How harmonic is the entropy of a droplet of water?

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Project aims

The proposed project is a theoretical study of the statistical physics of bound molecular clusters at temperatures where the structure is liquid-like, namely highly mobile and lacking in crystalline order. The aim is to test the use of the harmonic approximation in the calculation of the excess entropy of the cluster. This approach is suitable for solid-like clusters but could prove to be tenable for a range of temperatures above the melting point. The work will involve molecular dynamics simulation of clusters of different sizes and temperatures, together with a thermodynamic interpretation of the observed dynamical behaviour.

Background

The free energy of formation of a molecular cluster is a key quantity for understanding its stability against spontaneous disassembly into component molecules. It is also the main ingredient in determining the nucleation barrier that has to be overcome when a metastable or supersaturated gas converts itself into an aerosol of liquid droplets through the growth of molecular clusters[1]. There is great interest in understanding the way this happens, particularly since the generation of atmospheric aerosols from human-derived gas phase emissions constitutes the least understood mechanism of anthropogenic climate change.

Methods and objectives

The project will employ both theoretical and computational methods based on the use of the powerful molecular dynamics code LAMMPS. The work will involve building clusters of water described by the classical TIP4P/2005 force field and thermalising them at temperatures below the melting point. A variety of cluster shapes for a given number of water molecules will be investigated. A normal modes analysis of the trajectory taken by an equilibrated molecular cluster will produce a spectrum of vibrational frequencies, and theoretical analysis will be used to compute the harmonic entropy, an approximation based upon the assumption that all intermolecular interactions behave like Hookean springs. The associated *excess* entropies (with respect to the bulk condensed state) will be compared with computations previously obtained from molecular dynamics studies of liquid-like clusters[2]. They will also be compared with predictions from phenomenological models and where possible, from experimental data. Such an analysis has been performed for Lennard-Jones clusters[3] but not for clusters of complex molecules. A recent study has attempted to map the entropic behaviour of a oscillating rotor onto that of a liquid-like cluster[4]. Our objective is to explore whether the more elaborate properties of a harmonic solid structure are similarly preserved across the melting point. If successful, we would be able to develop a simplified phenomenological model of aerosol nucleation.

Benefits and opportunities for the student

Kirsten Bark recently completed a very thorough review of the literature of molecular clustering as part of her third year studies within the Natural Sciences degree programme[5]. She has shown considerable interest in further employment of the understanding that she has acquired. She is in a very good position to investigate a long-standing research question in the area, namely the adequacy of the harmonic approximation in the computation of cluster entropies. Tackling a challenging summer project between the third and fourth year of her MSci degree, with its need for self-propelled enquiry, will prepare her very well for a final year project. She will be able to deepen her knowledge of an area of physics and develop transferable skills in computing, reporting and communication, all of which will be invaluable for her future career.

Work plan

A programme of work lasting eight weeks, starting on June 11th, will allow us to meet the objectives. The study will be based on mathematical analysis and computer simulation. The research will be supervised by Prof. Ian Ford with the added involvement of PhD student Luke Davis who has expertise in molecular dynamics modelling. The following set of milestones is envisaged. *Week 1.* Literature review of the use of the harmonic approximation for computing the entropy of solid clusters. *Week 2.* Familiarisation with the operation of the LAMMPS molecular dynamics code. *Weeks 3-5.* Extraction of frequencies of normal modes of oscillation for solid clusters of water of various sizes and shapes. *Weeks 6-7.* Extrapolation of the harmonic entropy of solid water clusters to temperatures above the melting point, and comparison with the entropies of liquid water clusters derived from other sources. *Week 8.* Report writing.

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[1] I.J. Ford, *Statistical mechanics of nucleation: a review*, Proc. Instn Mech. Engnrs Part C: J. Mech. Eng. Sci. 218 (2004) 883.

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