at short times. \(\tau_{mol}\) is the time needed on average for the \(R \rightarrow P\) transition to occur, after the activation of reactants. Its time scale is that of the internal molecular motions that allow the thermalization of the reaction coordinate. During \(\tau_{mol}\) the excess potential energy of the reaction coordinate is being transferred to the other internal degrees of freedom and to the external environment. On the other hand, \(\tau_{xxn}\) is the time needed in order to reactivate the reaction coordinate starting from reactants at equilibrium, i.e. the actual average time required for a complete transition from a stable, equilibrated, species to the other one. The connection in Eq. 5.13 allows one to extract kinetic data from an equilibrium simulation by exploiting the spontaneous fluctuations of the variable \(n(t)\). By observing how small thermal fluctuations spontaneously disappear in the equilibrated system one obtains the same information accessible by artificially displacing the system from equilibrium and following its subsequent relaxation. The latter approach is often adopted in kinetics: for instance, one applies an abrupt variation of temperature of 5-10 K and examines the rate at which the concentration of reactants adjusts to the new equilibrium conditions (or compositions). The perturbation imposed must be small in order to apply several approximations based on the small concentration difference with respect to the equilibrium values. An approach analogous to the experimental one has been used in the simulations of Edberg et al.\(^{174}\) aimed at calculating the kinetic constant for the trans-gauche isomerization of n-butane in solution.\(^1\) They started from an all-trans configuration and obtain the rate constant from the exponential relaxation of concentrations towards the equilibrium values. Brown et al.\(^{173}\) simulated the same system\(^{173}\) through the same equilibrium approach as ours (i.e., they started from an equilibrated mixture of trans and gauche n-butane) and obtained results in good agreement with those of Edberg. However the approach followed by Edberg is questionable because each molecule is initially “immersed” in a

\(^1\)As the iodine recombination became a prototype model to study non activated processes in solution, the trans-gauche isomerization of n-butane is frequently exploited as a model of an activated process with a small reaction barrier\(^{141}\)
solvent far from equilibrium, which does not represent correctly the environment surrounding it in a real situation.

The method we use here is suitable for any activated process that shifts the reactive system between two primary regions of stability, possibly with some modifications to the final equations, for example in the case where the number of molecules is not conserved in the reaction. We remark again that this approach is well distinct from the standard, “reactive flux” way to obtain the kinetic constant for an activated process, which has also recently been applied to the study of very slow diffusive processes in zeolites.\textsuperscript{175-179} For activated process with very high barriers it is the only suitable method because even a single trajectory lasting several $\tau_{x,n}$ (as those we carried out) would require too large computer times. Nevertheless we shall show that, for barriers up to $5 \kT$ and with the present reaction model, it is possible to follow a single equilibrium trajectory for times long enough to provide both the kinetic constant and its approximation based on the transition-state theory (see next section). Indeed, Eq. 5.13 and Eq. 5.14 highlight that the connection between $c(t)$ and the reaction kinetics can provide all the information related to the reaction rate ($k$) and the dynamics of the barrier crossing ($k_{T,ST}$). The relaxation of $c(t)$, incorporating any kind of dynamical process involved in the transfer process, as among the others possible barrier recrossings, provides data not accessible through a direct analysis of the trajectory. Moreover the application of the reactive flux method is not easy or direct: both the phases described above entail problems often very difficult to face, as the accurate sampling of the phase space region close to the transition state in the first phase, and the production of independent initial conditions (positions and velocities of the solvent-solute system corresponding to the transition state) in the second phase.\textsuperscript{180-184} Finally note that the short duration of the dynamical trajectories in the reactive flux method cannot allow to explicitly highlight phenomena occurring over time scales larger than about 10 ps (the typical duration of reactive flux trajectories). Obviously this does not mean that such phenomena are not relevant in the reaction dynamics, but only that the reactive flux method, and the corresponding constants, are independent on them, in the sense that it does not need such information. The method based on Eq. 5.13 on the other hand explicitly depends on the long-time dynamics and may allow to focus on aspects occurring on such larger time scales. We can therefore say that – for the system under study – the method adopted is probably the best choice.

5.2.3 TST approximation

The transition state theory (TST) approximation to $k$ may be evaluated by the short time gradient of $c(t)$:

$$ k_{TST} = -\frac{dc}{dt} \quad (t \to 0+) \quad (5.14) $$

It can be shown\textsuperscript{52,161} that Eq. 5.14 is equivalent to the Wigner's assumption that every trajectory which crosses the transition state with positive velocity (i.e., directed towards the products) will always lead to the products, without recrossing the barrier before the complete deactivation. This assumption can break down, for example, if the
environment hinders the barrier passage through frequent collisions with the activated complex in the transition state domain. The activation step preceding the barrier crossing and the dissipation of the excess potential energy following the passage, which also influence the "true" reaction rate and its deviations from the TST approximation, are also strongly dependent on the solvent action. A decrease of \( k \) compared to \( k_{\text{TST}} \) could be caused by a very low coupling between the reaction coordinate and its surroundings. For example if no dissipation occurs shortly after the passage in the products well the reaction coordinate will recross the transition state and many recrossings will be observed. Other effects can further complicate the overall picture, such as the intramolecular coupling between the reaction coordinate and other internal, non reactive degrees of freedom or the sharpness of the potential curve in the transition region, etc. If the barrier crossing was immediate and no recrossings occurred then Eq. 5.13 would be valid also in the short-time region, i.e. the relaxation function would decay as a single exponential and the rate constants in Eq. 5.13 and Eq. 5.14 would obviously coincide. In other words TST corresponds to assume a single-exponential relaxation of \( c(t) \) at all times.

5.3 Simulations

5.3.1 Accuracy of the calculated rate constants

The effect of increasing the barrier height \( V_0 \) was firstly examined. By varying the \( \omega_0 \) parameter \( V_0 \) was increased from the low 2 \( k_B T \) value to the more significant 5 \( k_B T \). It must be remarked that longer trajectories are needed for higher \( V_0 \) values because the number of significant events (i.e., barrier crossings) decreases with higher barriers. A \( c(t) \) function smoothly decaying to zero is needed in order to get an accurate fit of Eq. 5.13: the rate constants were calculated by the slope of a logarithmic plot of \( c(t) \). The transient, short-time part of the log-plot was not included in the fitted region. The statistical accuracy of the obtained values of \( k \) can be tested by comparing the log plots of the \( c(t) \) functions computed from trajectories of different length. For this purpose we report in Fig. 5.3 the partial results of a 40 ns run in silicalite with \( V_0 = 5 k_B T \). The logarithms of the correlation functions computed from increasingly longer portions of the overall trajectory are shown.

The slope of the plots converges to a constant value after 5 ns only; in other words, for the system under study, a trajectory of 5 ns seems to be long enough to give an accurate rate constant in the worse (highest barrier) case. However, in order to further reduce the errors in the computed \( k \) considerably longer trajectories were carried out. MD runs of 10, 20 and 40 ns were carried out for \( V_0 = 2 k_B T, 3 k_B T \) and 5 \( k_B T \), respectively. The error present in the calculated values of the rate constants (estimated from the standard deviation of the constants obtained from different trajectories) turns out to be less than 10% for the 5 \( k_B T \) barrier case which, giving rise to the lowest number of crossings, should be affected by higher errors than the other cases. The length of the simulations carried out ensures that the configurational space is adequately sampled; the reactive system explores the two sides of the bistable potential according to a near-Boltzmann distribution (Fig. 5.4).

Due to the symmetry of the potential, in an equilibrated system some properties
5.3 Simulations

**Fig. 5.3:** Logarithms of the \( c(t) \) functions as calculated from trajectories of different length; lower curve: 1 ns; upper curves: 4-40 ns

**Fig. 5.4:** Normalized distributions of the \( u_\parallel \) coordinate for the simulations with \( V_0 = 3 \, k_B T \) compared with the ideal Boltzmann distribution
must be fulfilled: we indeed verified that \(\langle \tau(t) \rangle \sim 0.5\) in all simulations and the number of crossings in either direction is practically the same (the direct and reverse rate constants \(k_f\) and \(k_r\) are equal to one-half of the overall \(k\)). The symmetry of the system also entails that the \(k_{\text{TST}}\) calculated by Eq. 5.14 exactly matches the value calculated according to:

\[
k_{\text{TST}}^{\text{BC}} = \frac{2N_{\text{BC}}}{\tau_{\text{RUN}}} \quad (5.15)
\]

where \(N_{\text{BC}}\) is the total number of barrier crossings and \(\tau_{\text{RUN}}\) is the simulation length.\(^{154}\) As TST assumes that every barrier crossing actually leads to reaction the direct (or reverse) rate constant in such approximation is given by \(N_{\text{BC}}/\tau_{\text{RUN}}\). The inverse of the latter ratio represents the mean lifetime of the \(A-C\) or \(B-C\) species, therefore Eq. 5.15 corresponds to what reported in the original paper of Allen and Schefield.\(^{154}\) for the studied system \(\tau_{\text{TST}} = k_{\text{TST}}^{-1}\) is given by half of the mean lifetimes in either well.

### 5.3.2 TST and non-TST events

The \(c(t)\) functions obtained for the 2 \(k_B T\), 3 \(k_B T\) and 5 \(k_B T\) barrier height are shown in Fig. 5.5; the logarithms of \(c(t)\) are plotted in the insets. Tab. 5.1 reports the rate constants resulting from the various simulations.

**Table 5.1: Kinetic constants (ns\(^{-1}\))**

<table>
<thead>
<tr>
<th>(k)</th>
<th>Silicalite</th>
<th>ZK4</th>
<th>CCl4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_0/k_B T = 2)</td>
<td>94.2</td>
<td>73.1</td>
<td>110</td>
</tr>
<tr>
<td>(V_0/k_B T = 3)</td>
<td>38.9</td>
<td>31.8</td>
<td>37.8</td>
</tr>
<tr>
<td>(V_0/k_B T = 5)</td>
<td>5.5</td>
<td>4.3</td>
<td>9.4</td>
</tr>
<tr>
<td>(\circ)</td>
<td>49.2</td>
<td>35.9</td>
<td>-</td>
</tr>
</tbody>
</table>

\| \(k_{\text{TST}}\)         | Silicalite | ZK4 | CCl4 |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(V_0/k_B T = 2)</td>
<td>275</td>
<td>245</td>
<td>297</td>
</tr>
<tr>
<td>(V_0/k_B T = 3)</td>
<td>135</td>
<td>105</td>
<td>123</td>
</tr>
<tr>
<td>(V_0/k_B T = 5)</td>
<td>25</td>
<td>18.7</td>
<td>24.4</td>
</tr>
<tr>
<td>(\circ)</td>
<td>126</td>
<td>118</td>
<td>-</td>
</tr>
</tbody>
</table>

\(\circ\) Simulations with stronger zeolite-sorbate interactions, see below

In first column of Tab. 5.2 the total numbers of observed transfers, or barrier crossings, are shown. This value includes all crossings, i.e. a sequence of \(n\) close crossing-recrossing events is counted \(n\) times. In the second column of Tab. 5.2 any such sequence is grouped to count it as a single event only, so as to obtain an effective and more representative number of actual crossings. In the third and fourth columns the number and the percentage of crossings which do not immediately recross the barrier after shortly visiting the product side are reported. A non-recrossing event was defined as a

\(^1\)In this symmetric process both the forward and reverse reactions are identical and the term "product" can be referred both to \(A-C\) or \(B-C\) species, depending on the direction of the first barrier crossing.
5.3 Simulations

Fig. 5.5: Normalized correlation functions (Eq. 5.13) for the different barrier heights studied. (a): $V_0=2 k_B T$; (b): $V_0=3 k_B T$; (c): $V_0=5 k_B T$. Dashed line: ZK4; continuous line: silicalite; dot-dashed line: $CCl_4$. The insets show the logarithm of the $c(t)$ functions. Note the different scales on the time axes.

barrier passage neither immediately preceded nor followed by another (re)crossing; in the following we will term it "TST" event as it basically corresponds to the transition state theory assumption.

A sample TST trajectory is shown as the dashed curve in Fig. 5.6 while the solid curve is representative of a typical recrossing event. We see that, after crossing the barrier and reaching the repulsive wall of the product side, in the non-TST case the reaction coordinate is directly driven back to the reactant side while in the other case it quickly thermalizes. All the observed recrossings are like this one: they are not determined by any friction exerted by the environment while the system is on the barrier, but arise from an ineffective thermalization immediately after the crossing: the recrossing time is $\sim 1$ ps.

The distinction made between TST and non-TST events is useful to understand some qualitative features of the reaction on the basis of the observed percentages of TST events (see below), but it could not be directly and quantitatively associated to the rate constants $k$ in Tab. 5.1. The latter are the exact values, as shown above, because the decay of the $c(t)$ function is controlled by many events that cannot be easily accounted for with a simple definition of TST crossings. The latter numbers only represent a rough estimate of the real number of reactant-product transitions that could give the
Table 5.2: Analysis of barrier crossings and effective transitions

<table>
<thead>
<tr>
<th></th>
<th>Total crossings (•)</th>
<th>Effective crossings (•)</th>
<th>TST transitions (•)</th>
<th>% TST transitions</th>
<th>Crossings per transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicalite</td>
<td>2 k_B T</td>
<td>1371</td>
<td>520</td>
<td>236</td>
<td>45.4</td>
</tr>
<tr>
<td></td>
<td>3 k_B T</td>
<td>675.5</td>
<td>278</td>
<td>136.5</td>
<td>49.1</td>
</tr>
<tr>
<td></td>
<td>5 k_B T</td>
<td>124</td>
<td>61.5</td>
<td>35.2</td>
<td>57.3</td>
</tr>
<tr>
<td></td>
<td>∙</td>
<td>630</td>
<td>313</td>
<td>159.5</td>
<td>51.0</td>
</tr>
<tr>
<td>ZK4</td>
<td>2 k_B T</td>
<td>1223</td>
<td>471</td>
<td>203</td>
<td>43.1</td>
</tr>
<tr>
<td></td>
<td>3 k_B T</td>
<td>529</td>
<td>256</td>
<td>131</td>
<td>51.2</td>
</tr>
<tr>
<td></td>
<td>5 k_B T</td>
<td>93.7</td>
<td>52</td>
<td>31</td>
<td>59.6</td>
</tr>
<tr>
<td></td>
<td>∙</td>
<td>589.5</td>
<td>311.5</td>
<td>169.5</td>
<td>54.4</td>
</tr>
<tr>
<td>CCl₄</td>
<td>2 k_B T</td>
<td>1486</td>
<td>547</td>
<td>238</td>
<td>43.5</td>
</tr>
<tr>
<td></td>
<td>3 k_B T</td>
<td>612.5</td>
<td>298</td>
<td>150</td>
<td>50.3</td>
</tr>
<tr>
<td></td>
<td>5 k_B T</td>
<td>121.1</td>
<td>71.5</td>
<td>44.5</td>
<td>62.2</td>
</tr>
</tbody>
</table>

○ Simulations with stronger zeolite-sorbate interactions, see below

• Normalized to 10 ns

Fig. 5.6: Reaction coordinate profile for a “TST” barrier crossing (dashed line) and for a recrossing event (solid line).
5.3 Simulations

exact \( k \) values through an expression analogous to Eq. 5.15. Indeed, the \( k \) calculated through the number of TST crossings underestimate the values of Tab. 5.1 for 2 \( k_B T \) and 3 \( k_B T \) barriers while for \( V_0 = 5 k_B T \) the exact rate constants are overestimated. The discrepancy arises from the definition of TST event and in particular from the necessarily arbitrary choice of the time interval without recrossings that must elapse before the event could be considered a TST one. The "no-recrossing" interval has been chosen to be 4 ps: this is slightly longer than the average recrossing timescale, but shorter than the reaction time \( \tau_{rxn} \) in all cases. The first requirement excludes from the TST crossing number those transitions in which the recrossing occurs slightly later than the average; the second point is important to distinguish between recrossings and actual reactions. There are mainly two source of error in this definition: (a) if a barrier crossing is followed by just two (or any even number) quick recrossings, the net result is a reactant-product transition, but one not included in the overall TST crossing number while still contributing to the decay of \( c(t) \) and thus affecting the \( k \) value; this kind of errors leads to underestimate \( k \); (b) the recrossing can occasionally occur shortly after the 4 ps limit since the first passage but in this case it could not be recorded and the number of TST events is erroneously increased, leading to an overestimation of \( k \). It thus seems that the weight of (b) events is greater for the highest barrier, while the (a) events dominate for the two lower barriers. It is not easy to verify these points, or to give a more accurate definition of TST event based for example on a time interval different than 4 ps for the recrossings, because of the distinct reaction times \( \tau_{rxn} \) for each barrier height. For instance, after increasing the time limit for the recrossings to 16 ps, the recalculated number of TST crossings gives a better estimate of \( k \) for \( V_0 = 5 k_B T \); nevertheless the same time limit is not suitable for the lower barriers because it would overlap with the time scale for the reaction (\( \tau_{rxn} \approx 182 \) ps for \( V_0 = 5 k_B T \) in silicalite, but it falls to 26 ps for 3 \( k_B T \), and \( \approx 11 \) ps for 2 \( k_B T \)). Another improvement could arise by including all the transitions with an even number of passages in the TST crossing number but this would be complicated by the longer time needed for the transitions characterized by more than one crossing, which should be taken into account in some other way. All these effects are automatically included in Eq. 5.13 and there is no need of further efforts to get a more accurate TST crossing number. The numbers of Tab. 5.2 will only be used for a qualitative comparison between the different environments.

5.3.3 Comparison of reaction rates in the different environments

The reaction rates shown in Tab. 5.1 decrease with higher barriers following a linear, Arrhenius-like, behavior when \( \ln(k) \) is reported vs. \( V_0 / k_B T \) (filled symbols in Fig. 5.7); actually the curves in the zeolites are almost parallel, while CCl\(_4\) shows a more irregular trend, with a rate constant falling just below the silicalite one only for \( V_0 = 3 k_B T \). The transition-state approximated constants show a more linear trend than the effective constants (open symbols in Fig. 5.7). In all cases ZK4 appears to be the least effective environment in promoting the atom transfer. The rate constants in silicalite are always closer to those obtained in CCl\(_4\) and only for the highest 5 \( k_B T \) barrier the liquid definitely appears as the most effective environment (Tab. 5.1 and Fig. 5.5).
Fig. 5.7: Arrhenius plot of the data in Tab. 5.1; filled symbols: $k$, empty symbols: $k_{TST}$.

Since with the present model the long-range diffusional approach of the reactants has little influence on the reaction rate, the observed different rates in the two silicates are mainly due to their different effectiveness in the activation-deactivation of the reaction coordinate. Some factors could determine this different efficiency: notwithstanding the potentials describing all inter- and intramolecular interactions are identical, the internal vibrational modes of the two silicates show differences due to the different crystal structures. This is quite clear from the vibrational spectra reproduced by the present model of the framework (Fig. 3.2). Therefore the guest-host vibrational coupling could make a structure more active on the basis of a more effective energy exchange between the reaction coordinate and the framework. In order to check this hypothesis the total energy along the reaction coordinate, defined as:

$$E_{\parallel} = V[u_{\parallel}(t)] + \frac{1}{2}m\dot{u}_{\parallel}^2(t)$$ (5.16)

has been averaged over all TST crossings. The first term in Eq. 5.16 is the potential energy along the reaction coordinate (retaining only the $u_{\parallel}$ terms of Eq. 5.3), and the second term is the corresponding kinetic energy. The non-TST events have not
been included in the average because they would complicate the interpretation of the energy curves. We found more convenient to include in the averaged ensemble only the TST events because they are isolated and then uncorrelated from each other, thus better representative of a typical barrier passage. Moreover such events have a higher statistical weight in the ensemble including all crossings: they always directly lead to the products, thus giving the most important contribution to the rate constants. Fig. 5.8 shows the average total and kinetic energies for the $V_0 = 3 \ k_B T$ case.

![Figure 5.8](image)

**Fig. 5.8:** Total (a) and kinetic (b) energy of the reaction coordinate averaged over all non-crossing transitions for the $V_0 = 3 \ k_B T$ case. $t = 0$ corresponds to the crossing of the barrier.

