Excess energies of \( n \)- and \( i \)-octane molecular clusters

Hanna Vehkamäki and Ian J. Ford

Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, United Kingdom

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Cloud chamber data for the nucleation of droplets from supersaturated \( n \)- and \( i \)-octane vapors are analyzed using nucleation theorems. We obtain the excess energies of pure and mixed component molecular clusters with sizes ranging from 19 to 58 molecules. We plot this information in the form of an excess energy surface for a range of cluster compositions. Since the two species are similar we also combine the data into a plot of excess energy against the total number of molecules in the cluster. We show that the capillarity approximation fails to predict the critical cluster composition, though it does provide a rough estimate of the excess energy of a specified cluster. © 2001 American Institute of Physics. [DOI: 10.1063/1.1351874]

I. INTRODUCTION

Doster et al.\(^1\) have presented measurements of the rate of nucleation of droplets from pure \( n \)-octane and \( i \)-octane vapors, and from mixtures of the two species, obtained using a cloud chamber. The nucleation rates are determined as functions of the temperature \( T \) and the supersaturations, \( S_n \) and \( S_i \), of the \( n \)- and \( i \)-octane vapors, respectively. \( S_n \) is defined as the ratio \( p_s/p_{n,\text{pure}}(T) \), where \( p_{n,\text{pure}}(T) \) is the saturated vapor pressure over pure liquid \( n \)-octane, and \( p_s \) is the partial pressure of \( n \)-octane vapor in the chamber. \( S_i \) is defined similarly. We have used the two-component nucleation theorems\(^2\) to analyze the nucleation rate data, obtaining information about the excess energies of small one and two component molecular clusters of these species. We describe the nucleation theorems in Sec. II, the fit to the data in Sec. III, the extracted cluster properties in Sec. IV, and draw some conclusions in Sec. V.

II. NUCLEATION THEOREMS

The nucleation theorems are based on kinetic and thermodynamic models of the process of nucleation. We assume that the nucleation rate \( J \) can be expressed as \( J=J_0 \exp (-W^*/kT) \), where \( W^* \) is the work of formation of the critical cluster: the cluster which is equally likely to grow or decay under the prevailing conditions in the chamber. \( J_0 \) is the kinetic prefactor, which can be estimated,\(^3\) and \( k \) is the Boltzmann constant. According to the (first) nucleation theorem\(^4\)–\(^7\) the number of molecules of \( n \)-octane, \( \Delta n_n^* \), in the critical cluster is given by

\[
\Delta n_n^* = -\left( \frac{\partial \ln J}{\partial \ln S_n} \right)_{S_i,T} = -\left( \frac{\partial \ln J_0}{\partial \ln S_n} \right)_{S_i,T},
\]

and a similar equation provides a relation between \( \Delta n_i^* \), the number of molecules of \( i \)-octane in the critical cluster, and the partial derivative of \( \ln J \) with respect to \( \ln S_i \).

The second nucleation theorem\(^8\)–\(^10\) gives the excess energy of the critical cluster (the energy of the cluster minus the energies its constituent molecules would have in the pure bulk liquids at the same temperature and pressure) as

\[
E_n^* = \left( \frac{\partial \ln J}{\partial T} \right)_{S_i,s_n} - \left( \frac{\partial \ln J_0}{\partial T} \right)_{S_i,s_n} kT^2.
\]

Thus the dependence of \( J \) upon \( T \) gives the excess energy of a cluster whose molecular composition can be determined through the dependence of \( J \) upon the vapor supersaturations. Different experimental conditions correspond to critical clusters of various sizes, and so if sufficient data is available, properties of clusters of a variety of sizes and at different temperatures can be determined. This is the method which has been used previously to obtain plots of excess energy against size for a number of single component molecular clusters,\(^8\)–\(^10\) and more recently for a binary system.\(^2\)

For single component systems, the dependence of the prefactor \( J_0 \) on temperature and supersaturation is known,\(^9\) while for multicomponent vapors, estimates for the derivatives of the prefactor have to be made based on classical nucleation theory.\(^5\) These estimates are believed to be reasonably robust, and the physico-chemical data needed to make them (and also to perform classical calculations of the cluster composition) are presented in the Appendix and by Doster et al.\(^1\) Another matter is that the theorems given above are derived assuming the vapor is an ideal mixture of ideal gases: corrections to this approximation have been found to be unimportant and we so ignore them.\(^10\)

III. FITTING THE DATA

In order to make use of Eqs. (1) and (2), we have to fit a function to the data to relate \( \ln J \) to \( T, S_i, \) and \( S_n \). Generalizing the fitting function used by Doster et al.\(^1\) we chose to use the form

\[
\ln J(T,S_\xi) = \ln(aT+b) + \frac{eT+d}{S_\xi} + eS_\xi + f
\]