The trend observed in the three environments is very similar: the transfer process starts less than 2 ps before the crossing (this is more evident from the developing oscillations in the kinetic energy curves and from the trend of some geometrical properties of the reactive complex analyzed below), then the three curves are practically superimposed 1 ps before and after the crossing. The same similar behavior is also observed for the other barrier heights examined. Therefore the differences between the reaction rates in the two silicates cannot be ascribed to a faster energy transfer in silicalite. The rate at which the activated complex climbs the energy barrier along the reaction coordinate and then transfers the excess energy into the other degrees of freedom is roughly the same in all "solvents".
5.3.4 Mechanism of the activated process

If the geometry of the $A - C - B$ species is studied during the reactive crossings, we can conclude that the transfer mechanism is practically unchanged in the three environments. Indeed the trend of the main geometrical parameters observed during the barrier crossing (Fig. 5.9) shows that the main features of the transfer are the same in all cases. Note that the extensive averaging over many crossing trajectories considerably smoothes out the oscillations of the reported parameters due to their different phase (look, for example, at the differences between Fig. 5.6 and Fig. 5.9a).

![Graphs showing various parameters](image)

**Fig. 5.9:** Some geometrical properties of the reactive complex averaged over all non-recrossing transitions for the $V_0 = 3 k_B T$ case. (a) reaction coordinate $u_\parallel$; (b) $\angle CAB$ angle (in degrees); (c) $B - C$ distance; (d) $u_\perp$ coordinate, describing the perpendicular distance of the $C$ particle from the $A - B$ axis. Note that the reactant and product species are $A - C$ and $B - C$, respectively. continuous line: silicalite; dashed line: ZK4; dotted line: CCl$_4$

The averaged curves give also some insight into the transfer mechanism, together with the direct inspection of the computer-animated evolution of some selected MD trajectories near to the transition. We report in Fig. 5.10 several snapshots extracted from a reactive trajectory, which illustrate the exchange dynamics.

While the $A - B$ dumbbell is slowly oscillating around 4-5 Å the $C$ particle quickly rotates around the $A$ one, and during this rotation it continuously moves from the
<table>
<thead>
<tr>
<th>-200 fs</th>
<th>-145 fs</th>
<th>-125 fs</th>
<th>-120 fs</th>
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</thead>
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<td></td>
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<td>-100 fs</td>
<td>-90 fs</td>
<td>-75 fs</td>
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<tr>
<td>38 fs</td>
<td>45 fs</td>
<td>60 fs</td>
<td>98 fs</td>
</tr>
</tbody>
</table>

**Figure 5.10:** Snapshots taken from a reactive trajectory near to the barrier crossing at $t \sim 0$ fs
"internal" region between $A$ and $B$ (corresponding to the lower values of the $\angle CAB$ angle) to the external region at greater angles. This is clearer in Fig. 5.11, where the angle in a sample single trajectory is shown. Fig. 5.9b shows that $\angle CAB$ is minimum at $t=0$: indeed the transfer usually occurs after the light particle has moved to the internal region, almost aligned to the $A-B$ axis.

![Graph](image)

**Fig. 5.11:** Evolution of $\angle CAB$ angle (degrees) in a sample reactive trajectory: note the occurrence of a collision with the zeolite at $t=-2$ ps.

The dynamics of the transfer can then be roughly described in this way: following the activation the $A-C$ bond starts to oscillate with higher amplitudes and on each next rotation that brings the $C$ species in the favorable region between $A$ and $B$, $C$ gets increasingly closer to $B$ (look at the minimum at -0.8 ps in Fig. 5.9c) until the $A-C$ bond can be broken and the $B-C$ species is almost simultaneously formed. The snapshot taken near $t=0$ show that the activated complex, i.e. the geometry adopted at $t=0$, is almost linear: the CAB angle is at a minimum of 15° (Fig. 5.9b) and the normal distance $u_\perp$ from the $A-B$ axis converges to a minimum at $t=0$ (Fig. 5.9d). Moreover the only (slight) difference in mechanism between the three environments can be seen in the evolution of $u_\perp$: in CCl4 the $C$ species is kept closer to the axis connecting the heavy particles and the transition state configuration is a little more compact than in the silicates.

The energy curves in Fig. 5.8 and the described mechanism are representative of the crossing events only, and they show that, once the reaction coordinate is activated, the following dynamics is mostly independent on the environment. However they could not take into account the longer time interval (on the order of $\tau_{\text{exn}}$) between the reactive events, i.e. the time needed to "prepare" the atom transfer. The action of the environ-
ment on this time scale mainly affects structural and equilibrium properties that should then be crucial in determining the observed differences. The faster transfer rate in silicalite probably stems from a higher activation frequency: the time needed to reactivate an equilibrated species should be shorter than in ZK4. This seems to emerge from both the \( k_{\text{TST}} \) values in Tab. 5.1 and the (net) crossing numbers in Tab. 5.2, which are always higher in silicalite. Indeed, the almost constant percentage of TST events (with fixed \( V_0 \)) in all environments confirms that none of them is more effective in favoring the thermalization of the excited reaction coordinate after the barrier passage, i.e. in preventing the recrossings. Therefore a higher number of “attempted transitions” (net events in Tab. 5.2) will presumably lead to higher rate constants as the probability of success is roughly constant. Moreover looking at the Arrhenius parameters for the straight fits to the log plots in Fig. 5.7, reported in Tab. 5.3, we see that, while the effective activation energy \( E^\ddagger \) is the same in the two zeolites, the preexponential term is considerably higher in silicalite, presumably reflecting the higher “collision frequency” between the reactants which ultimately leads to the higher number of transfers.

**Table 5.3: Arrhenius parameters (*)**

<table>
<thead>
<tr>
<th></th>
<th>Silicalite</th>
<th>ZK4</th>
<th>CCl4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A ) (ns(^{-1}))</td>
<td>649 ±8</td>
<td>515 ±12</td>
<td>492 ±26</td>
</tr>
<tr>
<td>( E^\ddagger /V_0 )</td>
<td>0.95 ±0.02</td>
<td>0.95 ±0.03</td>
<td>0.80 ±0.09</td>
</tr>
</tbody>
</table>

\( (*) k = A \exp(-E^\ddagger/k_B T) \)

While the logarithmic curves in the two zeolites are fairly linear and then easily comparable, the Arrhenius parameters in the liquid solvent are less linear and then affected by higher errors. However, within the error bars, the activation energy in CCl4 is about 20% lower than \( V_0 \) while the zeolites shows a decrease of only 5%. While \( V_0 \) is the potential energy barrier to transfer, i.e. the gas-phase activation energy depending only on the intramolecular interactions, the effective barrier is usually altered by the additional contribution of the environment.\(^{186}\) Thus in the liquid solvent the static contribution changing the relative energies of reactive species (both at the bottom of the potential wells and at the barrier top) seems to be more important than in zeolites. In other words, for this model reaction the liquid is probably more effective in lowering the energy barrier compared to the zeolitic environments. This effect could also be connected to the more compact arrangement of the transition state in CCl4 highlighted above. Anyway the liquid solvent appears markedly more efficient than zeolites in the activation of reactants only for \( V_0 = 5 k_B T \). The *trans-gauche* conformational isomerization of n-butane shows a very similar energy barrier and has been simulated in zeolites by June et al.\(^{187}\) They obtained reaction rates in silicalite considerably lower than in liquid n-butane (i.e., when the solvent is made by the reactive species themselves). This agrees with our results with a similar barrier, albeit the studied processes are considerably different. The authors ascribe the observed results to the trapping of the molecule in the silicalite pores, which hinders the isomerization process. Nevertheless in our case other effects can also determine the higher efficiency of the liquid: for instance, the static effects described above, which modify the energy of reactive species and transition state, or the better matching between the masses of \( A \) and \( B \) species (131.3 g mol\(^{-1}\)) with that of CCl4 (153.8 g mol\(^{-1}\)), compared to the zeolite oxygens; this could favour
the reaction through more effective collisions in the liquid.

5.4 Structural effects on the reaction rate

5.4.1 Effect of the zeolite topology: distribution of reactive transitions in different regions

We observed that silicalite induces the activation of the reaction complex more frequently than ZK4, giving rise to a larger number of “attempts” of transition. This in turn leads to a larger reaction rate on the basis of the very similar behavior of the two silicates close to the reactive event. We then have to understand what determines the better long range effectiveness of silicalite, by looking at the equilibrium and structural properties. In silicalite the reaction complex moves along straight and zigzag channel sections and their intersections, thus experiencing significantly different environments, each one imposing different constraints to the reaction. This can in principle lead to multiple rate constants\(^{187}\) whose mean values are probably those shown in Tab. 5.1. ZK4 offers a more uniform and less confining environment to the reactive event, consisting of large cages (whose dimensions are even larger than the channel intersections in silicalite) connected by very narrow windows with diameter not much greater than that of the A and B particles. This structural difference should be the main source of the different behavior observed in this particular process. In order to elucidate the influence of specific regions on the reaction the transitions occurring in silicalite were divided on the basis of the region occupied by the CM at the barrier crossing time. This mapping is based on the exact classification of the region (straight channel, zigzag channel or intersection) visited by the sorbate at a particular time. This is not an easy task, and rather complex methods have been previously devised to distinguish the three regions.\(^{175}\) We adopted a method of mapping that will be described below (INSERISCI RIF.), which allows to classify the visited region on the basis of the x and y coordinates alone. We mapped the position of the A – C – B center of mass (again for the TST crossings) whenever \(u_{||}\) changed sign (i.e., at each barrier passage). At that time the A – C – B center of mass is close to the position of the transferring C species: indeed, at the transition state, the distances of C from A and from B are roughly equal and the A – C – B arrangement is almost linear, as seen before. The percentage of crossings found in each region is reported in Tab. 5.4; the values in parentheses are the fractions of the whole trajectory spent in the same region.

<table>
<thead>
<tr>
<th>(V_{0}/k_{B}T)</th>
<th>% Straight channel</th>
<th>% Zigzag channel</th>
<th>% Intersection</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>23.3 (24.7)</td>
<td>34.6 (38.1)</td>
<td>42.1 (37.2)</td>
</tr>
<tr>
<td>3</td>
<td>23 (22.7)</td>
<td>33.3 (39.2)</td>
<td>43.7 (38.1)</td>
</tr>
<tr>
<td>5</td>
<td>22.8 (23.9)</td>
<td>40.0 (39.5)</td>
<td>37.1 (36.6)</td>
</tr>
</tbody>
</table>

From the reported data it seems that the distribution of reactive events in silicalite is mainly statistic: the fraction of crossings occurred in each region closely reflects the time fraction spent there by the reaction complex in the MD trajectory, that is at
equilibrium. If a specific region favored the transfer reaction the percentage of events found in that region would be higher than the fraction of time spent there. We see that, for the straight channel, the two percentages are always identical, while (for barrier heights of 2 \( k_B T \) and 3 \( k_B T \)) the intersections seem more favorable for the reaction compared to the zigzag channels. However the differences are small and completely disappear for the highest barrier. Therefore the fact that the reaction complex spends more time in the channels than in the intersections (in about 62% of the full trajectory the complex is found in a channel) is presumably not the reason of the higher reaction rates in silicalite: in the intersections the reaction occurs with the same, if not higher, probability.

Turning to the ZK4 case we calculated the distributions of reactive events and of trajectory points located at a particular distance from the center of the (closest) window (Fig. 5.12a) and from the center of the cage hosting the \( A - C - B \) system (Fig. 5.12b). Now considerable differences are clearly visible. In the first case the main difference between the two distributions (reactive events vs. equilibrium trajectory) is the absence of reactive crossings in the region near the windows, where the reaction complex spends a non negligible fraction of time, albeit lower than the time spent in the cage (the main maximum in the figure). Fig. 5.12b shows the same phenomenon from another point of view: the reaction complex always avoids the cage center and it is preferentially adsorbed 3-4 Å apart, i.e., near the cage walls. This is a common behavior for molecules sorbed at low concentration in all-silica zeolites with large cages.\(^{63,188}\)

Much more important is the fact that, although the reactive crossings preferentially occur at similar distances from the cage center, a non-negligible tail at higher distances is present in the trajectory distribution and disappears in the distribution of reactive crossings. This tail corresponds again to the region near the windows, which seems to be definitely unfavorable for the transfer reaction.

### 5.4.2 Effect of the zeolite topology: contour maps for the coordinates

In order to further investigate the latter point the three-dimensional distribution functions\(^{189}\) of both the center of mass and of single \( A \) (and, equivalently, \( B \)) species in the zeolite cavities were calculated for the full trajectory with \( V_0 = 3 k_B T \). For ZK4 one eighth of the unit cell containing exactly one cage at its center was divided in 25x25x25 small cubes (with side ~ 0.5 Å). The coordinates of the sorbates were reported in this “subcell” through inverse symmetry operations and we calculated how many configurations (single trajectory points) were placed in each cube. A 3-D histogram is then built, whose visualization in two dimensions is possible by looking at the population of a slice of parallel cubes. Any pair of directions is equivalent due to the cubical symmetry of ZK4; we take \( x \) and \( y \), thus by fixing \( z \) we select the height at which the 3-D cube is observed. With \( z = L/4 \) (where \( L \) is the cell edge) one extracts the \( xy \) section with the cage center in the middle. The two contour plots in the upper part of Fig. 5.13 represent the corresponding projections for \( A \) and \( B \) coordinates and for their center of mass. If the same procedure is repeated for the whole cell of ZK4, one obtains a larger map, which includes four interconnected cages, shown in the lower
Fig. 5.12: Distribution of the positions of reactive crossings (solid lines) and of the 
whole trajectory (dotted lines) with respect to: (a) the closest window center; (b) the 
cage center, for the ZK4 run with $V_0 = 3 k_B T$.

part of Fig. 5.13. It is evident that both the heavy particles tend to be located in the 
cage, near the window entrances; at least one out of the two is always placed in these 
sites. Looking at the contour plot of the center of mass positions it is clear that the 
other one can be placed in the same cage (with the $A - B$ axis roughly aligned with 
the cage wall) or in the adjacent cage, with the center of mass placed at the window 
center (evidenced by the relative maxima at $(6,12)\AA$, $(12,6)\AA$, etc. in the lower right 
figure).

As seen before the latter arrangement does not allow the $C$-transfer to occur prob-
ably because the rotation of the light particle around the “donor” center shifting it 
close to the “acceptor” is considerably hindered inside the narrow windows. This is 
therefore one of the main reasons of the lower transition rates in ZK4. Indeed from 
the probability distributions of Fig. 5.12 the fraction of configurations with the center 
of mass placed near the windows can be estimated as 15±17%, to be compared with 
the $\sim 22\%$ increase in the rate constant going from ZK4 to silicalite ($V_0 = 3 k_B T$). 
The further small rate difference in favor of silicalite might denote that also the con-
figurations with both the heavy centers in the same cage of ZK4 (thus experiencing a 
larger rotational freedom) are not as favorable as the conformations adopted in silical-
ite. One hint in this direction comes from the mean interaction energies between the

\footnote{Remember that the unit cell of ZK4 includes eight cages, four centered in the $z = L/4$ plane and 
four in the $z = 3L/4$ plane, thus in this case we are looking at the first four cages}
5.4 Structural effects on the reaction rate

Fig. 5.13: Projections on the xy-plane of the three-dimensional distribution function of the coordinates in ZK4. Darker areas correspond to higher densities. The upper figures represent the cage centered at $(L/4, L/4, L/4)$ and the lower ones the four cages centered in the $z=L/4$ plane. The figures on the left reports the distribution of $A$ and $B$ positions, while on the right the center of mass distributions are shown.
guest reaction complex and the host framework, given by:

\[
\langle U_{ACB-Z} \rangle = \langle U_{A-Z}^{J} \rangle + \langle U_{B-Z}^{J} \rangle + \langle U_{C-Z}^{J} \rangle
\]

(5.17)

The obtained values, referred to the runs with \( V_0 = 3 \ k_B T \), are \( \langle U_{ACB-Z} \rangle = -57.6 \) kJ mol\(^{-1}\) for silicalite and -38.0 kJ mol\(^{-1}\) for ZK4. The \( A-C-B \) complex is adsorbed much more strongly in silicalite, due to the larger number of oxygens that can closely interact with it. In ZK4 the molecule can only interact with the oxygens in the nearest cage wall and the absence of a near opposite wall determines the lower adsorption energy. In fact, the average number of first neighbors oxygen atoms is 15.4 for silicalite and 9.3 for ZK4. These numbers have been calculated by integrating the oxygen-heavy atom rdf’s in the 0.5 Å interval, which is the range covered by the first peak in the rdf’s shown in Fig. 5.14.

![Graph showing radial distribution functions for oxygen-A(B) species in silicalite and ZK4](image)

**Fig. 5.14:** Radial distribution functions oxygen-A(B) species in silicalite and ZK4

The contour plots for the silicalite run, shown in Fig. 5.15 were calculated by dividing the unit cell in 40x40x27 cubes (so that the side is still ~ 0.5 Å as for the ZK4 distributions). When the slice is taken in the \( yz \) plane, with \( z=0 \) Å, the straight channel is shown (Fig. 5.15a-b) while in Fig. 5.15c-d the \( xz \) slice with \( y=b/4 \), representing the sinusoidal channel, is contoured.

In the straight channel some different configurations for the reactive complex are possible. Comparing the distributions of the heavy species (Fig. 5.15b) with that of their center of mass (Fig. 5.15a) and remembering that the \( A-B \) distance is always close to 4 Å it seems that the most common arrangements are two: i) those with one heavy atom in the intersections (located at \( y=5 \) and 15 Å) and the other in the channel; ii) the configurations with both atoms in the channel, arranged with the \( A-B \) axis
5.4 Structural effects on the reaction rate

![Graphs](image)

**Fig. 5.15:** Projections of the three-dimensional distribution function of the coordinates in silicalite. Darker areas correspond to higher densities. (a) C.M. coordinates in the straight channel; (b) single $A(B)$ species in the straight channel; (c) C.M. coordinates in the sinusoidal channel; (d) single $A(B)$ species in the sinusoidal channel;
oblique with respect to the channel axis and with the center of mass roughly at the
center of the channel. The latter configuration maximizes the attractive interactions
with the zeolite, by placing both the centers in close contact with the walls. Turning
to the distributions in the sinusoidal channel, we see that here only one arrangement is
possible, with both atoms placed along the channel and the center of mass located well
inside the channel. Indeed the results of Tab. 5.4 show that while the molecule remains
trapped in this arrangement for a rather long time the transfer of the light particle can
be slightly hampered, compared to the transfer probability when the center of mass is
in an intersection or in the straight channel: these regions allow for a greater freedom
of the reactive system. This phenomenon, albeit less marked, is similar to the complete
absence of transfer events when the center of mass of the molecule is locked in a ZK4
window.

5.4.3 Calculation of work involved in the transition

Another important effect has been highlighted by calculating the work done on
reactants by the solvent, which is a suitable measure of the guest-host interaction
during the reactive event. The work done by the $i$-th oxygen on reagent site $j$ up to
time $\tau$ following the barrier crossing (at $t=0$) is:

$$w_{ij}(t) = \int_0^{\tau} f_{ij} \cdot \mathbf{v}_j(t) dt$$  \hspace{1cm} (5.18)

where $f_{ij}(t)$ is the force exerted on atom $j$ by atom $i$ and $\mathbf{v}_j(t)$ is the velocity vector
of the $j$ atom. The total work done on the reactive complex by the $i$-th solvent atom
during the time $\tau$ is then:

$$w_i(\tau) = \sum_j w_{ij}(\tau)$$  \hspace{1cm} (5.19)

where the index $j$ runs over the three reagent atoms $A$, $B$, $C$. Following each barrier
crossing the work $w_i(\tau)$, with $\tau = 2$ ps, was determined for each zeolite oxygen $i$.
These atoms were then ranked by their corresponding value of $w_i(t)$ in such a way that
atom 1 did the more positive work in the 2 ps following the crossing, while atom 384
(the last oxygen) did the more negative work. Note that atoms doing positive work
are transferring energy to the reactants, while a negative $w_i$ denotes that atom $i$ is
removing energy from the $A - C - B$ complex during the two picoseconds following
the barrier passage. This calculation was repeated for all the observed crossings, thus
associating to each passage the corresponding ordered sequence of $w_i(\tau)$ with $i$ ranging
from 1 to 384. After averaging over all crossings, one obtains the average work done by
atom 1 (i.e. the work made on average by the atom which transfers the largest amount
of energy to reactants), by atom 2, up to atom 384 (representing the work made on
average by the atom which drains the largest amount of energy from reactants). This
average work is represented as thin lines in Fig. 5.16 for the systems with $V_0 = 3 k_B T$.
In both zeolites the work done by most oxygens is near zero: only a small fraction
of atoms does significant work, both positive and negative. By further examining
these fractions, shown in the insets of Fig. 5.16 it results that in silicalite the atoms doing positive work give a larger contribution than the corresponding atoms in ZK4; likewise the work done by the fraction of atoms doing negative work is again larger (more negative) for silicalite. In other words, even though in both zeolites few oxygens are directly involved in the energy transfer after the reaction, the interaction of these “active” atoms with the reagents is more effective in silicalite.

![Diagram](image)

**Fig. 5.16:** Thin lines: ranked work done on the reagents by the zeolite oxygen atoms; atoms are ranked according to their maximum value of work done (see text) in the 2 ps following each barrier crossing. The two insets show with higher detail the ranked work done by the 16 atoms doing the more positive and the more negative work. Thick lines: cumulative work done by the oxygen atoms (integral of the ranked work over the oxygens).

This point also emerges from the trend of the cumulative work done by the oxygen atoms, shown as thick lines in Fig. 5.16: the contribution of the few atoms doing positive work is about 20 kJ mol\(^{-1}\) in silicalite, and 13.4 kJ mol\(^{-1}\) in ZK4. This difference is counterbalanced by the atoms doing negative work which are again more effective in silicalite. Therefore the total work done on the reagents, i.e.

\[
w(\tau) = \sum_i w_i(\tau) \tag{5.20}\]
where the index \(i\) runs over all oxygens, is similar in both environments. Since we considered the work done in the interval following the barrier crossing, \(w(2 \text{ ps})\) is negative, corresponding to the energy flux from reactants to the environment. The fact that the overall work done on reactants in 2 ps is comparable in the two zeolites reflects the similar trend in the energy curves of Fig. 5.8 the energy removed from the reactive complex after 2 ps is about the same in the different environments. However this seems to arise from the cancellation of the larger positive and negative work contributions in silicalite. On one hand the net result is that close to the barrier crossing the energy transfer occurs with similar rates; on the other hand, the larger efficiency of silicalite oxygens both in accepting and transferring energy to the triatomic may be involved in the higher reaction rates observed on longer time scales.

5.5 Other general aspects

5.5.1 Validity of TST and intermolecular coupling

An important point emerging from Tab. 5.1 is that TST considerably overestimates the rate constants in all cases (the \(k_{TST}^{'}\)'s are always 2-4 times larger than the "true" constants). This is due to a high recrossing probability, which leads to a decrease of \(k\) compared to \(k_{TST}\). Many recrossings may arise when the coupling to the environment is low, in particular with a not too high reaction barrier: the reaction coordinate, after crossing the barrier, retains most of its excess energy, and quickly recrosses the transition state after having visited the products side for a short time (\(\sim \tau_{m,}\)). As shown in the trajectory of Fig. 5.6 our system usually leads to recrossings of this kind\(^6\). We see in Tab. 5.2 (fourth column) that the percentage of nonrecrossing (TST) transitions increases with greater barrier heights in all environments, and the last column shows that the mean number of crossings per single event is a decreasing function of the barrier height. Then a higher barrier correctly leads to a lower recrossing probability, but the tendency to recross the barrier (violating the TST assumption) remains rather high in all cases accounted for. The reactive complex \(A - C - B\) possesses only a few internal degrees of freedom over which the reaction coordinate may distribute its excess energy; thus, in absence of a strong coupling between these non-reactive degrees of freedom and the external bath, a great part of the excess activation energy is likely to flow again into the reaction coordinate before being transferred to the solvent, thus favoring the recrossing. If the number of internal degrees of freedom that can equipartition energy with the reaction coordinate on the time scale of the crossing is higher (like, for example, in the isomerization of a polyatomic molecule) then the dissipation could be more efficient even at very low coupling with the solvent.\(^{191-193}\) In order to investigate the effect of the coupling to the external bath, two more 20 ns simulations in silicalite and ZK4, with \(V_0 = 3 k_B T\), were performed with a three times deeper minimum for the interaction between the zeolite and the two heavy bodies; all the other parameters were left unchanged. This corresponds to a higher "friction" exerted by

\(^6\)This is the so-called inertial regime,\(^{190}\) which dominates in low-coupling conditions. The opposite case is the Kramer's regime, where the reaction coordinate is strongly coupled to the solvent; in such case, when the system is on the barrier top, the frequent collisions with the solvent can hinder the passage before the system can reach the products region.
the host (i.e., the attractive forces exerted on the solute are stronger) and not, strictly speaking, to a more effective guest-host (external) coupling; nevertheless some related information could be gained also in this way. The results are reported in Tab. 5.1 and Tab. 5.2. Compared to the runs with weaker intermolecular interactions, \( k \) increases both for silicalite and ZK4. The higher \( k \) values arise from an increased total number of (net) crossings and from a slightly higher percentage of nonrecrossing events. The increase in the rate constants shows the non-negligible influence of the guest-host interactions in this process and confirms that the high nonrecrossing probability observed for this system is connected to the weak intermolecular coupling. More work is needed to assess the exact nature of its action, which cannot easily be associated with the effects discussed so far. For example the structural properties, such as the distributions in the cavities, considerably change when the attractive guest-host forces are modified and the considerations made above may be no more valid. The general properties of the two zeolitic structures highlighted before are likely to affect many processes where the intermolecular coupling is low, but things may change when the coupling is very strong.

### 5.5.2 Dependence on the \( A-B \) force constant

Finally we tested the effect of lowering the force constant for the \( A-B \) interaction (\( a \) in Eq. 5.5) to one-half of its previous value. This corresponds to a “loosely bound” complex in which the \( A-B \) distance may reach higher values (up to 7-8 Å). The rate constants, for the runs with \( V_0 = 3 \kappa_B T \), are reported in Tab. 5.5. Compared to the previous rates there obviously is a net decrease as the reactants are on average farther from each other. ZK4 gives rise to the more marked decrease (-90%) followed by silicalite (-50%) and CCl4 (-30%). It is interesting to note that the further increase in the difference between the rates in the two silicates is not due to a different distribution of the \( A-B \) distances: as in the previous runs the distributions in silicalite and ZK4 are identical. The structure does not apparently affect the relative distance of reactants.

<table>
<thead>
<tr>
<th></th>
<th>silicalite</th>
<th>ZK4</th>
<th>CCl4</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k )</td>
<td>26.2</td>
<td>16.6</td>
<td>26.7</td>
</tr>
<tr>
<td>( k_{TST} )</td>
<td>96</td>
<td>80.9</td>
<td>105.3</td>
</tr>
</tbody>
</table>

The overall trend is unchanged with respect to the previous runs with \( V_0 = 3 \kappa_B T \): \( k(\text{ZK4}) < k(\text{silicalite}) \sim k(\text{CCl4}) \), showing that the general features observed for this process are not heavily sensitive to the internal (as opposed to the external, or intermolecular) parameters adopted, in particular to the choice of a “tightly bound” complex. Actually, only if we loosened the \( A-B \) bond at the point that a CCl4 molecule could easily slip between the heavy atoms (which would require \( A-B \) separations of about 10 Å) we would obtain considerably different rates in the liquid solvent. But in such case the dynamics of the transfer would significantly differ from the process studied so far: the reactants might considerably separate from each other and their relative diffusion would affect the rates. Moreover such simulations would require very long MD runs in order to observe a fair number of transitions and the application of
the present method would not be any longer suitable.

5.6 Final remarks

It has been shown that useful information concerning the mechanism and the kinetics of activated transfer processes in zeolites can be obtained from a standard correlation functions analysis applied to classical equilibrium Molecular Dynamics trajectories, as long as the energy barrier separating reactants and products is not too high. The small size of the light $C$ particle compared to the heavier $A - B$ ones mainly reduces the problem to the interaction of the $A - B$ substrate with the environment. The diffusional constraints imposed on the relative $A - B$ motion further emphasize the importance of the coupling between these masses and their surroundings. The adopted model is also a suitable tool to test the basic assumptions implicit in the TST approximation. It is known that standard TST, when applied to a heavy-light-heavy particle transfer reaction, may be seriously in error: the rapid motion of the light particle within the force field of the two slowly moving substrate species leads to considerable recrossings of the transition state.\(^{186}\) We indeed verified such behavior, further associating it to the low intermolecular coupling; the actual rate constants measured are considerably lower than their TST estimates. The main point emerging from the simulations is the greater effectiveness of siliclite in the long-range activation of reactants, as compared with ZK4. The rate constants in the latter environment are always lower even considering the (low) error affecting the computed values. The observed differences are not overwhelming, as can be expected on the basis of the simplicity of the adopted reaction model that involves only short range guest-host interactions and intentionally excludes the diffusive approach of the reactants from the reactive dynamics. From the presented data it may be inferred that the most favorable environment for an exchange process of a light particle in zeolite cavities should be a fairly confining one, in order to maximize the attractive guest-host interactions. When the three centers are located in the large cages of ZK4 their interaction with the zeolite is limited to the atoms of the near wall, as opposed to siliclite where a stronger interaction arises from the cylindrical and more confining structure, even in the intersections. At the same time an excessive confinement suppresses the transfer, as seen in the ZK4 windows and, to a lesser extent, in the sinusoidal channels of siliclite. This phenomenon is probably due to the limitation of the rotational freedom experienced by the light particle: the excitation of such motion seems to be essential in the reaction path. Moreover, we observed that an increased intermolecular coupling lead to a larger difference between $k$(siliclite) and $k$(ZK4); at the same time the general trend (i.e., the relative order of the rates in the three environment) does not change after modifying the internal potential parameters so as to loosen the $A - B$ "bond". This seems to prove that the qualitative features observed are not entirely determined by the internal force field of the reactive complex and the influence of the environment, albeit small, plays an important role in driving the transfer reaction. It has been shown that, as long as the dynamics of the activated complex is concerned, the energetic and mechanical behavior of the reactive system is not solvent-dependent. Therefore the observed rate differences should arise mainly from the different "preparation" of the activation process, which is driven by the environ-
ment. The stronger interactions with the more confining silicalite framework together with the hindering of the transfer when the complex is located in the ZK4 windows seem to be the main structural effects determining the observed behavior. In addition to these effects also the different effectiveness of the small number of “active” oxygens doing considerable work in silicalite and ZK4 should be considered. Even though the total work is comparable in the two zeolites, due to the large compensation between atoms depositing energy in the reactive complex and atoms removing energy from it, it is likely that this point may play an important role in determining the rate differences observed on longer time scales ($\sim \tau_{\text{rxn}}$) than those characterizing the barrier passage ($\sim \tau_{\text{mol}}$).
Activated processes: the exchange reaction
Chapter 6

The two-step model for diffusion in silicalite

6.1 Diffusion models and correlation effects

The confinement within zeolitic cavities may lead to important effects related to the anisotropy of the microporous structure; being subjected to a confinement that is repeated in space according to the periodicity of the crystal structure, the sorbed molecules move along well-defined and distinct paths in the three cartesian axes, on the basis of guest-host interactions of different kind and intensity along each direction. Clearly, isotropic zeolites such as those with cubical symmetry like A and Y does not show these phenomena, which are instead present for example in zeolites ZSM-5 (silicalite I), ZSM-11 (silicalite II) and chabazite.\(^{194-196}\) The particular structure of silicalite channels determines an easier motion along the straight channels compared to that in the sinusoidal ones, where the diffusion is obviously slower. Indeed, the order \(D_y > D_x \gg D_z\) is typically observed for the component of the diffusion coefficient. As a system of channels directed along \(z\) is absent, the motion along this direction is only possible after a specific (and complicated) sequence of displacements along the two kinds of channels. Looking at Fig. 6.1 we see that the molecule can diffuse along \(z\) only when it is located in the sinusoidal channel; in those channels there is a strict alternation of sections directed towards positive and negative \(z\), while keeping \(x\) as average direction. Therefore if a molecule moves over two consecutive sinusoidal sections, non net displacement along \(z\) will occur. However if the molecule carries out one (or any odd number) displacement along the straight channel between the two jumps in the zigzag sections, an effective displacement of \(c\) Å along \(z\) will result, as indicated in the figure.

It is then clear that the motion along \(z\) will necessarily be slower than in the two other directions, being dependent on the probability that the molecule follows such tortuous path. The propagation along \(y\) or \(x\) does not show similar restrictions, as the two channels are precisely directed along those directions. The strict connection between the motion along \(z\) and that in the two channel systems bring about another effect: the monodimensional diffusion coefficients are not independent on each other, but they must be connected by a relation somewhat reflecting the previous discussion. By rep-
Fig. 6.1: A schematic view of the network of channels in a silicalite unit cell. Continuous lines represent the principal axes of channels; the displacement highlighted by the thick lines illustrates the sequence of displacements corresponding to a net displacement of $c$ (13.383 Å) along $z$

representing the diffusion in silicalite as a random walk between adjacent intersections, Kärger\textsuperscript{194} obtained a simple relation between the three components of the diffusion coefficient:

\[ \frac{a^2}{D_x} + \frac{b^2}{D_y} = \frac{c^2}{D_z} \tag{6.1} \]

where $a$, $b$ and $c$ are the unit cell edges. This expression may easily be associated to the previous discussion: it shows that the mean propagation time along $z$ is the sum of the corresponding times of diffusion along $x$ and $y$, each one normalized to the distance covered in a single jump.

It should be remarked that the only assumption made in deriving Eq. 6.1 is the basic assumption of random walk theory (section 3.4.5): the molecular propagation is considered to be independent on the previous "history" of the molecule, or equivalently any correlation between two subsequent displacements is absent. In other words one assumes that in the time between a jump and the next one the molecule completely looses the memory of its previous motion, so that any subsequent displacement will be absolutely independent on the previous ones. In the case of silicalite, one assumes that when a molecule reaches an intersection it will then move to one of the four adjacent intersections with a probability independent on its previous trajectory, thus independent on the intersection from which it came from. The validity of this assumption may be ascertained by applying Eq. 6.1 to the measured components of the diffusion tensor. The experimental measurements of $D$, based on pulsed NMR techniques, are affected by considerable errors (up to 50\%) due to the fairly small dimensions of the zeolite crystals employed in the analysis*. However it is possible, by carrying out the NMR measure-

*In order to measure the true intracrystalline diffusivity through NMR it is necessary that in the
ments over oriented crystals, to determine the diffusivity in the z direction and in the perpendicular xy plane,\textsuperscript{197,198} thus obtaining the anisotropy factor \( f = \frac{1}{2}(D_x + D_y)/D_z \) (note that \( D_{xy} = \frac{1}{2}(D_x + D_y) \)). Following Eq. 6.1, \( f \) should ideally change with the \( D_x/D_y \) ratio as shown in Fig. 6.2, with a minimum value of \( \sim 4.4 \) when \( D_x = D_y \). This is the lower limit of the anisotropy factor for a random-walker in silicalite.

![Diagram](image.png)

**Fig. 6.2:** Anisotropy factor plotted versus the \( D_x/D_y \) ratio, according to the correlation rule Eq. 6.1

The available experimental data concerning the diffusion of methane, ethane and CF\(_4\) are not in contrast with this limit.\textsuperscript{197-199} The rather large error affecting such measurements does not allow definitive conclusions to be drawn. MD simulations directly provide the values of \( D_x \), \( D_y \) and \( D_z \), allowing to calculate \( f \) and also a direct estimate of the “random walk” value of \( D_z \). In the latter case the \( D_x \) and \( D_y \) values obtained from the simulation are introduced in Eq. 6.1 and the obtained \( D_z \) will then be compared with the value obtained from the simulation, which in this context takes the role of “experimental” data to test the theory. The available data for small and/or spherically symmetrical species like methane and xenon are in good agreement with the predictions of the random walk model.\textsuperscript{70,149,151,200} Nevertheless the simulations of Dumont et al.\textsuperscript{201} showed that for ethane and propane the deviations from the random walk rule are more marked with respect to methane. Moreover simulations with a flexible model for the silicalite framework\textsuperscript{202,203} show that the ethane diffusion consists of a series of jumps occurring every 20-30 ps in the straight channels and every 70 ps in the sinusoidal channels. Albeit the length of such simulations (100 ps) is too short to draw quantitative conclusions, we see that in the case of ethane there is a larger probability that the molecule, after reaching the intersection, keeps moving in the same direction, instead of randomly jumping from a channel to the other. In prac-

observation time (about a millisecond) the molecule does not diffuse out of the crystal (whose diameter is in the micrometer range); the larger the available crystals, the better this condition will be verified.
tice it could be expected that non-spherical molecules like linear alkanes might show considerable deviations from the random walk behavior. For instance, the hydrocarbon chain may act as an effective guide to direct the molecular propagation of relatively long molecules, favoring the keeping of the direction as opposed to the previous hypothesis of total randomness. Indeed, several recent simulations of long-chain linear alkanes seem to confirm this point: Maginn et al.\textsuperscript{50,204} observed that the longer chains have a lower tendency to move between the two channel systems, i.e. they keep a strong conformational memory and tend to be localized in a single channel system; this behavior is more marked at low temperatures. In a more accurate description of the diffusive motion the possible correlation between subsequent displacements between intersections should be taken into account. This purpose has been reached, at least as a first approximation, by representing the molecular diffusion as a sequence of \textit{pairs} of jumps ("two-steps") between adjacent intersections, as opposed to the random walk sequence of single displacements. In the random walk model each event is a jump from an intersection to another adjacent one, while in this extension two subsequent jumps (where the molecule crosses \textit{three} intersections) are coupled to give a single, two-step, event. Clearly, different kinds of two-step events are possible, each one affecting to a different extent the total diffusivity. The description of the trajectory of a sorbed molecule in terms of the appropriate sequence of two-steps incorporates the possible correlation within each couple of subsequent jumps. Indeed, we are going to express the mean square displacement along each direction through the average number of different two-step events: this allows avoiding the assumption of complete loss of memory between the single jumps. For instance the tendency of a molecule to continue (or not to continue) in the same direction from which it came from is directly considered in the two-step model equations, which include the numbers of coupled events in the same direction, as well as the switches of direction, and so on. In other words, the diffusive memory can (if present) affect the diffusion coefficients estimated through the two-step model, while in the random walk model such influence cannot be directly included.

The investigation of the existence and entity of correlation effects is an important and actual problem, for instance to test the applicability of stochastic jump diffusion models such as Kinetic Monte Carlo (KMC)\textsuperscript{205-209} to study diffusive phenomena in zeolites. In such methods, after determining the position and the relative energies of adsorption sites in the zeolite, as well as the activation energy and the kinetic constants for each possible jump, a stochastic trajectory is generated for the molecules diffusing in the zeolitic pores. In this trajectory jumps are usually non correlated: the molecule carries out a random walk between the sorption sites. This allows to considerably extend the time scales accessible to the simulation, because the "molecular" details involved in the exact dynamical evolution of the system are left out of the calculations. KMC methods are then often based on the same assumption of the random walk model: absence of correlation between subsequent jumps, which should be then carefully checked before applying them. It is necessary to ascertain if, for a particular sorbent-sorbate system, the diffusion may effectively be separated into a sequence of jumps in random directions, and up to what concentration/temperature the assumption keeps its validity. When correlation effects are important the applicability of KMC methods is more difficult; it is however possible to include correlation effects in KMC models by modifying them on the basis of correlation factors determined analytically\textsuperscript{209} or by
MD simulations. An interesting alternative could be to adapt our two-step model to KMC simulations in silicalite: actually the basic input of such simulations are the rate constants for each possible jump, which are usually determined from the corresponding activation energies, previously calculated. The mean times and probabilities corresponding to each two-step event (obtained from our MD simulations) provide an alternative way for calculating such rate constants. From their values it should be possible to generate - following the KMC algorithm - an appropriate stochastic (but more accurate) sequence of two-step jumps, extended to very long space and time scales. In practice, instead of generating a random walk between sorption sites, a two-step trajectory - automatically incorporating most part of the correlation present - would be produced.