\(^*\)Current address: Department of Physics, P.O. Box 9, 00014, University of Helsinki, Finland.
for pure n-octane and i-octane. The suffix $\xi$ corresponds to $n$ or $i$, and the coefficients $a, b, c, d, e,$ and $f$ are fitting parameters (different values for each pure case). This function produces a good fit not only to the pure vapor experimental data of Doster et al.,$^1$ but also to the pure n-octane data of Rudek et al.$^{11}$ Doster et al. have also measured nucleation rates for three mole fractions of $i$-octane in the vapor mixture: $X = 1/2, X = 1/4,$ and $X = 3/4$. Figures 4–6 of Doster et al.$^1$ suggest that for such mixtures of $n$-octane and $i$-octane the nucleation rate is a smooth function of the combined effective supersaturation $S^* = S_{n}^{\xi \cdot 1/4} + S_{i}^{\xi \cdot 3/4}$. Guided by the apparent similarity of the plots of $J$ as function of $S^*$ in the mixed cases to the plots of $J$ as a function of $S_\xi$ in the pure cases we chose to fit the nucleation rate in the mixed cases using the form

$$
\ln J(T, S_n, S_i) = \ln J(T, S^*) = \ln(aT + b) + \frac{cT + d}{S^*} + eS^* + f.
$$

(4)

We fitted each of the mixed vapor datasets, with $X = 1/2, X = 1/4,$ and $X = 3/4,$ separately. It must be noted that since $S_n$ and $S_i$ are combined into one variable, the above form with a fixed $X$ leads to a firm relation between $(\partial \ln J/\partial \ln S_n)_{S,T} = (1 - X)(\partial \ln J/\partial \ln S^*)_{T} = \Delta n_n^*$ and $(\partial \ln J/\partial \ln S_i)_{S,T} = X(\partial \ln J/\partial \ln S^*)_{T} = \Delta n_i^*$ and thus the mole fraction in the critical cluster $x^* = \Delta n_n^*/(\Delta n_n^* + \Delta n_i^*) \approx X$ is fixed for a certain $X$. This obviously restricts the generality of our analysis. In any case, the set of experimental points available leads to a restriction of this kind. The data points for each $X$ happen to form lines in the three dimensional $(T, S_n, S_i)$ space. We can actually find an equation for these lines, that is we can solve one of the variables as a function of two others; for example, $S_i = S_i(T, S_n)$. This means that from these data we are not able to derive independently the partial derivatives with respect to all three variables. Our approach is further supported by the fact that $i$-octane and $n$-octane molecules are very similar, and therefore it is likely that the mole fraction of the cluster closely reflects the mole fraction of the vapor.

Further support is given by the classical theory, based on the capillarity approximation, which predicts that $x^* = X$ holds accurately for the mixture of $n$-octane and $i$-octane. Note that in this paper $x^*$ is the mole fraction of the entire nucleus including surface excess effects, not the mole fraction of the core of the cluster (for more details on the subject see Laaksonen et al.$^{12}$).

We noticed that a subset of measurements with $X = 1/4$ and $266.0 \text{K} < T < 276.2 \text{K}$ showed a reduction in nucleation rate as the supersaturation of $i$-octane is increased, while the temperature and supersaturation of $n$-octane are kept constant. Including this subset within the fitting procedure caused the fit to behave unphysically, and thus we discarded this set, in the belief that it suffers from inaccuracies in the measurements.

Figures 1(a) and 1(b) show examples of the goodness of the fit. We studied the uncertainty of the fit (and hence the derived cluster properties) by using a modified fitting function where the coefficient $e$ was multiplying $\ln S^*$ rather than $S^*$. Figure 1(b) also shows the classical nucleation rate curves for pure $i$-octane at five different temperatures. The curves are considerably shifted to the left, and the slopes differ as well.

### IV. CLUSTER PROPERTIES

Classical nucleation theory also yields predictions for the numbers of molecules in the critical cluster. Of course, they should not be trusted since the application of bulk material properties to small molecular clusters is hard to justify. The method for obtaining the classical values is explained elsewhere.$^{2,12}$ Figures 2 and 3 (for pure $i$-octane, and mixed clusters, respectively) compare the classical predictions for the $i$-octane molecular content of the critical clusters with those obtained from the experimental data.

The molecular numbers of $i$-octane in the critical cluster according to classical theory are shown on the horizontal axis, and are compared with other values on the vertical axis. First, the line representing classical data provides a one to one correspondence for reference purposes. The vertical bars show estimated error bars for the classical values. The method of obtaining the classical error estimates is explained in the Appendix. For mixed clusters (Fig. 3) we have also shown the number of $i$-octane molecules in the core of the cluster. The circles show the experimental values for the mo-
clusters at lower temperatures. In Fig. 3 the varying mole
experiments as well as classical theory give smaller critical
sizes than those calculated from the classical theory. This is
quite unable to account for the critical sizes deduced from
the measurement temperature is also shown in Fig. 2.