The study of the deviations from the behaviour predicted by random walk correlation rules analogous to Eq. 6.1 and derived under the hypothesis of absence of diffusive memory may also highlight some particular aspects of the diffusive process. Bär et al. studied the diffusion anisotropy in the zeolite chabazite; it is a natural zeolite, so that crystals of large dimensions are available for an accurate experimental measurement of diffusive anisotropy. The authors observe that the diffusion anisotropy experimentally determined in chabazite is larger than what expected on the basis of uncorrelated propagation; this may suggest the existence of additional transport barriers hindering diffusion along \( z \) (the principal axis of the chabazite cavities). It is clear that this kind of information cannot be directly obtained by the single components of the diffusion coefficient alone, but only by comparing their ratio with that predicted by an appropriate correlation rule. The already mentioned simulations of Maginn et al. highlighted that at high temperatures also long-chain species tend to satisfy more closely the correlation rule in silicalite: if we interpret the fast loss of diffusive memory (implicit in the correlation rule) as due to a facile migration between the two channel systems, such observation is very important. It shows that, if a porous section is obstructed by side products, this does not completely inhibit the access to such section: indeed, if the diffusants are small enough or if the temperature is high, the tridimensional network of channels in silicalite allows to circumvent the obstacle through an alternative (albeit tortuous) path. Therefore the loss of activity of the zeolite catalyst due to the formation of pore-obstructing species is a more crucial problem at low temperature and for longer chain species. This concept is strictly connected to the so-called “molecular traffic control” or MTC, which is the property by which zeolites with different channels, interconnected in the three dimensions, induce reactants and products to move in different channels, on the basis of different guest-host interactions. Indeed simulations of multicomponent systems seem to point out that different molecules in a mixture occupy the different sections of the porous system with different probabilities. The problem is then shifted to the behavior of the molecules after they approach an intersection with the other channel, where reactant and products interact and possibly react. Once again it appears important to understand and predict the tendency of a molecule to continue its path in the same direction (same channel) after the intersection, compared to the possibility of changing channel.

These are some of the fields where the monodimensional diffusion coefficients and the diffusion models (with the corresponding correlation rules) can provide information useful to understand the molecular propagation in zeolites.
6.2 The two-step model

The basic idea of the model is to combine two subsequent ("single-step") displacements between intersections in a coupled (or "two-step") event. The molecular propagation is now considered as a sequence of two-step displacements. There are basically three kinds of such coupled displacements: a) 2 steps in the straight channel, b) 2 steps in the zigzag channel or c) an interchange between straight and zigzag channels. Fig. 6.3 shows examples for these three possibilities.

![Diagram](image)

**Fig. 6.3:** The same schematic view of Fig. 6.1; now the thick lines illustrate examples of the three main two-step displacements: \((ss')\), two consecutive jumps in the straight channel, in the same direction; \((zz')\), two consecutive jumps in the zigzag channel, in the same direction; \((sw)\), switch of channel from straight to zigzag or vice versa.

Let us look at the probabilities that, on its way through three subsequent intersections, a molecule crosses two straight channels \((p_{ss})\), two zigzag channels \((p_{zz})\), a straight channel followed by a zigzag one \((p_{sz})\) or a zigzag channel followed by a straight one \((p_{zs})\). If the motion is uncorrelated, then these probabilities can be written as:

\[
p_{ss} = p_s^2 \quad p_{zz} = p_z^2 \quad p_{sz} = p_{zs} = p_s p_z
\]  

where \(p_s\) and \(p_z\) are the single-step probabilities that the molecule exits from an intersection to a straight channel or to a zigzag one, respectively. Note that Eq. 6.2 obviously obeys the condition:

\[
p_{ss} + p_{zz} + p_{sz} + p_{zs} = (p_s + p_z)^2 = 1
\]  

Note that the coupled displacements in the straight or zigzag channels could be both in the same direction \((p_{ss}^2 \text{ and } p_{zz}^2)\) or in opposite directions \((p_{ss}^2 \text{ and } p_{zz}^2)\): in
this last case the first and the third intersections are identical, i.e. the molecule returns to the starting intersection after having visited a neighbouring one. Obviously, \( p_{ss} = p_{ss}^s + p_{ss}^o \) and \( p_{zz} = p_{zz}^s + p_{zz}^o \). If we want to express the components \( \langle \Delta x^2(t) \rangle \), \( \langle \Delta y^2(t) \rangle \) and \( \langle \Delta z^2(t) \rangle \) of the mean square displacement as a function of the measured numbers of coupled displacements, it is very important to distinguish between the coupled displacements in the same and in opposite directions. These last events do not take part in the overall motion of the molecule. Moreover, as visible from Fig. 6.1, the total displacement during one two-step event clearly depends on the individual steps: two displacements in the same zigzag direction lead to a displacement of \( a \) along \( x \) (\( a/2 \) being the distance between two intersections along the zigzag channel, i.e. the length of each single-step); two displacements in the same straight direction lead to a displacement of \( b \) along \( y \) (\( b/2 \) being the distance between two intersections along the straight channel); finally, each switch event (with probability \( p_{sw} = p_{sz} + p_{zs} \)) leads to displacements of \( a/2 \), \( b/2 \) and \( c/2 \) along \( x \), \( y \) and \( z \) directions, respectively. This happens because an \( a/2 \) displacement followed by a \( b/2 \) one (or vice versa) necessarily implies a \( c/2 \) displacement along the \( z \) direction. Therefore, the correct expressions for the monodimensional mean square displacements (MSD) should be:

\[
\langle \Delta x^2(t) \rangle = n_{zz}^s(t)a^2 + n_{sw}(t)(a/2)^2 \tag{6.4}
\]

\[
\langle \Delta y^2(t) \rangle = n_{zz}^o(t)b^2 + n_{sw}(t)(b/2)^2 \tag{6.5}
\]

\[
\langle \Delta z^2(t) \rangle = n_{sw}(t)(c/2)^2 \tag{6.6}
\]

where the \( n(t) \)'s are the numbers of coupled events detected in an observation time \( t \). The correctness of these expressions may be verified by showing their coincidence with the correlation rule for random propagation. For this purpose, we express the numbers of coupled events as a function of the numbers \( n_s \) and \( n_z \) of single-steps. In the case of random propagation, we have \( p_{zz}^s = p_{zz}^o \) (any difference between them indicates deviations from strict randomness). In the following the time-dependency of the \( n \) event numbers will not be explicitly indicated, therefore \( n \) should be read \( n(t) \), and so on. From Eq. 6.2 we find:

\[
p_{zz} = p_{zz}^s + p_{zz}^o \underbrace{=}_{\text{random case}} 2p_{zz}^s = 2p_{zz}^o \tag{6.7}
\]

whence:

\[
p_{zz}^s = p_{zz}^o = \frac{1}{2} p_z = \frac{1}{2} (n_z/n)^2 \tag{6.8}
\]

We may use the notation:

\[
p_{zz}^s = n_{zz}^s/n_2 \tag{6.9}
\]
where \( n_2 = n_{ss} + n_{zz} + n_{sw} \) is the total number of coupled steps. It is equal to one-half of the total number \( n \) of single steps, because every coupled event is composed of two single-steps:

\[
n = 2 \, n_2
\]  

(6.10)

Thus, from Eq. 6.8, Eq. 6.9 and Eq. 6.10:

\[
n_{zz}^s = n_{zz}^o = \frac{1}{4} n_2^2/n
\]  

(6.11)

With analogous calculations, one obtains:

\[
n_{ss}^s = n_{ss}^o = \frac{1}{4} n_2^2/n
\]  

(6.12)

On the other hand, we can write:

\[
\text{random case}
\]

\[
p_{sw} = p_{sz} + p_{zs} \quad \Rightarrow \quad 2p_{sz} = 2p_{zs} = 2p_sp_z
\]  

(6.13)

whence:

\[
n_{sw}/n_2 = 2 \, n_sn_z/n_2
\]  

(6.14)

and finally:

\[
n_{sw} = n_sn_z/n
\]  

(6.15)

Substituting in Eq. 6.4 - Eq. 6.6 the quantities \( n_{zz}^s \), \( n_{ss}^s \) and \( n_{sw} \) by the relations Eq. 6.11, Eq. 6.12 and Eq. 6.15 as resulting for random propagation from intersection to intersection, one obtains:

\[
\langle \Delta x^2(t) \rangle = n_z(a/2)^2
\]  

(6.16)

\[
\langle \Delta y^2(t) \rangle = n_s(b/2)^2
\]  

(6.17)

\[
\langle \Delta z^2(t) \rangle = n_sn_z/n \, (c/2)^2
\]  

(6.18)

From Eq. 6.16 - Eq. 6.18 we obtain:
\[
\frac{a^2}{4\langle \Delta x^2(t) \rangle} + \frac{b^2}{4\langle \Delta y^2(t) \rangle} = \frac{1}{n_z} + \frac{1}{n_s} = \frac{n}{n_s n_z} = \frac{c^2}{4\langle \Delta z^2(t) \rangle}
\] (6.19)

which, due to:

\[
\langle \Delta x^2(t) \rangle = 2D_x \, t \quad \langle \Delta y^2(t) \rangle = 2D_y \, t \quad \langle \Delta z^2(t) \rangle = 2D_z \, t
\] (6.20)

is nothing else than the correlation rule, Eq. 6.1.

We then showed the general validity of Eq. 6.4 - Eq. 6.6, which represent the core of the two-step model. Another interesting development is the derivation of a correlation rule between the components of the diffusion coefficient analogous to Eq. 6.1. In this case it should also include the deviations from the ideal behavior of absence of correlation. Such deviations can be calculated as difference between the numbers of coupled events and those predicted in absence of correlation:

\[
\Delta n_{zz}^s = n_{zz}^s - \frac{1}{4} n_z^2 / n
\] (6.21)

\[
\Delta n_{zz}^o = n_{zz}^o - \frac{1}{4} n_z^2 / n
\] (6.22)

\[
\Delta n_{ss}^s = n_{ss}^s - \frac{1}{4} n_s^2 / n
\] (6.23)

\[
\Delta n_{ss}^o = n_{ss}^o - \frac{1}{4} n_s^2 / n
\] (6.24)

\[
\Delta n_{sw} = n_{sw} - n_s n_z / n
\] (6.25)

By introducing the latter equations, Eq. 6.4 - Eq. 6.6 may be transferred into:

\[
\langle \Delta x^2(t) \rangle = \frac{1}{4} a^2 (n_z + 4 \Delta n_{zz}^s + \Delta n_{sw})
\] (6.26)

\[
\langle \Delta y^2(t) \rangle = \frac{1}{4} b^2 (n_s + 4 \Delta n_{ss}^s + \Delta n_{sw})
\] (6.27)

\[
\langle \Delta z^2(t) \rangle = \frac{1}{4} c^2 (n_s n_z / n + \Delta n_{sw})
\] (6.28)
or:

\[
\frac{a^2}{4(\Delta x^2(t))} = \frac{1}{n_z + 4 \Delta n_{zz} + \Delta n_{sw}} \approx \frac{1}{n_z} - \frac{4 \Delta n_{zz}}{n_z} - \frac{\Delta n_{sw}}{n_z^2} \tag{6.29}
\]

\[
\frac{b^2}{4(\Delta y^2(t))} = \frac{1}{n_s + 4 \Delta n_{ss} + \Delta n_{sw}} \approx \frac{1}{n_s} - \frac{4 \Delta n_{ss}}{n_s} - \frac{\Delta n_{sw}}{n_s^2} \tag{6.30}
\]

\[
\frac{c^2}{4(\Delta z^2(t))} = \frac{1}{\frac{n_m}{n} + \Delta n_{sw}} \approx \frac{1}{n_s} + \frac{1}{n_z} - \Delta n_{sw} \left[ \frac{1}{n_s^2} + \frac{1}{n_z^2} + \frac{2}{n_s n_z} \right] \tag{6.31}
\]

where we have made use of the fact that \( n_z \gg (4 \Delta n_{zz} + \Delta n_{sw}) \) in Eq. 6.29; \( n_s \gg (4 \Delta n_{ss} + \Delta n_{sw}) \) in Eq. 6.30 and \( n_s n_z \gg n \Delta n_{sw} \) in Eq. 6.31. The values reported in the following validate these approximations. Combining Eq. 6.29 - Eq. 6.31 yields:

\[
\frac{a^2}{4(\Delta x^2(t))} + \frac{b^2}{4(\Delta y^2(t))} \approx \frac{c^2}{4(\Delta z^2(t))} \approx \frac{4 \Delta n_{zz}}{n_z^2} - \frac{4 \Delta n_{ss}}{n_s^2} + \frac{2 \Delta n_{sw}}{n_s n_z} \tag{6.32}
\]

whence via Eq. 6.20:

\[
\frac{a^2}{D_x} + \frac{b^2}{D_y} \approx \frac{c^2}{D_z} = \frac{32 \Delta n_{zz}}{n_z(n_z/t)} - \frac{32 \Delta n_{ss}}{n_s(n_s/t)} + \frac{16 \Delta n_{sw}}{n_s n_z/t} \tag{6.33}
\]

Finally, combining Eq. 6.16 - Eq. 6.18 with Eq. 6.20, in first order approximation the quantities \( n_z/t \) and \( n_s/t \) on the right side of Eq. 6.33 may be replaced by \( 8 D_z/a^2 \) and \( 8 D_y/b^2 \), respectively, while the quantity \( n_s n_z/t \) may be replaced by \( 8nD_z/c^2 \). Thus one obtains the generalized correlation rule:

\[
\frac{a^2}{D_x} \left[ 1 + \frac{4 \Delta n_{zz}}{n_z} \right] + \frac{b^2}{D_y} \left[ 1 + \frac{4 \Delta n_{ss}}{n_s} \right] = \frac{c^2}{D_z} \left[ 1 + \frac{2 \Delta n_{sw}}{n} \right] \tag{6.34}
\]

which we shall call generalized rule because it does not arise from any basic assumption concerning the diffusive motion of the molecules. It quantitatively relates the diffusivities in \( x \) and \( y \) direction to the diffusivity in \( z \) direction, if subsequent displacements between the channel intersections are correlated. As to be expected, any preferential continuation of propagation in the same type of channel segment which - according to Eq. 6.21 and Eq. 6.23 - corresponds to positive \( \Delta n_{zz} \) and \( \Delta n_{ss} \) values, leads to a decrease in \( D_z \) in comparison with the prediction of the correlation rule, Eq. 6.1, for completely random propagation. Moreover, any preferential tendency to switch channel segment, entailing positive \( \Delta n_{sw} \) values, leads to an increase of \( D_z \) in comparison with the value predicted by Eq. 6.1. Note also that both rules coincide in complete absence of diffusive memory (\( \Delta = 0 \)).
6.3 Applications of the two-step model: diffusion of ethane in different conditions

6.3.1 Interaction potentials

As a first test of the two-step model it has been applied to interpret the diffusive motion of ethane molecules at different loading and temperatures. Besides verifying the efficiency of Eq. 6.4 - Eq. 6.6 in the prediction of the MSD components, it is interesting to evaluate the extent of correlation effects for a non-spherical, but rather small molecule. The simulation box consists of two unit cells of silicalite superimposed along the z axis. The intra- and intermolecular potential describing ethane has been previously proven to be suitable to accurately reproduce several experimental properties of the ethane-silicalite system, like sorption heat and diffusion coefficient.\textsuperscript{81,82} Ethane is modeled by two point sites representing methyl groups, the site-to-site intermolecular potential between two methyl groups of different molecules, as well as between a methyl and a zeolitic oxygen, are of the Lennard-Jones form. The Jorgensen's parameters\textsuperscript{213} for liquid ethane have been used for the CH\textsubscript{3}-CH\textsubscript{3} interaction: $\sigma=3.775\text{Å}$ and $\epsilon=0.867\text{kJ mol}^{-1}$; the CH\textsubscript{3}-O\textsubscript{xo} parameters are $\sigma=3.461\text{Å}$ and $\epsilon=0.811\text{kJ mol}^{-1}$, which had been chosen because they give an adequate description of the methane-silicalite system, as shown in previous simulations.\textsuperscript{71} Indeed they proved to be suitable to model the CH\textsubscript{3}-O interaction too. The full flexibility of both the ethane molecule and the zeolite framework are taken into account; the C-C bond oscillation is described through a Morse potential with parameters derived from spectroscopic data.\textsuperscript{214} Dissociation energy $D_c=351.381\ \text{kJ mol}^{-1}$, equilibrium distance $r_o=1.536\ \text{Å}$ and C-C stretching frequency 945 cm\textsuperscript{-1}, corresponding to $\beta=1.8408\ \text{Å}^{-1}$.

Four MD simulations at 300 K have been carried out, with 1, 2, 4 and 6 ethane molecules per unit cell. The equilibration run length was 400 ps, during which the atom velocities, starting from zero, were adequately rescaled to achieve the desired temperature. Having previously\textsuperscript{81,82} established that a 3 ns “production” run with 4 ethane molecules per unit cell gave a good statistical accuracy, we extended the length of the trajectories with lower loadings to 12 ns for 1 ethane/u.c., and to 6 ns for 2 ethane/u.c., in order to obtain a reasonably accurate sampling of the phase space in all cases. Another two simulations of 3 ns at 400 K and 500 K were carried out with 4 molecules/u.c. to study the effect of temperature. The center of mass coordinates of ethane molecules were stored every 32 fs (the time step is always 1 fs).

6.3.2 Coordinates’ mapping

The analysis of the motion is based on an accurate mapping of the different zones in which the micropores of silicalite can be divided, in order to establish with high precision the region (straight or zigzag channel or intersection) visited by a molecule at a certain time. The projection of a trajectory in the $xy$-plane (Fig. 6.4, run at 500K) shows that the various zones (straight channels, zig-zag channels and intersections) are well-defined using only these two coordinates. Note that the sinusoidal channels (segments along $z$) in the figure appear as straight once projected onto the $xy$ plane. The enlargement of a part of Fig. 6.4, shown in Fig. 6.5, allows a better understanding
of the criteria adopted to divide the \( xy \)-plane in:

1. straight channel sections: rectangles with edges 5.2 Å (along \( y \)) and 4.8 Å (along \( x \)) centered at \( x=0, \pm 10, \pm 20, \ldots \) and \( y=0, \pm 10, \pm 20, \ldots \)

2. zig-zag channel sections: rectangles with edges 5.2 Å (along \( x \)) and 4.8 Å (along \( y \)), centered at \( x=\pm 5, \pm 15, \pm 25, \ldots \) and \( y=\pm 5, \pm 15, \pm 25, \ldots \)

3. intersections between two orthogonal channels: squares with edges of 4.8 Å, centered at \( x=0, \pm 10, \pm 20, \ldots \) and \( y=\pm 5, \pm 15, \pm 25, \ldots \)

![Graph](image)

**Fig. 6.4:** Projection in the \( xy \)-plane of the trajectory of an ethane molecule in silicalite (3 ns at 500 K).

It must be remarked that the channel sections are often considered longer than 5.2 Å, and the width of the intersections, projected on the plane, can be lower than 4.8 Å. Indeed the only requirement is that such lengths must sum to 10 Å and in principle every combination that satisfies this criterion could be chosen. But, looking at the \( xy \)-projection of our trajectories, we found this division more suitable to describe them. In our case, it is very important to know when a particle reaches or leaves an intersection (see below), and with shorter intersection edges some cases would not have been correctly considered. In that case many events would not be correctly dealt with because: a) a larger number of oscillations channel-intersection would be observed while the molecule moves at the boundary between the two regions; b) a not negligible number of points not belonging to any of the previously discussed regions would be recorded. By extending the region covered by the intersection these problems are minimized and no further difficulties arise. This map keeps a general validity and it is possible to use it to locate and define the zone occupied by any molecule in silicalite.
Fig. 6.5: Enlargement of a portion of Fig. 6.4, showing the details of the intersection centered at \( x=0 \text{ Å}, y=5 \text{ Å} \).

Some errors could stem from the application of the geometrical criterion described above to these trajectories. The conservation of the total linear momentum \( P \) of our system (which is zero, as the initial velocities are) leads to a resulting non-zero linear momentum for the framework. This momentum, albeit small, results in a slow translational motion of the whole framework\(^1\), which does not affect much the values of the diffusion coefficients and other dynamical variables, but could be very important when the coordinates of the particles are mapped on the basis of the initial position of the framework, as in the present case. For example, after 3 ns, we found in some cases displacements of 2-3 Å of the \( x \) coordinate of all framework atoms compared to the starting values, indicating a slow overall translational motion along \( x \) (obviously, the displacement could also be observed in other directions). We easily solved this problem by referring the stored coordinates of the guest particles to the initial position of the framework center of mass, i.e., before the storage to disk, the position vectors \( \mathbf{r}_i \) of each particle were scaled as:

\[
\mathbf{r}_i(t) = \mathbf{r}_i(t) - \Delta \mathbf{r}_{cm,zeo}(t)
\]

where \( \Delta \mathbf{r}_{cm,zeo}(t) \) is the difference between the position of the framework center of mass at time \( t \) and its initial position, at \( t = 0 \). The trajectories obtained in this way are then suitable for the right application of the geometrical mapping criterion, because the motion of the particles is always referred to the same (initial) geometry of

\(^1\) \( P = P_{zeo} + P_{ads} \) (where \( P_{zeo} \) and \( P_{ads} \) are the linear momentum of the framework and of the sorbed molecules, respectively. As the initial value of \( P \) is zero, the sum \( P_{zeo} + P_{ads} \) will be zero for the whole simulation. This entails \( P_{zeo} = -P_{ads} \) at every step: in other words when \( T \neq 0 \) a small but nonzero linear momentum is always present on the framework. Therefore, as \( P = M v_{CM} \) (where \( M \) is the total mass and \( v_{CM} \) is the center of mass velocity of the framework) the slow translation of the framework is an effect of the conservation law.
the framework. This correction leads to very small variations in the calculated diffusion coefficients compared to the values obtained without the correction for the framework motion.

6.3.3 Calculating the average numbers of two-step events

In the $xy$-plane every intersection could then be identified as a couple of integers $(l,m)$ corresponding to the intersection center, expressed in Å. The path of a molecule is described in terms of the succession of different intersections reached, i.e., in terms of the corresponding sequence of $(l,m)$ pairs. This sequence is then analyzed starting from the first intersection, and establishing what kind of coupled displacement has led the molecule to the second and then to the third intersection; this step is then repeated starting from the second intersection in the series, and so on. Results are averaged over all molecules. The number and the duration of each kind of single and two-step displacements found are recorded and averaged. Note that all subsequent intersections are taken as origins in order to achieve the best statistics as possible. But the applications of the two-step model, which is based on jumps from the first to the third intersection, then from the third to the fifth one, and so on, requires that the event numbers calculated in this way must be divided by two. It should be noted that in Eq. 6.4 - Eq. 6.6 the time-dependence of the monodimensional MSD's is associated to the time dependence of $n^s_{zz}$, $n^s_{ss}$ and $n_{sw}$. One simple but inaccurate way to proceed could be to calculate the $n^s_{zz}$, $n^s_{ss}$ and $n_{sw}$ values from the full trajectory (averaging over all molecules); then the $t$ value would be equal to the trajectory length $\tau_{RUSN}$. But some inaccuracy stems from the fact that only one trajectory would be considered in each case, and moreover the time evolution of the MSD’s could not be followed in this way. It is more interesting to study the time evolution of the MSD’s as calculated by Eq. 6.4 - Eq. 6.6, in order to better assess their validity by comparison with the values obtained through the standard method (Eq. 3.25). The latter datum has the role of "experimental" value against which the theoretical model can be validated. Moreover the $n_t$ and $n_z$ numbers of "single" events will be also calculated, in order to apply and test the random walk equations Eq. 6.16 - Eq. 6.18.

The extended time dependence of the numbers of events can be extracted from the trajectory of each single molecule according to the following scheme:

1. the sequence of $N_i$ intersections visited by the molecule is mapped.
2. the index $j$ runs from 2 to $N_i$.
3. all the sequences of $j$ intersections included in the full ($N_i$) one are separately studied, so as to obtain the average number and duration of each kind of event observed in a typical sequence of $j$ intersections with a calculation similar to that typically performed for correlation functions. Actually when $j$ is small the trajectory contains a large number of sequences of $j$ intersections. Such sequences are examined one at a time, so as to determine the kind and number of jumps connecting the first to the last intersection for each sequence. The final average will be more accurate when $j$ is small because a large number of samples are included, just like in the calculation of correlation functions, whose statistical accuracy gets worse at long times.
4. the time \( \tau \) needed to cross \( j \) intersections is simultaneously averaged over all such sequences, and the average numbers of events found in the path along \( N_i \) intersections are then assigned to the time \( \tau \).

In this way it becomes possible to account for the time dependence of the event numbers and Eq. 6.4 - Eq. 6.6 as well as Eq. 6.16 - Eq. 6.18 can be applied, giving the monodimensional and total MSD predicted by the new and the random walk models.

### 6.3.4 Diffusion coefficients from the random walk and two-step models

In Fig. 6.6 the three mean square displacement curves calculated according to Eq. 6.4 - Eq. 6.6 (2-step model), Eq. 6.16 - Eq. 6.18 (random walk model) and Eq. 3.25 (standard MSD calculation) are shown for each case studied here. It is immediately clear that both the diffusion models considered always overestimate the MSD with respect to the standard, “true” value obtained from Eq. 3.25. At the same time, it is evident that the 2-step model always gives a better estimate of the mean square displacement: actually this model only slightly overestimates the “true” MSD value in its linear region (80-240 ps), whose slope was chosen to measure the diffusion coefficient values. The agreement seems to improve at higher temperatures: at 500 K (Fig. 6.6f) the two curves are very close. It is interesting to note that the curves calculated according to Eq. 6.4 - Eq. 6.6 and Eq. 6.16 - Eq. 6.18 always show a very linear trend, also at longer times than those shown, while the MSD calculated by Eq. 3.25 is more sensitive to the higher statistical inaccuracy with increasing correlation time, showing a less linear trend at longer times. This is probably due to the thorough analysis of the trajectories carried out in the calculation of the event numbers as a function of the time.

The diffusion coefficients obtained from a linear fit to the “real” MSD curves calculated by Eq. 3.25 in the 80-240 ps region are reported in Tab. 6.1 and Tab. 6.2, indicated by the (a) notation. There is only a slight decrease with increasing loading from 2 to 4 ethane molecules/unit cell, while a net decrease is observed going to 6 molecules/u.c, where probably the stronger interactions between the sorbed molecules mutually hinder their motion. Anyway we are not interested in the effect of loading on diffusivity, but in verifying the validity of models and the extent of correlation effects at the different concentrations.

The “anomalous” behavior observed for the 2 mol./u.c. simulation (see also below) emerges also when the anisotropy factor \( f \) is calculated. All studied cases but that with 2 mol./u.c give values greater than 4.4. The \( f \) values calculated by the random walk diffusivities is always exactly 4.4, that is the lower limit obtained analytically by taking \( p_s = p_z = 0.5 \). This condition does not need to be verified - the random walk model only requires that the probability of each jump should be independent on the previous displacement, but \( p_s \) can be different from \( p_z \), giving \( f > 4.4 \) - however for ethane the number of single steps along straight and zigzag channel segments does not vary considerably, so that \( p_s \sim p_z \) and \( f \) calculated with the random walk equations Eq. 6.16 - Eq. 6.18 exactly matches 4.4. The increase with the temperature is discussed in previous works,\(^{81,82}\) where the Arrhenius parameters for the diffusion process were calculated and discussed.
**Fig. 6.6:** Mean square displacement curves obtained according to 2-step model (dashed line), 1-step model (dot-dashed line) and standard method (solid line). (a): $T=300$ K, 1 molecule/u.c.; (b): $T=300$ K, 2 molecules/u.c.; (c): $T=300$ K, 4 molecules/u.c.; (d): $T=300$ K, 6 molecules/u.c.; (e): $T=400$ K, 4 molecules/u.c.; (f): $T=500$ K, 4 molecules/u.c.
Table 6.1: Ethane diffusion coefficients at different loadings (/10^{-9} \text{ m}^2 \text{ s}^{-1}): (a) standard method; (b) two-step model; (c) random walk model

<table>
<thead>
<tr>
<th>Loading (mol/u.c.)</th>
<th>D</th>
<th>D_x</th>
<th>D_y</th>
<th>D_z</th>
<th>f</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
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<td>5.7</td>
<td>13.1</td>
<td>1.8</td>
<td>5.2</td>
</tr>
<tr>
<td>(b)</td>
<td>7.6</td>
<td>8.6</td>
<td>12.2</td>
<td>2.1</td>
<td>4.9</td>
</tr>
<tr>
<td>(c)</td>
<td>9.6</td>
<td>13.4</td>
<td>12.4</td>
<td>2.9</td>
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</tr>
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<td></td>
<td></td>
</tr>
<tr>
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<td>8.3</td>
<td>2.0</td>
<td>3.5</td>
</tr>
<tr>
<td>(b)</td>
<td>7.6</td>
<td>8.2</td>
<td>12.6</td>
<td>2.0</td>
<td>5.2</td>
</tr>
<tr>
<td>(c)</td>
<td>10.4</td>
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<td>13.8</td>
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</tr>
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<tr>
<td>(a)</td>
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<td>5.5</td>
<td>9.1</td>
<td>1.2</td>
<td>6.3</td>
</tr>
<tr>
<td>(b)</td>
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<td>7.6</td>
<td>10.7</td>
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<td>5.7</td>
</tr>
<tr>
<td>(c)</td>
<td>8.7</td>
<td>12.4</td>
<td>11.0</td>
<td>2.7</td>
<td>4.3</td>
</tr>
<tr>
<td>6</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>3.0</td>
<td>2.9</td>
<td>5.3</td>
<td>0.7</td>
<td>6.0</td>
</tr>
<tr>
<td>(b)</td>
<td>4.8</td>
<td>5.1</td>
<td>7.9</td>
<td>1.3</td>
<td>5.0</td>
</tr>
<tr>
<td>(c)</td>
<td>7.2</td>
<td>10.0</td>
<td>9.4</td>
<td>2.2</td>
<td>4.4</td>
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</table>

Table 6.2: Ethane diffusion coefficients at different temperatures (/10^{-9} \text{ m}^2 \text{ s}^{-1}): (a) standard method; (b) two-step model; (c) random walk model

<table>
<thead>
<tr>
<th>T (K)</th>
<th>D</th>
<th>D_x</th>
<th>D_y</th>
<th>D_z</th>
<th>f</th>
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<td></td>
</tr>
<tr>
<td>(a)</td>
<td>5.3</td>
<td>5.5</td>
<td>9.1</td>
<td>1.2</td>
<td>6.3</td>
</tr>
<tr>
<td>(b)</td>
<td>6.7</td>
<td>7.6</td>
<td>10.7</td>
<td>1.6</td>
<td>5.7</td>
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<tr>
<td>(c)</td>
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<td>2.7</td>
<td>4.3</td>
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<td>400</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>8.0</td>
<td>7.7</td>
<td>14.7</td>
<td>1.5</td>
<td>7.5</td>
</tr>
<tr>
<td>(b)</td>
<td>9.6</td>
<td>11.2</td>
<td>15.1</td>
<td>2.5</td>
<td>5.3</td>
</tr>
<tr>
<td>(c)</td>
<td>12.0</td>
<td>16.7</td>
<td>15.7</td>
<td>3.7</td>
<td>4.4</td>
</tr>
<tr>
<td>500</td>
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<td></td>
</tr>
<tr>
<td>(a)</td>
<td>11.0</td>
<td>8.1</td>
<td>22.5</td>
<td>2.3</td>
<td>6.7</td>
</tr>
<tr>
<td>(b)</td>
<td>12.1</td>
<td>13.8</td>
<td>19.1</td>
<td>3.4</td>
<td>4.8</td>
</tr>
<tr>
<td>(c)</td>
<td>15.4</td>
<td>19.9</td>
<td>21.7</td>
<td>4.8</td>
<td>4.3</td>
</tr>
</tbody>
</table>
More information could be obtained looking again at Tab. 6.1 and Tab. 6.2, where the diffusion coefficients obtained from the MSD’s calculated by the models are also reported. The (b) and (c) notations there indicate values obtained from the two- and one-step model, respectively. The main source of error for the random walk model appears to be the far too high value of $D_x$, which is even slightly higher than the corresponding $D_y$ value in almost all cases. Indeed, the $D_y$ values obtained according to the two models are always similar. The diffusional anisotropy characteristic of silicate, which should lead to $D_y$ values significantly greater than $D_x$, is not reproduced at all with the direct application of Eq. 6.16 - Eq. 6.18: the $f=4.4$ value shown by the random walk model actually indicates absence of anisotropy ($D_x \sim D_y$, look also Fig. 6.6).

Tab. 6.3 and Tab. 6.4 report the numbers of single- and two-step events found in the simulations, together with their respective probabilities. The last two columns report the total numbers of single-steps and two-steps recorded. In order to compare to each other the event numbers, the values obtained for $\tau = 1$ ns have been listed. This choice of $\tau$ is not crucial for the comparison of the results, due to the very linear trend of the MSD curves calculated by Eq. 6.4 - Eq. 6.6 and Eq. 6.16 - Eq. 6.18 at different times. It could be argued that the reported numbers of events are rather small; actually, if we increased the observation time $\tau$, we would obtain larger numbers, but affected by higher errors, due to the lower number of time intervals of duration $\tau$ included in the average. For example, if we took $\tau = 3$ ns for the 4 ethane/u.c. case, we would obtain the largest event numbers as possible ($\tau$ being equal to the full trajectory length), but at the same time they would be considerably inaccurate (having been computed from a single time interval). The accuracy of the numbers obtained with $\tau = 1$ ns is doubtless better, with the present trajectory length. In order to record as many events as possible, also with good statistical accuracy, very long trajectories would be needed, but this would also require prohibitive calculation times.

First, it is interesting to observe the total number of events $n_2$. While, on one hand, these numbers obviously increase with temperature, on the other hand the trend with different loadings is not so clear, showing a maximum for 2 mol./u.c, and a net decrease with higher loadings. This point reflects in some way the trend of the diffusion coefficients versus ethane loading. Turning to the specific event numbers, it should be remarked that the only case in which a significant difference between $n_s$ and $n_z$ is present is the 500 K simulation; in all the other cases the difference is very small and cannot explain alone the diffusional anisotropy of ethane, as we already saw examining the diffusion coefficients predicted by the random walk model. In other words a “single-step” model, when applied in this direct way, fails to reproduce the observed differences in the monodimensional diffusion coefficients. Indeed, looking at Eq. 6.16 - Eq. 6.18, any difference between $D_y$ and $D_x$ could only arise from $n_s > n_z$, but we obtain $n_s \sim n_z$ in almost all cases. On the other hand, Eq. 6.4 - Eq. 6.6 show that the anisotropy should result from a difference between the number of “double-straight” events $n_{ss}^e$ and the number of “double-zig-zag” events $n_{zz}^e$, which is actually always present ($n_{ss}^e \sim 2 n_{zz}^e$). Therefore, the two-step model seems to work better also in the prediction of the diffusional anisotropy.
**Table 6.3:** Average numbers (probabilities) of events per molecule at different loadings after 1 ns

<table>
<thead>
<tr>
<th>loading (mol./u.c.)</th>
<th>$n_s$</th>
<th>$n_z$</th>
<th>$n_{ss}^s$</th>
<th>$n_{ss}^o$</th>
<th>$n_{zz}^s$</th>
<th>$n_{zz}^o$</th>
<th>$n_{sw}$</th>
<th>$n_{sz}$</th>
<th>$n_{zs}$</th>
<th>$n_1$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.53 (0.501)</td>
<td>26.46 (0.499)</td>
<td>4.16 (0.157)</td>
<td>4.44 (0.168)</td>
<td>1.98 (0.075)</td>
<td>6.58 (0.248)</td>
<td>9.32 (0.352)</td>
<td>4.66 (0.176)</td>
<td>4.65 (0.176)</td>
<td>53.0</td>
<td>26.5</td>
</tr>
<tr>
<td>2</td>
<td>29.97 (0.507)</td>
<td>29.02 (0.492)</td>
<td>4.60 (0.156)</td>
<td>5.84 (0.198)</td>
<td>1.86 (0.063)</td>
<td>8.11 (0.275)</td>
<td>9.07 (0.307)</td>
<td>4.53 (0.154)</td>
<td>4.53 (0.154)</td>
<td>59.0</td>
<td>29.5</td>
</tr>
<tr>
<td>4</td>
<td>23.04 (0.48)</td>
<td>24.95 (0.52)</td>
<td>3.78 (0.157)</td>
<td>4.05 (0.169)</td>
<td>1.99 (0.083)</td>
<td>6.79 (0.283)</td>
<td>7.37 (0.307)</td>
<td>3.68 (0.154)</td>
<td>3.68 (0.153)</td>
<td>48.0</td>
<td>24.0</td>
</tr>
<tr>
<td>6</td>
<td>19.78 (0.494)</td>
<td>20.21 (0.506)</td>
<td>2.77 (0.139)</td>
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<td>20.0</td>
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</table>

**Table 6.4:** Average numbers (probabilities) of events per molecule at different temperature after 1 ns

<table>
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<tr>
<th>loading (mol./u.c.)</th>
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</thead>
<tbody>
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<td>300</td>
<td>23.04 (0.48)</td>
<td>24.95 (0.42)</td>
<td>3.78 (0.157)</td>
<td>4.05 (0.169)</td>
<td>1.99 (0.083)</td>
<td>6.79 (0.283)</td>
<td>7.37 (0.307)</td>
<td>3.68 (0.154)</td>
<td>3.68 (0.153)</td>
<td>48.0</td>
<td>24.0</td>
</tr>
<tr>
<td>400</td>
<td>32.72 (0.495)</td>
<td>33.27 (0.505)</td>
<td>4.93 (0.149)</td>
<td>5.85 (0.177)</td>
<td>2.86 (0.087)</td>
<td>8.20 (0.249)</td>
<td>11.13 (0.337)</td>
<td>5.56 (0.169)</td>
<td>5.56 (0.169)</td>
<td>66.0</td>
<td>33.0</td>
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<tr>
<td>500</td>
<td>46.46 (0.534)</td>
<td>40.53 (0.466)</td>
<td>6.09 (0.140)</td>
<td>9.24 (0.213)</td>
<td>2.86 (0.066)</td>
<td>9.52 (0.219)</td>
<td>15.70 (0.363)</td>
<td>7.88 (0.181)</td>
<td>7.88 (0.182)</td>
<td>87.0</td>
<td>43.5</td>
</tr>
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</table>
6.3.5 Qualitative interpretation of the diffusive mechanism for ethane

But how do the diffusion coefficients influence by slight variations in the \(n_{zz}^s\), \(n_{ss}^s\) and \(n_{sw}\) numbers? From Eq. 6.4 - Eq. 6.6, by putting \(a \sim b \sim 20 \AA\), one obtains:

\[
\Delta x^2(t) \approx 400 [n_{ss}^s(t) + n_{zz}^s(t)] + 245 n_{sw}(t)
\] (6.36)

This equality shows that the total number of switches has a much lower weight on the overall MSD than the sum of the numbers of straight-to-straight and zigzag-to-zigzag coupled events. Actually, this sum is about six events/molecule for the 1, 2, and 4 mol./u.c. cases, and falls to about four for the 6 mol./u.c. loading, in which case a net decrease of the diffusion coefficient was observed. The same sum rises to \(\sim 8\) at 400 K and to \(\sim 9\) at 500 K, but also with a significant increase in \(n_{sw}\). We saw that the behavior of the diffusion coefficient as a function of the loading shows a similar trend, so we can assume that the diffusive mechanism is strongly influenced by the possibility that ethane can carry out long displacements in the same direction, and less influenced by its tendency to switch channel. In other words the diffusive memory appears to assist the diffusion, at least for small molecules like ethane. Further insight into this point stems from the analysis of the event probabilities, which are not influenced by the different total number of events in the various cases. As shown in the histograms of Fig. 6.7, the least probable event is clearly the “zigzag-to-zigzag” (zzs) double-step in the same direction, while the most probable one is again the double-zigzag step, but in opposite directions. The general trend is: \(p_{zz}^s < p_{ss}^s \sim p_{sz} = p_{sz} \leq p_{sz}^o < p_{zz}^o\). Note that \(p_{sw} = 2 p_{sz} = 2 p_{sz}\), but a meaningful comparison should obviously be separately made with each of the two possible switch events.

Indeed, when a molecule leaves an intersection, two out of the four possible jumps correspond to a channel switch, one to the keeping of direction, and the last to the “bouncing back” towards the intersection visited just before. Therefore \(p_{zz}^s\) and \(p_{ss}^s\) as well as \(p_{sz}^o\) and \(p_{zz}^o\) should be compared with half the switch probabilities. Moreover, being the \(s\)-\(z\) and \(z\)-\(s\) switches equivalent due to the time reversibility of MD trajectories, it follows \(p_{sz} = p_{zs} = 1/2 p_{sz}\), and we could include either \(p_{sz} \) or \(p_{zs}\) into the order of probabilities underlined above. It is remarkable that the general trend is almost unchanged in all conditions, indicating that the diffusion mechanism should not be influenced by the different loading and temperature. This mechanism seems to indicate that, when an ethane molecule coming from a zigzag channel reaches an intersection, it will often reverse its motion, coming back to the previous intersection; on the other hand, a molecule coming from a straight channel has almost equal probabilities to continue in the same direction, to switch to a zigzag channel or to return to its starting intersection.