The temperature increases in the figure from left to right, so
we have plotted every tenth point from the entire data set and show error bars only for selected points. We also show the temperatures corresponding to the experimental points.

The molecular content of the critical cluster. We also show error bars to indicate uncertainties in the values extracted from the experimental data. For clarity, we have plotted only every tenth point, approximately, and have shown error bars only for selected points. The relative importance of the prefactor is indicated using cross symbols, by displaying the molecular content that would be extracted from the data by ignoring the $S_i$ dependence of $J_0$. It is seen that the contribution arising from the prefactor is almost imperceptible for the pure clusters, but with mixed clusters the contribution increases slightly with the size of the cluster. The classical theory is quite unable to account for the critical sizes deduced from the data. The measurement temperature is also shown in Fig. 2. The temperature rises in the figure from left to right, so experiments as well as classical theory give smaller critical clusters at lower temperatures. In Fig. 3 the varying mole

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V. CONCLUSIONS

Nucleation theorems relate properties of the critical molecular cluster to the dependence of the nucleation rate on experimental control parameters such as the temperature and vapor supersaturations. Using theorems for two-component nucleation, we have analyzed droplet formation rate data for recent experiments involving pure n- and i-octane vapors, and mixtures of the two.

The largest mixed cluster studied contains 48 molecules, 35 of which are i-octane, and the smallest contains 19 molecules with only 10 i-octane molecules. We were also able to study pure i-octane clusters ranging in size from 24 to 58 molecules, and pure n-octane clusters from 19 to 24 molecules in size. There is an uncertainty of about 5 to 10% in these numbers. Classical nucleation theory provides estimates which are quite at odds with these sizes. The key second nucleation theorem for multicomponent cluster formation allows us to determine the excess energies of these clusters: the energies of the clusters minus the energies each constituent molecule would have in single component liquids at the same temperature and pressure. The excess energy will comprise, to a first approximation, a bulk mixing energy, and a surface energy due to unsatisfied bonds (undercoordination).

The excess energies of the clusters have been displayed in the form of an energy surface over cluster composition. We have gone on to convert the energy surface into a plot of excess energy against the total number of molecules in the critical cluster. This time, the classical theory is seen to give a reasonable estimate for the energy of a cluster of a given size. However, due to the inability to predict critical sizes, the classical theory provides a poor model of nucleation rates, as shown by Doster et al.[1]

The data we have analyzed here, and elsewhere[8–10,2 provide a wealth of information about the small, short-lived molecular clusters that control the nucleation of droplets from metastable vapors. This information could be useful as reference material in numerical studies of the structure of these clusters.

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APPENDIX: PHYSICOCHEMICAL DATA

The properties of i-octane and n-octane liquids (densities \( \rho_{i.o.} \), surface tensions \( \sigma_{i.o.} \) and saturated vapor pressures \( p_{i.o.}^{\text{pure}} \) and \( p_{n.o.}^{\text{pure}} \)) are given by Doster et al.[1]

The liquid phase is assumed to be ideal, and thus the activities \( a_i(x_{\text{bulk}}, T) = p_i^{\text{x}}(x_{\text{bulk}}, T)/p_i^{\text{pure}}(T) \), with \( i = n, i \), take the simple forms \( a_n(x_{\text{bulk}}, T) = x_{\text{bulk}} \) and \( a_i(x_{\text{bulk}}, T) = 1 - x_{\text{bulk}} \), where \( p_i^{\text{x}}(x_{\text{bulk}}, T) \) is the saturated vapor pressure of component \( i \) over a flat surface of liquid mixture with i-octane bulk mole fraction \( x_{\text{bulk}} \).

The molecular masses are \( m_i = m_n = 144.23 \times 1.66057 \times 10^{-27} \text{kg} \). The latent heats of evaporation \( L_i \) for the pure liquids are evaluated using the Clausius–Clapeyron equation:

\[
\frac{d p_i^{\text{pure}}}{dT} = \frac{L_i}{T(v_{i,\text{bulk}} - v_i)}.
\]

If we assume that the molecular volume in the liquid \( v_{i,\text{bulk}} \) is negligible compared with that in the saturated vapor \( v_{i,\text{vap}} \), we get

\[
L_i(T) = kT^2/p_i^{\text{pure}} dp_i^{\text{pure}}/dT.
\]

To estimate the uncertainty of the classical predictions we have used slightly modified fits for the density and surface tension. Not only the absolute values but also the composition and temperature derivatives of these quantities have to be changed to perform a relevant sensitivity analysis. At most, the uncertainty in surface tension and density were taken to be 5%. As for the activities, we considered the mixture ideal even when performing the sensitivity analysis.