The overall timelength of single-events was calculated as:

\[
t_1 = p_s t_s + p_z t_z
\] (6.37)

while for the coupled events we have:

\[
t_2 = p_s^s t_{ss}^s + p_s t_{ss}^o + p_z t_{zz}^o + p_z^o t_{zz}^o + p_{sw} t_{sw}
\] (6.38)
Fig. 6.7: Histograms of probabilities of coupled events for the simulations at different loading (left) and temperature (right).

The mean timelengths of various events are reported in Tab. 6.5 and Tab. 6.6. Obviously the relation \( t_2 = 2t_1 \) is exactly obeyed.

### Table 6.5: Average timelengths of displacements (ps) for ethane at different loadings

<table>
<thead>
<tr>
<th>loading (mol./u.c.)</th>
<th>( t_s )</th>
<th>( t_z )</th>
<th>( t_{ss}^s )</th>
<th>( t_{ss}^o )</th>
<th>( t_{zz}^s )</th>
<th>( t_{zz}^o )</th>
<th>( t_{sw} )</th>
<th>( t_{sz} )</th>
<th>( t_{zs} )</th>
<th>( t_1 )</th>
<th>( t_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.75</td>
<td>19.74</td>
<td>31.48</td>
<td>34.88</td>
<td>41.48</td>
<td>37.83</td>
<td>40.32</td>
<td>38.26</td>
<td>42.38</td>
<td>18.74</td>
<td>37.5</td>
</tr>
<tr>
<td>2</td>
<td>17.41</td>
<td>16.69</td>
<td>34.35</td>
<td>31.28</td>
<td>42.36</td>
<td>30.40</td>
<td>37.45</td>
<td>34.38</td>
<td>40.51</td>
<td>17.04</td>
<td>34.08</td>
</tr>
<tr>
<td>4</td>
<td>20.94</td>
<td>21.20</td>
<td>38.17</td>
<td>38.42</td>
<td>45.83</td>
<td>39.64</td>
<td>47.56</td>
<td>44.49</td>
<td>50.62</td>
<td>21.08</td>
<td>42.1</td>
</tr>
<tr>
<td>6</td>
<td>25.99</td>
<td>24.16</td>
<td>48.87</td>
<td>50.83</td>
<td>61.52</td>
<td>45.98</td>
<td>52.45</td>
<td>50.93</td>
<td>53.98</td>
<td>25.07</td>
<td>50.14</td>
</tr>
</tbody>
</table>

### Table 6.6: Average timelengths of displacements (ps) for ethane at different temperatures

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( t_s )</th>
<th>( t_z )</th>
<th>( t_{ss}^s )</th>
<th>( t_{ss}^o )</th>
<th>( t_{zz}^s )</th>
<th>( t_{zz}^o )</th>
<th>( t_{sw} )</th>
<th>( t_{sz} )</th>
<th>( t_{zs} )</th>
<th>( t_1 )</th>
<th>( t_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>20.94</td>
<td>21.20</td>
<td>38.17</td>
<td>38.42</td>
<td>45.83</td>
<td>39.64</td>
<td>47.56</td>
<td>44.49</td>
<td>50.62</td>
<td>21.08</td>
<td>42.1</td>
</tr>
<tr>
<td>400</td>
<td>14.42</td>
<td>15.80</td>
<td>25.79</td>
<td>27.22</td>
<td>33.16</td>
<td>30.01</td>
<td>33.21</td>
<td>31.74</td>
<td>34.67</td>
<td>15.12</td>
<td>30.21</td>
</tr>
<tr>
<td>500</td>
<td>11.09</td>
<td>12.06</td>
<td>21.67</td>
<td>18.95</td>
<td>26.41</td>
<td>22.51</td>
<td>25.79</td>
<td>24.30</td>
<td>27.28</td>
<td>11.54</td>
<td>23.11</td>
</tr>
</tbody>
</table>

The observed trend as a function of the loading shows similar values for the overall timelengths in the 1 and 2 mol./u.c. cases, and a net decrease going to higher loadings: \( t_2 \approx 50 \text{ ps} \) for the 6 mol./u.c. case. This trend again reflects the anomalous situation already observed for the event numbers: the 2 mol./u.c. case presents the highest average number of events, and the lowest average event timelength. Note that this point not necessarily leads to a greater total MSD: actually, the above averages regard all events, including those in opposite directions, and do not take into account the different distributions and probabilities of each event. Indeed, the two MSD curves
for the 1 and 2 mol./u.c. cases, calculated by Eq. 6.4 - Eq. 6.6, are very close at all times. The increase of the temperature leads to the expected overall decrease of event timelengths ($t_1$ and $t_2$). The slowest events are the switches and the zigzag-to-zigzag displacements in the same direction, in practically all cases, while the other three displacements are always 5-10 ps faster (Fig. 6.8). Moreover, it should be remarked that the straight-to-zigzag interchange is always significantly faster than the zigzag-to-straight one (Tab. 6.5 and Tab. 6.6). This phenomenon could be interpreted on the basis of the orientational decorrelation of the molecule in silicalite$^{187}$ and will be thoroughly discussed in the following.

**Fig. 6.8:** Histograms of timelengths of coupled events for the simulations at different loading (left) and temperature (right)

### 6.3.6 Application of the generalized correlation rule

The validity of the generalized correlation rule (Eq. 6.34) can be tested by comparing the simulated $D_z$ (i.e., given by Eq. 3.25 and Eq. 3.26) with the value predicted on the basis of the simulated $D_x$ and $D_y$ and the deviations $\Delta$ of the two-step event numbers from their corresponding values expected in absence of correlation, Eq. 6.21 - Eq. 6.25. If the generalized correlation rule gives a reliable description of the interdependency of the three components of the diffusion coefficient, its $D_z$ will be in agreement with the simulated one. The $\Delta$ values are reported in Tab. 6.7. Note that these values are differences between numbers averaged over all molecules and over all 1 ns time intervals present in the MD trajectories, so that they should be read as $\Delta n_{zz}^s$ ($t = 1$ ns), and so on.

Clearly the sum of all the deviations, including $\Delta n_{zz}^o$ and $\Delta n_{ss}^o$ must be close to zero: making use of Eq. 6.21 - Eq. 6.25 and of the equality $n = 2n_2$, one obtains:
Table 6.7: Deviations of the two-step event numbers from their theoretical (uncorrelated) values; the relative deviations are in parentheses

<table>
<thead>
<tr>
<th>Loading (mol./u.c.)</th>
<th>$\Delta n_{zz}^s$</th>
<th>$\Delta n_{ss}^s$</th>
<th>$\Delta n_{sw}^o$</th>
<th>$\Delta n_{zz}^o$</th>
<th>$\Delta n_{ss}^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.32(-0.66)</td>
<td>0.84(0.2)</td>
<td>-3.92(-0.42)</td>
<td>3.28(0.5)</td>
<td>1.12(0.25)</td>
</tr>
<tr>
<td>2</td>
<td>-1.71(-0.92)</td>
<td>0.79(0.17)</td>
<td>-5.67(-0.62)</td>
<td>4.54(0.56)</td>
<td>2.03(0.44)</td>
</tr>
<tr>
<td>4(300 K)</td>
<td>-1.25(-0.63)</td>
<td>1.01(0.27)</td>
<td>-4.61(-0.62)</td>
<td>3.55(0.52)</td>
<td>1.28(0.32)</td>
</tr>
<tr>
<td>4(400 K)</td>
<td>-1.33(-0.46)</td>
<td>0.88(0.18)</td>
<td>-5.36(-0.48)</td>
<td>4.01(0.49)</td>
<td>1.80(0.31)</td>
</tr>
<tr>
<td>4(500 K)</td>
<td>-1.86(-0.65)</td>
<td>-0.10(-0.02)</td>
<td>-5.88(-0.37)</td>
<td>4.8(0.50)</td>
<td>3.04(0.33)</td>
</tr>
<tr>
<td>6</td>
<td>-1.46(-1.34)</td>
<td>0.32(0.11)</td>
<td>-4.17(-0.72)</td>
<td>3.55(0.58)</td>
<td>1.75(0.42)</td>
</tr>
</tbody>
</table>

$$\sum \Delta = \Delta n_{zz}^s + \Delta n_{zz}^o + \Delta n_{ss}^s + \Delta n_{ss}^o + \Delta n_{sw} =$$
$$n_{zz}^s + n_{zz}^o + n_{ss}^s + n_{ss}^o + n_{sw} +$$
$$- 2 \cdot \frac{1}{4} n_z^2/n - 2 \cdot \frac{1}{4} n_s^2/n - n_z n_s/n =$$
$$= n - (n_z^2 + n_s^2 + 2n_z n_s)/n = 0 \quad (6.39)$$

Eq. 6.39 entails that any deficiency (excess) of a specific kind of event will be balanced by an accompanying excess (deficiency) of another kind of event. The values in parentheses in Tab. 6.7 are the corresponding relative deviations ($\Delta n_{zz}^s/n_{zz}^s$, etc.), which are more suitable for a qualitative discussion. The motion in straight channels shows the smallest deviations: in particular for the $ss^s$ events, more important for the effective displacement, the deviations decrease with increasing temperature and loading. The other events show a less regular trend; the deviations from completely random motion are always negative for the $n_{sw}$ and $n_{zz}^s$ terms, entailing that such events are less probable than what expected in absence of memory; on the other hand the coupled displacements in opposite directions are always more frequent than what predicted by the random hypothesis. Therefore when a molecule enters an intersection from a sinusoidal channel, it has a greater tendency to return to its previous intersection, compared to a random propagation, while if it enters the intersection from a straight channel it manifests a greater tendency to move forward in the same direction than to come back or to turn into the zigzag channel. These considerations agree well with those made discussing the jump probabilities.

Tab. 6.7 shows that correlation effects are not negligible for ethane molecules diffusing in silicalite, notwithstanding the duration of a single step (about 20 ps at 300 K, see Tab. 6.5) may appear as long enough to cancel the directional memory and randomize the motion of a short molecule like ethane. The question arises, if these deviations are only due to correlation effects; actually, looking again at Eq. 6.39, only a few switches are observed because the molecule tends to maintain its direction of motion, in particular along $y$, and this is mainly a “memory” effect. At the same time, the shape of zig-zag channels determines the occurrence of many “bouncing-back” events, and this may be considered both a kinetic and a correlation (“memory”) effect.
Tab. 6.8 compares the $D_z$ values obtained by the standard method (Eq. 3.25 - Eq. 3.26) to those obtained by inserting the “experimental” $D_z$ and $D_y$ (i.e., obtained by Eq. 3.25 and Eq. 3.26) into the correlation rule expressions, Eq. 6.1 and Eq. 6.34. The modified correlation rule does not always predict $D_z$ values better than the first-approximation rule, Eq. 6.1, but for the runs with 4 and 6 molecules/u.c. the introduction of the deviations seems to work in the right way, i.e. Eq. 6.34 gives $D_z$ values closer to the right (second column) ones. It is rather surprising that, although the two-step equations Eq. 6.4 - Eq. 6.6 predict a more accurate MSD than the random walk ones (Eq. 6.16 - Eq. 6.18), and we also showed the existence of non-negligible correlation effects, the new correlation rule is not clearly better than the original rule. We shall clarify in the following the reasons for this discrepancy. At the moment it is sufficient to remark that a completely random description for the ethane diffusion is surely inappropriate, notwithstanding the ratios between the monodimensional components of the diffusion coefficient may in many cases follow the random walk correlation rule.

**Table 6.8:** $D_z$ values obtained by the standard method, by the first correlation rule and by the modified correlation rule ($/10^{-9}\text{m}^2\text{s}^{-1}$)

<table>
<thead>
<tr>
<th>loading (mol/u.c.)</th>
<th>$D_z$ (standard)</th>
<th>$D_z$ (Eq. 6.1)</th>
<th>$D_z$ (Eq. 6.34)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.8</td>
<td>1.78</td>
<td>1.69</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>1.51</td>
<td>1.36</td>
</tr>
<tr>
<td>4(300 K)</td>
<td>1.2</td>
<td>1.54</td>
<td>1.32</td>
</tr>
<tr>
<td>4(400 K)</td>
<td>1.5</td>
<td>2.26</td>
<td>2.03</td>
</tr>
<tr>
<td>4(500 K)</td>
<td>2.3</td>
<td>2.67</td>
<td>2.67</td>
</tr>
<tr>
<td>6</td>
<td>0.7</td>
<td>0.84</td>
<td>0.79</td>
</tr>
</tbody>
</table>

### 6.4 Application of the two-step model: diffusion of halogens and triatomics

The study of ethane diffusion through the two-step model provided several information on the diffusive mechanism and on the extent of correlation effects as a function of the different loading and temperature. We shall apply the same analysis to MD trajectories of several diatomic and triatomic molecules sorbed in silicalite at fixed loading and temperature. This allows to study the effect of mass and dimension of sorbates and to extend the above considerations concerning the efficiency of the two-step model in describing the diffusion of different species in silicalite. The molecules considered here represent through effective potentials chlorine, bromine and iodine molecules, and the triatomic species CO$_2$ and CS$_2$. As for ethane the adsorbent system consists of two silicalite cells; the temperature is 300 K and only a single sorbate molecule is included, that is we simulate infinite dilution. This clearly requires longer MD trajectory compared to the case in which several sorbates are present leading to better statistics. In order to adequately sample the phase space in this case we carried out 20 ns trajectories for each studied system, each one preceded by an equilibration run of 900 ps at 300 K. As for ethane, positions and velocities of each atom have been stored every 32 fs, apart
from the spectrum calculation (see below).

6.4.1 Details of the interaction potentials for the sorbed species

The intramolecular bond of the sorbates is modeled through a Morse potential. The parameters (shown in Tab. 6.9) have been obtained from the vibrational spectra of halogen molecules, with small changes based on recent data.\(^{215,216}\) The intramolecular interactions of CO\(_2\) and CS\(_2\) are modeled by means of the potential of Zhu et al.\(^{217,218}\) taking the following form:

\[
V(r_1, r_2, \theta) = k_1[(r_1 - r_{eq})^2 + (r_2 - r_{eq})^2] + k_2(r_1 - r_{eq})(r_2 - r_{eq}) + k_\theta(\theta - \theta_{eq})^2
\]

(6.40)

where \(r_1\) and \(r_2\) are the distances of the central carbon atom from the two oxygen (for CO\(_2\)) or sulphur (for CS\(_2\)) atoms, and \(\theta\) is the \(\angle\text{O-C-O}\) or \(\angle\text{S-C-S}\) angle; \(r_{eq}\) and \(\theta_{eq}\) are the corresponding equilibrium values. The adopted parameters are shown in Tab. 6.10; we verified that this simple potential gives an excellent reproduction of the vibrational spectra of both triatomic molecules. We separately calculated the Fourier transforms of the velocity autocorrelation function for the carbon and oxygen (sulphur) atoms\(^1\) and the resulting spectra are shown in Fig. 6.9 and Fig. 6.10. The experimental spectrum\(^{214}\) for gaseous CO\(_2\) has two bands at 667 cm\(^{-1}\) (bending, two degenerate modes) and 2349 cm\(^{-1}\) (asymmetric stretching); the symmetric stretching is IR-inactive and in the Raman spectrum gives rise to a band at 1337 cm\(^{-1}\) that is split by complex resonance effects into two peaks at 1285 and 1388 cm\(^{-1}\), in excellent agreement with Fig. 6.9. The IR spectrum for CO\(_2\) in silicalite\(^{219}\) shows slight changes, with two peaks at 662 and 2339 cm\(^{-1}\). The experimental frequencies of CS\(_2\) are 656, 397 and 1523 cm\(^{-1}\), again in very good agreement with Fig. 6.10.

<table>
<thead>
<tr>
<th>Table 6.9: Morse potential parameters for the halogen molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{eq}) (Å)</td>
</tr>
<tr>
<td>Cl(_2)</td>
</tr>
<tr>
<td>Br(_2)</td>
</tr>
<tr>
<td>I(_2)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 6.10: Harmonic potential parameters for the triatomic molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>(r_{eq}) (Å)</td>
</tr>
<tr>
<td>CO(_2)</td>
</tr>
<tr>
<td>CS(_2)</td>
</tr>
</tbody>
</table>

The Lennard-Jones potential is used to model all the intermolecular interactions between the atoms of the sorbates and the silicalite oxygens (no interactions between

\(^1\)The Nyquist criterion limits the largest observable frequency \(\nu_{max}\) to \((2\Delta)^{-1}\), where \(\Delta\) is the time interval between the data being transformed. We then took \(\Delta = 4\) fs (instead of 32 fs), corresponding to \(\nu_{max} = 4166\) cm\(^{-1}\).
**Fig. 6.9:** Vibrational spectrum of CO$_2$: Fourier transforms of VACF of carbon atom (continuous line) and the oxygen atoms (dashed line).

**Fig. 6.10:** Vibrational spectrum of CS$_2$: Fourier transforms of VACF of carbon atom (continuous line) and the sulphur atoms (dashed line).
the sorbed species are present; the interactions with the silicon atoms are neglected, because they are well shielded by the oxygen atoms covering the surface of the channels). For the diatomic species, the Cl-O, Br-O and I-O parameters are the same as for Ar-O, Kr-O and Xe-O, as previously explained. The self-interaction LJ parameters of Murthy et al.\cite{221} for carbon and oxygen atoms in CO$_2$ describe their interaction with the oxygen atoms through the standard combining rules. The Murthy intermolecular potential also includes a contribution due to the high quadrupole moment of CO$_2$, not included in our model. Such moment introduces an additional attractive contribution to the interaction forces, and it is important to take it into account, even if only approximately.\cite{8} In our case only one CO$_2$ molecule is adsorbed and no intermolecular quadrupole-quadrupole interaction are present. Moreover, in our harmonic model the charges present on the framework atoms are not explicitly considered, and thus there is no contribution to the intermolecular energy arising from the effect of the intrazeolite electric field on the molecular quadrupole moment. The exact inclusion of this interaction would be essential if any Al atoms and charged counterbalancing cations were present, or if a very accurate representation of the CO$_2$ motion was sought, faithfully describing, for example, the way in which the additional attractive contribution may affect the effective pore size. In this work such an accurate description is not required, as we are interested in the effects of molecular shape, size and mass over the diffusive behaviour, and the models we use are mainly intended to represent diatomic and triatomic species of different size and mass. Therefore for CO$_2$ we approximated the quadrupole-framework interaction by scaling the well depths $\epsilon_{O-O_{zeo}}$ and $\epsilon_{C-O_{zeo}}$ by 1.5, so as to obtain a good reproduction of the experimental heat of adsorption of CO$_2$ in silicalite,\cite{221} which is about 28 kJ mol$^{-1}$. This approximation leads to diffusion coefficients consistent with experimental data (see below). However it is likely that at finite loadings, with important quadrupole-quadrupole interactions, this kind of approximation may lose validity. Our model should be considered as representing a linear triatomic molecule, comparable to carbon dioxide only at infinite dilution, in a neutral environment. On the other hand, the Tildesley-Madden\cite{222} LJ parameters for carbon and sulphur in CS$_2$ have been taken without modifications, as in their paper CS$_2$ is modeled through a non-quadrupolar, effective three-site potential. All the intermolecular LJ parameters are reported in Tab. 6.11. The fact that $\sigma_{C-O_{zeo}}$ for CO$_2$ is lower than the corresponding value for CS$_2$ is connected to the different electronic distributions on the carbon atom for the two molecules:\cite{217} in CO$_2$ the electronic density on the carbon is shifted towards the oxygen and the C-O bonds, while in CS$_2$ both the carbon and the sulphur atoms transfer electronic density towards the C-S bonds. Moreover the contraction of the electronic density close to the carbon atom showed by recent \textit{ab initio}\cite{222} calculations validates the fact that for such molecule $\sigma_{C-O_{zeo}} < \sigma_{S-O_{zeo}}$.

\footnote{The attractive term in the Lennard-Jones potential, $-C/r^6$, only accounts for the induced dipole interactions. CO$_2$ has a large quadrupole moment giving a considerable contribution to the intermolecular attraction. This contribution can be indirectly included in the LJ potential by adjusting the parameters, or it can be explicitly considered by introducing an additional term, as in the work of Murthy et al.}
Table 6.11: Intermolecular (guest-host) Lennard-Jones potential parameters

<table>
<thead>
<tr>
<th>Interaction</th>
<th>( \sigma ) (Å)</th>
<th>( \epsilon ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl-O(_{zeo})</td>
<td>3.029</td>
<td>1.028</td>
</tr>
<tr>
<td>Br-O(_{zeo})</td>
<td>3.14</td>
<td>1.335</td>
</tr>
<tr>
<td>I-O(_{zeo})</td>
<td>3.2745</td>
<td>1.737</td>
</tr>
<tr>
<td>C(CO(<em>2))-O(</em>{zeo})</td>
<td>2.657</td>
<td>0.739</td>
</tr>
<tr>
<td>O(CO(<em>2))-O(</em>{zeo})</td>
<td>2.772</td>
<td>1.251</td>
</tr>
<tr>
<td>C(CS(<em>2))-O(</em>{zeo})</td>
<td>2.940</td>
<td>0.8015</td>
</tr>
<tr>
<td>S(CS(<em>2))-O(</em>{zeo})</td>
<td>3.025</td>
<td>1.516</td>
</tr>
</tbody>
</table>

6.4.2 Diffusion coefficients

The total MSD curves calculated with the standard method and with the two statistical models are shown in Fig. 6.11 for halogens and Fig. 6.12 for triatomic molecules. The corresponding partial and total diffusion coefficients, reported in Tab. 6.12, have been calculated by fitting a straight line to the MSD curves between 50 and 500 ps. The fitting interval here is larger than in the case of ethane, whose MSD curves (and in particular the standard MSD) stayed in the linear regime for a shorter time. The errors reported in Tab. 6.12 for the standard diffusion coefficients are obtained from a block analysis of data (Eq. 3.28) by dividing the trajectory in 20 blocks of 1 ns each. The errors range between 13 and 28%, with smaller values for the total \( D \)'s.

Table 6.12: Diffusion coefficients (\(10^{-8} \text{ m}^2 \text{ s}^{-1}\)) calculated through: (a) the standard MD method; (b) the random walk model; (c) the two-step model.

<table>
<thead>
<tr>
<th></th>
<th>( D )</th>
<th>( D_x )</th>
<th>( D_y )</th>
<th>( D_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(_2)</td>
<td>(a) 0.67±0.09</td>
<td>0.73±0.14</td>
<td>1.1±0.3</td>
<td>0.14±0.04</td>
</tr>
<tr>
<td></td>
<td>(b) 0.87</td>
<td>1.15</td>
<td>1.2</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>(c) 0.70</td>
<td>0.81</td>
<td>1.1</td>
<td>0.19</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>(a) 0.22±0.04</td>
<td>0.22±0.06</td>
<td>0.37±0.09</td>
<td>0.062±0.02</td>
</tr>
<tr>
<td></td>
<td>(b) 0.44</td>
<td>0.70</td>
<td>0.49</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td>(c) 0.30</td>
<td>0.39</td>
<td>0.42</td>
<td>0.083</td>
</tr>
<tr>
<td>Br(_2)</td>
<td>(a) 0.11±0.01</td>
<td>0.095±0.02</td>
<td>0.22±0.04</td>
<td>0.027±0.006</td>
</tr>
<tr>
<td></td>
<td>(b) 0.327</td>
<td>0.337</td>
<td>0.55</td>
<td>0.0955</td>
</tr>
<tr>
<td></td>
<td>(c) 0.155</td>
<td>0.16</td>
<td>0.261</td>
<td>0.0452</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>(a) 0.66±0.11</td>
<td>0.58±0.12</td>
<td>1.25±0.3</td>
<td>0.16±0.03</td>
</tr>
<tr>
<td></td>
<td>(b) 1.17</td>
<td>1.64</td>
<td>1.50</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>(c) 0.85</td>
<td>0.99</td>
<td>1.3</td>
<td>0.24</td>
</tr>
<tr>
<td>CS(_2)</td>
<td>(a) 0.28±0.05</td>
<td>0.19±0.04</td>
<td>0.59±0.15</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td></td>
<td>(b) 0.656</td>
<td>0.84</td>
<td>0.92</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>(c) 0.386</td>
<td>0.44</td>
<td>0.62</td>
<td>0.10</td>
</tr>
</tbody>
</table>
Fig. 6.11: Mean square displacement curves obtained according to 2-step model (dashed line), 1-step model (dot-dashed line) and standard method (solid line), for the halogen molecules.
Fig. 6.12: Mean square displacement curves obtained according to 2-step model (dashed line), 1-step model (dot-dashed line) and standard method (solid line), for the triatomic molecules: (top) CS₂; (bottom) CO₂.
6.4.3 Analysis of molecular motion

The calculation of the average number of events has been carried out by the same procedure adopted for ethane. The number of displacements as a function of the time has then been used to determine the two-step and random walk MSD curves according to Eq. 6.4 - Eq. 6.6 and Eq. 6.16 - Eq. 6.18. For a qualitative comparison we report in Tab. 6.13 the values after 1 nanosecond, together with the corresponding probabilities, shown as histograms in Fig. 6.13.

Table 6.13: Numbers and probabilities of displacements for the halogens, CO₂ and CS₂ after 1 ns

<table>
<thead>
<tr>
<th></th>
<th>$n_s$</th>
<th>$n_z$</th>
<th>$n_{ss}^s$</th>
<th>$n_{ss}^o$</th>
<th>$n_{zz}^s$</th>
<th>$n_{zz}^o$</th>
<th>$n_{sz}$</th>
<th>$n_{szw}$</th>
<th>$n_{sz}$</th>
<th>$n_{sz}$</th>
<th>$n_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.52)</td>
<td>(0.48)</td>
<td>(0.15)</td>
<td>(0.20)</td>
<td>(0.08)</td>
<td>(0.22)</td>
<td>(0.35)</td>
<td>(0.175)</td>
<td>(0.175)</td>
<td>(0.175)</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>(0.43)</td>
<td>(0.57)</td>
<td>(0.11)</td>
<td>(0.17)</td>
<td>(0.08)</td>
<td>(0.34)</td>
<td>(0.30)</td>
<td>(0.15)</td>
<td>(0.15)</td>
<td>(0.15)</td>
<td>32.5</td>
<td></td>
</tr>
<tr>
<td>I₂</td>
<td>11.977</td>
<td>7.023</td>
<td>0.908</td>
<td>4.042</td>
<td>0.303</td>
<td>2.169</td>
<td>2.075</td>
<td>1.041</td>
<td>1.037</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>(0.63)</td>
<td>(0.37)</td>
<td>(0.097)</td>
<td>(0.42)</td>
<td>(0.033)</td>
<td>(0.23)</td>
<td>(0.22)</td>
<td>(0.11)</td>
<td>(0.11)</td>
<td>(0.11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0.49)</td>
<td>(0.51)</td>
<td>(0.13)</td>
<td>(0.196)</td>
<td>(0.067)</td>
<td>(0.269)</td>
<td>(0.338)</td>
<td>(0.169)</td>
<td>(0.169)</td>
<td>(0.169)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS₂</td>
<td>19.896</td>
<td>17.104</td>
<td>2.218</td>
<td>5.466</td>
<td>1.16</td>
<td>5.128</td>
<td>4.528</td>
<td>2.263</td>
<td>2.266</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>(0.54)</td>
<td>(0.46)</td>
<td>(0.12)</td>
<td>(0.295)</td>
<td>(0.063)</td>
<td>(0.28)</td>
<td>(0.245)</td>
<td>(0.122)</td>
<td>(0.122)</td>
<td>(0.122)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 6.13: Histograms of probabilities for coupled displacements of halogens and triatomics

The total number of two-step displacements decreases going from Cl₂ to I₂, and from
CO₂ to CS₂, essentially following the order of molecular masses. The probabilities of
the various events provide a general picture of the preferred displacements for every
species. Two different trends are observed: \( p_{ss}^s > p_{sz}^o > p_{sz} > p_{sz}^s > p_{zz}^s \) for Cl₂, Br₂ and
CO₂, and \( p_{ss}^o > p_{sz}^o > p_{sz} \sim p_{sz}^s > p_{zz}^s \) for I₂ and CS₂. In all cases the least probable
event is the double-forward motion in the zigzag channel. The coupled displacements
in opposite direction are more frequent than those in the same direction, the switches
\((s - z \text{ or } z - s)\) are roughly half-way between these two events. The longer molecules
(iodine and carbon disulphide) have a lower tendency to switch direction; this could
be connected to the greater diffusive memory for such species. Moreover they show
a larger percentage of “bouncing-backs” along the straight channel, instead of along
the sinusoidal channel as it could have been expected on a steric-kinetic basis. Indeed
bromine happens to be the molecule with largest \( p_{zz}^o \). This does not necessarily imply
that longer molecules experiment a greater difficulty to move forward along the
straight channel than along the sinusoidal one. Indeed, if a molecule crosses a larger
number of straight sections (as emerging from the \( p_s \) and \( p_z \) values for I₂ and CS₂),
the number of “bouncing-backs” in the straight channel will increase independently on
the real tendency of straight channels to favor such events. On the other hand bromine
shows \( p_z > p_s \) and in this case the \((z - z')\) events acquire a greater statistical weight
with respect to the same events in the straight channels. In other words the order of probabilities
should take into account the possibility that \( p_s \) be different from \( p_z \),
as occurs mainly for the larger species. On the contrary ethane, chlorine and carbon
dioxide \( p_s \sim p_z \) and the conclusions drawn on the basis of the probability orders are
reliable enough. In order to highlight possible correlation effects for all the molecules,
we could ignore the displacements in opposite directions (which are of kinetic-steric
nature and further tend to complicate the interpretation of the diffusive mechanism)
and directly compare the \( p_{ss}^s \) and \( p_{sz} \) numbers, as well as \( p_{zz}^s \) and \( p_{zz} \) ones. If
the propagation is completely uncorrelated, on the basis of Eq. 6.2, Eq. 6.7 - Eq. 6.9 and
Eq. 6.13, the following expressions must hold:

\[
\frac{p_{ss}^o}{p_{sz}^o} = \frac{p_{zz}^s}{p_{zz}^s} = 1
\]

(6.41)

Any deviation from unity of the “randomization” ratios in Eq. 6.41 is to be ascribed
to correlations in the diffusive motion; a ratio >1 denotes tendency to keep the direction
of motion, while a ratio <1 denotes preference to “turn the corner”. With the separate
analysis of the two ratios we can independently investigate the diffusion in the two
channel systems, so as to avoid confusions due to the different numbers of straight
or zigzag sections visited. At the same time, not including in the comparison the
bouncing-backs, we are somewhat isolating the other two kinds of events, allowing a
better comparison, which would otherwise be obscured by the overwhelming number
of displacements in opposite directions. Tab. 6.14 shows that in the straight channel
the “continuations” are usually more probable than the switches, while in the zigzag
channel there is a better randomization of the motion. Obviously, the channel’s shape
is involved in this phenomenon, by bringing about a larger number of collisions that
effectively randomize the molecular velocities and the direction of propagation.

The motion of the heaviest iodine is practically uncorrelated in both channel sys-
Table 6.14: Randomization ratios in the two-channel systems (Eq. 6.41)

<table>
<thead>
<tr>
<th></th>
<th>$(p_{ss}/p_{sz})$</th>
<th>$(p_{s}/2p_{z})$</th>
<th>$(p_{zz}/p_{sz})$</th>
<th>$(p_{z}/2p_{s})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>1.59</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br₂</td>
<td>1.92</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I₂</td>
<td>1.03</td>
<td>1.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>1.60</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CS₂</td>
<td>1.66</td>
<td>1.24</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

tems, probably due to the longer residence times that allow a better thermalization. On the other hand, the longest molecule considered, CS₂, shows considerable diffusive memory in both channels, tending to maintain the direction of motion: the longer molecular axis acts as an effective guide to direct the molecular propagation. When moving in the zigzag channel no molecule except CS₂ shows any preferential tendency to continue its motion along the channel, and bromine and CO₂ actually prefer to “turn the corner” to the straight channel. Clearly, correlated jumps must arise from an insufficient thermalization between jumps, but the highlighted differences point out that this lack of thermalization is in turn strongly affected by some further parameters, such as the molecular shape and dimensions, as well as the intermolecular interactions with the channel walls, whose flexibility can be very important in the thermal equilibration of sorbates.⁷⁰ ⁷¹

Turning back to the probability order it is remarkable that the order found for Cl₂, Br₂, and CO₂ is the same previously observed for ethane. Each methyl group of ethane is larger than a iodine atom, while its mass is lower than half that of chlorine, and the carbon-carbon bond is shorter than the bond in Cl₂. If we consider the molecular length, defined as $r_{eq} + \sigma_{X-O_{zeo}}$ (X being Cl, Br or I) for the diatomic molecules and as $2r_{eq} + \sigma_{X-O_{zeo}}$ (X being O or S) for the triatomic species, one obtains ~ 5 Å for ethane and Cl₂, 5.1 Å for CO₂, 5.4 Å for Br₂, 5.9 Å for I₂, and 6.1 Å for CS₂: on the basis of the molecular length alone, Cl₂, CO₂ and ethane may be put roughly on the same level. Indeed the diffusion coefficients obtained for ethane at 1 mol./u.c. and Cl₂ and CO₂ at infinite dilution are very similar, in spite of the very different masses. Several factors, with opposite effect, could be involved in this point, such as the higher loading for ethane, and the differences in the single LJ parameters for the interaction with the zeolitic host. The attractive force exerted by the framework on the molecules may change considerably: the sorption heats calculated by the simulations are reported in Tab. 6.15. The observed trend, $q(Cl₂) < q(CO₂) < q(ethane)$, may partially counterbalance the (inverse) order of the masses, leading to very similar diffusion coefficients. However, a simpler line of reasoning takes into account only the molecular length into explaining such differences; this parameter seems to play an important role in determining the diffusive properties of linear molecules in silicate.

The average event timelengths, reported in Tab. 6.16 and as histograms in Fig. 6.14, give further insight into the diffusion mechanism. Clearly, the absolute values of these propagation times are mainly determined by the masses, but the relative speed of the different events for each species can in any case be of some interest. The fastest events are always the bouncing-backs along the straight channels, while as for ethane
Table 6.15: Sorption heats

<table>
<thead>
<tr>
<th>Substance</th>
<th>$q$ (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane (1 mol./u.c.)</td>
<td>31.2</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>25.1</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>37.6</td>
</tr>
<tr>
<td>I$_2$</td>
<td>58.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>27.3</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>45.2</td>
</tr>
</tbody>
</table>

The slowest are the consecutive displacements in the same direction along the zigzag channel, except for iodine, whose slowest two-step event is the bouncing-back along the zigzag channel. CS$_2$ (whose trend of event probabilities was similar to I$_2$) now shows a trend closer to the smaller species, reflecting the greater importance of the molecular weight in determining the event time lengths. As for ethane $t_{sz} > t_{sz}$ in all cases, with larger differences for the longer species, while as shown in Tab. 6.13 $p_{sz} \sim p_{sz}$, as to be expected on the basis of the time reversibility. This point deserves some comments: the time length of a two-step event is calculated as difference between the time of access to the last intersection ($C$ in Fig. 6.15) minus the time of access to the starting ($A$) intersection; therefore the “forward” $z$-$s$ event, starting at $t_0$ and ending at $t_2$, is distinct from the corresponding “backward” $s$-$z$ sequence of jumps, which starts at $t_3$ and is completed at $t_1$. Time reversibility strictly applies only to the fragment of trajectory between $t_1$ and $t_2$, and we have indeed verified that the time length of $s$-$z$ and $z$-$s$ events would be the same if calculated in such region, i.e. between the access to the last intersection and the exit from the first one. Therefore the basic reason for the longer time needed for the interchanges from zigzag to straight channels is that the crossing of an intersection towards a zigzag channel requires a longer time than the crossing towards the straight channel: the $t_3 - t_2$ intervals averaged over all switch events turn out to be shorter than the $t_1 - t_0$ intervals by an amount practically coinciding with the difference between $t_{sz}$ and $t_{sz}$. This also emerges in a more general context: we separately calculated the mean residence time in the intersections and distinguished the cases where the molecule subsequently reaches a straight or sinusoidal section. In the latter case the residence time in the intersection is longer, again with larger differences for heavier species.

---

*It could be argued that the central intersection ($B$) should give rise to the same phenomenon, but in any case the path between $t_1$ and $t_2$ (including the crossing of $B$) requires the same time in both directions, so that the exit from the first intersection is the crucial point*
### Table 6.16: Event timelengths (ps) for halogens and triatomics

<table>
<thead>
<tr>
<th>Gas</th>
<th>$t_{e}$</th>
<th>$t_{g}$</th>
<th>$t_{p_{g}}$</th>
<th>$t_{f_{g}}$</th>
<th>$t_{p_{f}}$</th>
<th>$t_{f}$</th>
<th>$t_{p_{f}}$</th>
<th>$t_{f}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂</td>
<td>19.3</td>
<td>21.9</td>
<td>37.7</td>
<td>46.4</td>
<td>42.6</td>
<td>44.0</td>
<td>44.0</td>
<td>41.1</td>
</tr>
<tr>
<td>Br₂</td>
<td>36.7</td>
<td>42.9</td>
<td>72.9</td>
<td>111.5</td>
<td>76.6</td>
<td>88.2</td>
<td>95.7</td>
<td>80.6</td>
</tr>
<tr>
<td>I₂</td>
<td>47.5</td>
<td>66.0</td>
<td>101.4</td>
<td>133.8</td>
<td>122.4</td>
<td>133.8</td>
<td>122.4</td>
<td>108.0</td>
</tr>
<tr>
<td>CO₂</td>
<td>14.6</td>
<td>16.4</td>
<td>26.5</td>
<td>28.3</td>
<td>38.8</td>
<td>32.9</td>
<td>35.9</td>
<td>31.0</td>
</tr>
<tr>
<td>CS₂</td>
<td>26.4</td>
<td>28.8</td>
<td>60.0</td>
<td>46.9</td>
<td>78.0</td>
<td>50.7</td>
<td>61.5</td>
<td>57.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 6.14: Histograms of timelengths for coupled displacements of halogens and tri-atomics

Fig. 6.15: Sketch of a channel switch projected in the x-y-plane: the shaded regions represent the intersections.

6.4.4 Orientational relaxation and channel switches

The interchange between the two channels, which is of great importance for molecules diffusing in silicalite, can be further examined by looking at the decay of the autocorrelation function (section 4.7.3) \( U(t) \) of the end-to-end versor directed along the molecular axis. In silicalite, decorrelation of the \( u_x \) and \( u_y \) components can only come about through interconversions from one channel type to another, while the \( u_z \) component is usually decorrelated in a shorter time, due to the rattling motion of the molecules in the channels, corresponding to fast oscillations of \( u_z \) around zero. We calculated the decorrelation times by fitting a straight line to the logarithm of the
normalised autocorrelation function of the components of \( \hat{u}(t) \); assuming an exponential relaxation, the slope of the straight line matches \(-1/\tau_d\), \( \tau_d \) being the decorrelation time. Actually, this method gives good results only for the longer species iodine and \( \text{CS}_2 \); the total correlation functions are shown in Fig. 6.16; the slow decay of the iodine and \( \text{CS}_2 \) functions is due to the slow decorrelation of their \( x \) and \( y \) components. For the shorter species the decay is so fast, even along \( x \) and \( y \), that it should be almost completely ascribed to the hindered rotations in the channels, rather than to actual straight-zigzag (or vice versa) migrations, and it could not provide reliable information about such processes.

**Fig. 6.16:** Orientational decorrelation functions

On the other hand, for the longer species the librations are less important and the orientational decorrelation is mostly determined by the switches of channel. Therefore we report in Tab. 6.17 the values obtained for bromine, iodine and carbon disulphide only. For the longer species \( \tau_x \) is considerably greater than \( \tau_y \), in agreement with the previous discussion and with the results of earlier MD simulations of \( n \)-butane and \( n \)-hexane in silicalite\textsuperscript{187,223} while for bromine \( \tau_y \) results slightly larger than \( \tau_z \). Fig. 6.17 shows the decay of the components of \( \hat{u}(t) \) for iodine; the behavior is similar to that observed by June et al.\textsuperscript{187} for butane in silicalite. In the case of chlorine, bromine and carbon dioxide the \( x \) and \( y \) curves are much closer to each other.

**Table 6.17:** Decorrelation times of the end-to-end versor and of its components (ps)

<table>
<thead>
<tr>
<th></th>
<th>( \tau )</th>
<th>( \tau_x )</th>
<th>( \tau_y )</th>
<th>( \tau_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Br}_2 )</td>
<td>11.5</td>
<td>9.3</td>
<td>13.1</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>123.1</td>
<td>183</td>
<td>101.5</td>
<td>11.8</td>
</tr>
<tr>
<td>( \text{CS}_2 )</td>
<td>31</td>
<td>41.8</td>
<td>26.4</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Recall that \( t_{zz} \) and \( t_{zx} \) are solely determined by the migrations between different types of channels, while the decay of \( U(t) \) can also be brought about by the librations in a single channel or intersection. Therefore it seems that only for the longest molecules,
Fig. 6.17: Component of the orientational decorrelation function for I\textsubscript{2} in silicalite

I\textsubscript{2} and CS\textsubscript{2}, the decorrelation of the end-to-end versor is completely determined by the channel interconversions. Maginn et al.\textsuperscript{204} obtain $\tau_x > \tau_y$ for butane and n-hexane, with decorrelation times between 200 and 300 ps. For C\textsubscript{7} and longer chains the decorrelation times become much longer (up to 1 ms) and the decorrelation along $y$ results the slowest: the long linear molecules can leave the straight channels only with great difficulty, probably because they tend to maintain the extended, energetically favorable alignment along such cavities.

### 6.4.5 Comparison of the diffusive models

As shown in Fig. 6.11 and Fig. 6.12, the MSD curves reproduced by the two-step model are always considerably closer to the “standard” one than those obtained by the random-walk model. As already found in the ethane case, Tab. 6.12 shows that both jump models always overestimate the standard values of the diffusion coefficients; however, those predicted according to the two-step model are in much better agreement with the reference values, which in turn should provide a good estimate of the “real” (experimental) data, as proven for ethane,\textsuperscript{81,82} while very few data do exist on the diffusion of halogens, CO\textsubscript{2} and CS\textsubscript{2} in silicalite. The already mentioned (section 4.7.1) experimental work of Kocirik et al. provides a lower limit to the diffusion coefficient for iodine in silicalite which is not in contrast to our data. The diffusion coefficient for CO\textsubscript{2} in silicalite at 300 K and 12 mol./u.c. has been estimated by PFG-NMR,\textsuperscript{224} the obtained value ($0.2 \cdot 10^{-8}$m\textsuperscript{2} s\textsuperscript{-1}) is smaller than ours, but the difference is probably due to the much larger loading in the experimental measurement.

The diffusion anisotropy is not well accounted for by the random walk model, which gives $D_y$ considerably larger than $D_x$ only for I\textsubscript{2}; actually, the two-step model also
fails to well reproduce such effect in the bromine case, where it gives $D_y \sim D_x$ (but
the random walk model in this case behaves even worse, predicting $D_x > D_y$). The
application of the random walk correlation rule and of the generalized correlation rule
to the calculation of $D_z$ from the standard $D_y$ and $D_x$ values (i.e., those denoted as
(a) in Tab. 6.12), gives rise to the values reported in Tab. 6.18.

Table 6.18: $D_z$ values obtained by the standard method, by the random walk correlation rule and by the generalized correlation rule ($/10^{-9}$ m$^2$ s$^{-1}$)

<table>
<thead>
<tr>
<th></th>
<th>$D_z$ standard</th>
<th>$D_z$ r.w. correlation rule</th>
<th>$D_z$ gener. corr. rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$_2$</td>
<td>1.38</td>
<td>2.00</td>
<td>1.83</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>0.62</td>
<td>0.62</td>
<td>0.60</td>
</tr>
<tr>
<td>I$_2$</td>
<td>0.27</td>
<td>0.30</td>
<td>0.29</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>1.57</td>
<td>1.77</td>
<td>1.75</td>
</tr>
<tr>
<td>CS$_2$</td>
<td>0.59</td>
<td>0.64</td>
<td>0.57</td>
</tr>
</tbody>
</table>

Nevertheless, both correlation rules are always fairly adequate: the smaller species give higher errors: for chlorine, $D_z$ is overestimated by 32% by the generalized rule and by 45% by the random walk rule, while for CO$_2$ both rules gives values larger by 12%. In the other cases the agreement is satisfactory. At the same time, we saw before that the direct calculation of total and monodimensional diffusion coefficients through the two-step model gave much better results than the random walk model. This apparent discrepancy, already noted for ethane, needs an explanation. The random-walk equations Eq. 6.16 - Eq. 6.18 considerably overestimate the monodimensional MSD’s and then the total $D$. The MSD of a molecule after $N$ jumps is:

$$\langle \Delta r^2(N) \rangle = \left\langle \left| \sum_{n=1}^{N} r(n) \right|^2 \right\rangle = \sum_{n=1}^{N} \langle |r(n)|^2 \rangle + 2 \sum_{n=1}^{N-1} \sum_{n'=1}^{N-n} \langle r(n) \cdot r(n + n') \rangle$$  \hspace{1cm} (6.42)

and the random-walk model neglects the cross terms in Eq. 6.42, assuming that the loss of memory is complete before each jump. However, Tab. 6.18 shows that:

$$\langle a^2(n_z) \rangle_{MD} < \left\langle \sum_{n=1}^{n_z} x(n)^2 \right\rangle = n_z \left( \frac{a}{2} \right)^2$$  \hspace{1cm} (6.43)

(the same is found for the other components), revealing that the contribution of cross terms in Eq. 6.42 is non-negligible and negative. In other words, if two consecutive jumps in either channels follow opposite directions, the net displacement is clearly zero. Therefore, such pair of jumps should be excluded from the $n_y$ ($n_z$) total number, but a single step model cannot take into account two consecutive jumps. However, when Eq. 6.16 - Eq. 6.18 are combined to obtain the first correlation rule Eq. 6.1, one takes the ratio of the monodimensional MSD’s, and this operation partially corrects the overestimation in the numerator as well as in the denominator: as a consequence, the correlation rule between $D_x$, $D_y$ and $D_z$ may often be adequate, even when the monodimensional MSD’s are not! The random walk equations can be in error but they
are still fairly valid when combined to give Eq. 6.1. The two-step model expressions perform much better in the prediction of monodimensional MSD’s, because they exclude all the pairs of consecutive events in opposite direction: indeed, they overestimate the “true” MSD’s to a much lesser extent. Roughly speaking, the two-step model includes in the sum of Eq. 6.42 the cross products \( r(n) \cdot r(n + 1) \), which have the largest weight in the overall sum (the diffusive memory decreases with the number of jumps). Actually, they cannot account for some higher order events which also give no net contribution to the overall motion, as for example two subsequent pairs of displacements in two opposite directions, therefore also the two-step model slightly overestimates the “true” MSD’s. Clearly, an higher order \( N \)-step model, with \( N > 2 \), would give an almost perfect match with the standard MSD. The \( N \) value should be proportional to the diffusive memory. However, as long as the correlation rules are concerned, it is not surprising that the modified correlation rule Eq. 6.34 does not always improve the first rule, Eq. 6.1: in both rules, overestimation errors are partially cancelled out; these errors are much higher in the random-walk expressions.

The inclusion in Eq. 6.34 of the deviations from complete randomness (Tab. 6.19) is anyway correct, though in some cases the modification of the correlation rule does not apparently lead to any improvements. Note again that \( \Delta n_{zz}^s \) and \( \Delta n_{ss}^s \) are always negative, indicating less events of such kind than in absence of correlation, compensated by the increase of events in opposite direction according to Eq. 6.39; for the longer species also \( \Delta n_{ss}^s \) changes from positive to negative. This indicates a further compensation mechanism acting in favor of Eq. 6.1 also in cases clearly correlated: a decrease in the number of switches (determining lower \( D_z \) values) is accompanied by an increase in the number of events in opposite direction (determining smaller \( D_x \) and \( D_y \) values). From a qualitative point of view, the heavy influence of “bouncing-backs” of steric nature over the \( \Delta n_{zz}^s \) and \( \Delta n_{ss}^s \) values makes them a barely accurate measure of the persistence of the diffusive memory, compared to the randomization ratios discussed above, which are by definition independent on the number of “bouncing-backs”. The only general observation stemming from Tab. 6.19 is the larger weight of “bouncing-backs” for iodine and carbon disulphide (more positive \( \Delta n_{zz}^O \) and \( \Delta n_{ss}^O \) values), which thus show much more negative values for the other deviations.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta n_{zz}^s )</th>
<th>( \Delta n_{zz}^O )</th>
<th>( \Delta n_{ss}^s )</th>
<th>( \Delta n_{ss}^O )</th>
<th>( \Delta n_{ss}^w )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}_2 )</td>
<td>-0.86(-0.44)</td>
<td>2.66(0.48)</td>
<td>0.35(0.09)</td>
<td>1.45(0.30)</td>
<td>-3.6(-0.41)</td>
</tr>
<tr>
<td>( \text{Br}_2 )</td>
<td>-1.0(-0.97)</td>
<td>2.16(0.51)</td>
<td>0.18(0.13)</td>
<td>0.99(0.46)</td>
<td>-2.33(-0.61)</td>
</tr>
<tr>
<td>( \text{I}_2 )</td>
<td>-0.34(-1.12)</td>
<td>1.52(0.70)</td>
<td>-0.98(-1.08)</td>
<td>2.15(0.53)</td>
<td>-2.35(-1.13)</td>
</tr>
<tr>
<td>( \text{CO}_2 )</td>
<td>-1.95(-0.89)</td>
<td>4.59(0.52)</td>
<td>0.24(0.05)</td>
<td>2.39(0.37)</td>
<td>-5.26(-0.48)</td>
</tr>
<tr>
<td>( \text{CS}_2 )</td>
<td>-0.82(-0.70)</td>
<td>3.151(0.614)</td>
<td>-0.457(-0.20)</td>
<td>2.79(0.51)</td>
<td>-4.67(-1.03)</td>
</tr>
</tbody>
</table>

Table 6.19: Deviations of the two-step event numbers from their theoretical (uncorrelated) values; relative deviations are in parentheses.
6.5 Final remarks

We attempted to throw light on the effects that the particle “memory” of its previous path may have on the overall propagation of linear and relatively short molecules in silicalite-type zeolites. It is often assumed that such effects should be most important only for long-chain alkanes with more than five carbon atoms, that can extend for the whole channel length (10 Å) and thus tend to keep the alignment for long times. However we found that a random-walk description is inadequate also for linear flexible species of 5-6 Å length, as emerges from the non-negligible deviations reported in Tab. 6.7 and Tab. 6.19. A more suitable description is given by the two-step model, which takes into account such deviations incorporating the memory present in two subsequent displacements. We showed that the validity of Eq. 6.1 is not a sufficient condition to ensure that molecular propagation in silicalite can be effectively represented by a sequence of noncorrelated jumps between channel intersections. The large applicability of such relation arises from several compensation effects that cancel and correct the errors introduced by the assumption of noncorrelated motion. Such errors are most evident when one calculates directly the MSD curves and the diffusion coefficients according to the random walk model. The two-step model greatly improves these predictions; its residual overestimation of MSD suggests that the diffusive memory does not completely vanish within two jumps, but also for the small molecules considered three or more jumps (covering at least 30 Å) can be necessary to induce an effective randomization of the motion. It is interesting to note that negative correlation effects emerge only at high loadings in Na-Y zeolites, where each jump leaves behind a vacancy which is likely to be reached again at the successive jump.\textsuperscript{55,209} The very different structure of silicalite entails different mechanisms and time scales for diffusion and makes such negative correlations important even at infinite dilution. This is a central point to consider in KMC simulations in silicalite, which will have to include correlation effects if a reliable description of the system is sought. The two-step model has proven to be useful also in the study of several aspects of the diffusive mechanism, such as duration and probability of the various displacements and the relative weight of the molecular librations with respect to the switches from a channel to another. It can be supposed that probabilistic models like this could open a new way to extend the space and time scales accessible to simulations. This arises from the considerable linearity (and good accuracy) observed for the MSD curves calculated with the two-step model, which in turn stems from the constant ratios between the event numbers calculated. Thus the probabilities and times obtained from a direct analysis of the trajectory can presumably define the diffusive behavior over much longer scales, compared to the standard analysis. For instance, these values could allow the application of a KMC simulation based on the two-step model, because they provide the basic rate constants corresponding to each kind of two-step jump.
Chapter 7

Conclusions

This thesis can be considered as the final development of a project aimed at determining the structural and energetic effects which influence the dynamics and reactivity of systems confined inside the zeolite cavities. It has been inspired by preceding simulations\[1,2\] where we highlighted the advantages of a flexible model for the lattice in reproducing the energy exchanges with the sorbates; a central requirement in order to use the same model to study reactive processes, but also to simulate the diffusion in the cavities.\[69\] If, one one hand, the empirical potentials used here does not allow the simulation of reactions involving the zeolite acid sites, on the other hand their simplicity and efficiency allow to probe space and time scales otherwise unreachable. We then shifted our interest to effect relevant over such scales, such as the action of different geometries of the cavities and then of a different confinement in simple reactive processes. In order to observe and understand such effects it is necessary that the dimensions of the simulated system cover at least a unit cell of the solid. Dynamical ab initio simulations of zeolite structures of big industrial relevance, but with several hundredths of atoms/unit cell, such as silicalite and ZK4 examined here, are presently out of reach event with the most powerful CPU normally available, and the situation will not presumably change much for several years. The use of empirical potentials vastly simplifies (and actually makes feasible) the simulation of such systems, which anyway should carefully be performed, taking into account the obvious limits implicit in the force fields adopted. From this perspective there are two essential points which in our opinion give a general validity to our simulations:

- the reactive processes studied are essentially prototypes of condensed-phase reactions, which have proven and still are useful to study the general effect of the solvent, independently of the particular reaction they represent.

- the information we obtain mainly stem from the comparison of data concerning probability, rate and reaction dynamics in different structures. In this way the properties of a specific structure can be highlighted in a direct and accurate way, not in absolute terms, but on the basis of the observed differences

We will not repeat here the observations made in the previous chapters, but only resume the main aspects and the future perspectives. First, we faced the study of a
simple dissociation-recombination process of halogens.\textsuperscript{225-227} The accuracy of the obtained results (and thus of the applied method) is supported by the good agreement between the recombination times observed for the liquid solvent in our simulations and in several experimental and theoretical studies, as well as the agreement between the diffusion coefficients and sorption heats in silicalite calculated by us and those reported in previous simulations and experimental works. We highlighted the major importance of structural effects which can often counterbalance an ineffective energy dissipation and lead to a high probability of recombination. Zeolites with a cage structure like ZK4 can show phenomena similar to the "cage effect" typical of liquids, forcing the recombination of dissociated fragments which are kept in the same cage. In more open, silicalite-like structures the dissociated radicals experiment a greater freedom, which could favor, in specific processes, the formation of different recombination products. This possibility could be studied by observing the behavior (in the two reference zeolites) of the molecular fragments, possibly different, obtained through the photochemical excitation of a number of molecules.

The interesting results obtained in the simulation of the recombination process have in fact encouraged the subsequent study of an activated reactive process,\textsuperscript{228} with analogous purposes. The transfer of a light particle between two heavier substrates is interesting in itself because many catalytic reactions in zeolites involve the transfer of light fragments (as protons) between the reactants. The further complexity introduced by an activation barrier placed between reactants and products allows the exploration of new aspects of the zeolites' action and required the application of particular techniques in order to obtain kinetic information in a reasonable CPU time. The most interesting aspect is the greater efficiency of the silicalite framework in promoting the reaction through the thermal activation of reactants. The explanation of this important aspect is not trivial and entails structural phenomena connected to the presence (in ZK4) of regions that inhibit the reaction, as well as energetical effects, made clear through the calculation of the work made by the zeolitic host during the reaction. The detailed study of the reaction mechanism and of the preferred conformations for the reaction complex inside each structure allowed an hypothesis to be formulated about the ideal microporous structure for this kind of processes.

The height of the barriers considered is not larger than 5$k_B T$. It could surely be interesting to study what effects come into action when much higher barriers are present. In that case the low probability of the reactive event (over the MD time scales) makes necessary the use of yet more sophisticated techniques to obtain accurate kinetic data. An interesting test could be the chair-boat isomerization of cyclohexane, which show a 20 $k_B T$ barrier at 300 K and can be modeled through an intramolecular potential with an exact, albeit complicated, definition of the reaction coordinate.\textsuperscript{193}

Recall that the choice of a particular zeolite for a specific process often derives from a "try and see" approach due to the absence of general information on the structure-activity relationship of different zeolites. The data obtained here are doubtless interesting from this point of view: we observed important and in some cases surprising effects. If some of these may appear in a posteriori accord with intuitive notions, as Whithnall and Wilson pointed out,\textsuperscript{163} it is very important to confirm with the Molecular Dynamics experiment such intuitive notions, in the present case concerning the effects of confinement and of the guest-host energetics. Other observed phenomena are of more
complex nature and then hardly predictable, like among the others the possible action of the breathing motion of ZK4 into helping bromine molecules to cross the windows connecting cages, or the greater efficiency of the silicalite oxygens in the thermal activation of reactants in an activated process. The combination of this information with the results of local quantum dynamics simulations, where the active sites are explicitly considered, could be the key for a better rationalization of the zeolite properties in the future.

In the same way the data obtained from the application of the two-step model\textsuperscript{229,230} could be used in KMC simulations to extend the time scales of observation of the diffusive motion in silicalite. The simulations of the diffusion of diatomic and triatomic species and the subsequent statistical analysis according to the random-walk and two-step models illuminated the frequent inadequacy of a random-walk description. A relevant aspect highlighted is that the validity of the random-walk correlation rule between the components of the diffusion coefficient is not a sufficient condition to assume, as often done in experimental and theoretical works, that the molecular propagation occurs by means of a series of random jumps between the sorption sites. Negative correlations are present, which often elude a simple analysis based on such rule, and must be carefully considered in every statistical description of diffusion in silicalite and similar structures. The two-step model adequately incorporates correlation effects and provides average times and probabilities of each kind of event, which could be used to generate a stochastic two-step (as opposed to random-walk) trajectory in the silicalite channels.
Appendix A

Computing programs and times

The simulations have been carried out through computer programs written in FORTRAN and developed in our laboratory. The core of the Molecular Dynamics code for the simulations of zeolites (harmonic model for the lattice) is made of about 6500 rows of code. It has been modified and adapted according to the specific simulations and problems considered here. We show in the following table the benchmarks of the CPU used for the simulations, for a typical system consisting of 576 atoms of the (flexible) lattice and 8 diatomic molecules sorbed.

<table>
<thead>
<tr>
<th>CPU-Model</th>
<th>RAM</th>
<th>SPECfp95</th>
<th>MD steps/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIGITAL DEC 3000 Mod.300</td>
<td>64 MB</td>
<td>3.65</td>
<td>32.4</td>
</tr>
<tr>
<td>IBM RISC/6000 3CT/39H</td>
<td>64 MB</td>
<td>10.2</td>
<td>34</td>
</tr>
<tr>
<td>Hewlett-Packard HP-9000 K460 4CPU</td>
<td>512 MB</td>
<td>20.2</td>
<td>48.7</td>
</tr>
<tr>
<td>Compaq AlphaServer DS20 2CPU</td>
<td>1 GB</td>
<td>76.1</td>
<td>522.8</td>
</tr>
</tbody>
</table>

The calculations have been carried out mainly on the IBM and HP workstations. In the following we report the CPU times approximately spent for the three groups of simulations performed.

<table>
<thead>
<tr>
<th>Study</th>
<th>MD steps/s</th>
<th>CPU time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation-Recombination</td>
<td>20÷25</td>
<td>1000 h</td>
</tr>
<tr>
<td>Transfer reaction</td>
<td>70÷100</td>
<td>1100 h</td>
</tr>
<tr>
<td>Diffusion (ethane)</td>
<td>25÷70</td>
<td>250 h</td>
</tr>
<tr>
<td>Diffusion (halogens and triatomics)</td>
<td>80÷110</td>
<td>400 h</td>
</tr>
</tbody>
</table>

The above rates vary according to the studied system and the CPU employed. Obviously such times only concern the “production” runs and do not include the statistical analysis of trajectories.
Appendix B

Publications

The main results of this thesis have been presented and published elsewhere as follows:

Chapter 4:

Chapter 5:
IV AIZ Conference, Como, September 1998

Chapter 6:
IV Liquid Matter Conference, Granada, July 1999
XXX Physical Chemistry Conference, Florence, September 1999
*Physical Chemistry Chemical Physics*, accepted for publication (2000)
Appendix C

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