

Thermodynamic properties of critical clusters from measurements of vapour–liquid homogeneous nucleation rates

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Two nucleation theorems are proved using small system thermodynamics. The first is well known and has been used before to determine the number of molecules in the critical nucleus controlling the nucleation of droplets from supersaturated vapours. The second appears to be new, and relates the temperature dependence of the nucleation rate to the excess internal energy of the critical cluster. An analysis of measured homogeneous nucleation rates can therefore provide the size, internal energy, free energy, and entropy of the critical cluster, which should provide important guidance for the construction of theoretical models of the process. This is illustrated using water, *n*-butanol and *n*-nonane nucleation data. While there is often a close correspondence between the droplet free energy and the form suggested by classical theory, the excess internal energy seems to show a linear dependence on molecular number, rather than the classical $2/3$ power behaviour. © 1996 American Institute of Physics. [S0021-9606(96)50642-2]

I. INTRODUCTION

The nucleation of a phase change often involves the formation of a critical molecular cluster. This is an agglomerate of the new phase which is in equilibrium with the original phase under the prevailing conditions: it is just as likely to grow as it is to decay back into the old phase. Although the homogeneous nucleation of liquid droplets from supersaturated vapours is the focus of attention in this paper, there are many systems where similar phenomena occur, such as freezing in undercooled liquids, and phase transformations and growth processes in solid state materials.¹

The study of phase equilibria involving spatial scales which are large compared to molecular sizes has long been a principal application of the methods of continuum thermodynamics. However, since critical clusters can often contain only a few tens of molecules, the use of continuum thermodynamics to describe such systems is of doubtful validity. A continuum approach also requires a cluster surface area to be defined, which is uncertain for such small structures. An approach often used instead is to apply the methods of statistical mechanics, since the molecular nature of the system can then be taken into account in constructing the relevant ensembles and partition functions. However, these approaches usually introduce particular choices of interaction potential,^{2,3} or require definitions of what precisely constitutes a cluster.^{4–6} The generality of thermodynamic predictions can be missing.

Classical nucleation theory builds on the continuum thermodynamics treatment of droplets by imposing the capillarity approximation, according to which small droplets are considered to have the same properties as bulk condensed phases, with bulk surface properties. This additional continuum assumption has also been viewed with suspicion, and other models have been proposed which introduce more microscopic features.^{7–10} However, classical nucleation theory compares well with these others in accounting for experi-

mental data. It would be an important goal to understand why the classical treatment of tiny droplets is as successful as it is, and also where and why it fails.

However, in order to investigate the failings of classical theory, it is necessary to question the underlying approach, namely the application of continuum thermodynamics to small clusters of molecules. In fact, this problem was addressed more than thirty years ago by Hill.^{11,12} His insight was that even though the methods of continuum thermodynamics cannot be used to analyse a small cluster, they are valid for treating a large ensemble of such systems. The thermodynamic relations which emerge are in terms of averages of system thermodynamic quantities over the ensemble. These relations can differ from those expected for large systems, although in the continuum limit they coincide. Furthermore, the questionable introduction of a well-defined cluster surface area can be avoided.

The method of small system thermodynamics deserves to be reviewed solely for the ease with which an expression for the work of formation of a critical cluster can be derived. This is done in Section II. However, it also allows a general analysis of the thermodynamics of droplets to proceed. The nucleation theorem,^{13,14} according to which the supersaturation dependence of measured nucleation rates is related to the number of molecules in the critical cluster, can be proved quite easily. Furthermore, an analogous relation between the temperature dependence of the nucleation rate and the cluster internal energy can be derived. This result is described in Section III and is then applied in Section IV using experimental data for the homogeneous nucleation of droplets of water, *n*-butanol and *n*-nonane from their vapours. Conclusions from this work are given in Section V. Finally, to demonstrate that the nucleation theorems are not restricted to the small system treatment, the basic results are also proved using continuum methods in the Appendix.

II. SMALL SYSTEM THERMODYNAMICS

Statistical mechanical models of clusters typically predict droplet free energies with various terms proportional to powers and logarithms of the number of molecules in the cluster.^{3,7} For bulk materials the linear terms dominate, but for small clusters the non-linear terms are also important. However, the thermodynamics of clusters has often been developed according to the Gibbs treatment, which assumes that the condensate and vapour can be modelled as though they were homogeneous bulk phases with extensive internal energies and entropies, proportional to the numbers of molecules in each. An additional surface phase is introduced with an excess free energy which carries the non-linear terms. This is defined on an arbitrary dividing surface separating the condensed and vapour phases. The well-known Tolman prediction of the size dependence of the surface tension emerges from this formalism.^{15,16} However, the Gibbs treatment is likely to be a poor approximation to real clusters when the number of molecules is small. The thermodynamics of small systems was developed by Hill^{11,12} in order to describe systems for which the free energy, entropy and internal energy are not extensive quantities. Model continuum phases and a surface phase do not appear in this treatment.

It is useful to compare the two approaches briefly. In the Gibbs treatment we consider a spherical condensed phase droplet held within a homogeneous vapour phase, with total system volume V , and in contact with particle and heat reservoirs. We shall use the terms droplet and cluster interchangeably. The temperature T and chemical potential μ are constant throughout. The internal energy, number of molecules and entropy E , N and S characterising the whole system are divided into contributions associated with the condensate and vapour separately (considered to be occupying volumes V_l and V_v respectively with $V = V_l + V_v$), and a third phase defined on a notional dividing surface of area A separating the two. A condition for the position of the dividing surface must also be chosen. For a change in phase entropy, volume and molecular content, the first law of thermodynamics gives the associated changes in internal energy of the liquid and vapour phases:

$$\begin{aligned} dE_l &= TdS_l - p_l dV_l + \mu dN_l, \\ dE_v &= TdS_v - p_v dV_v + \mu dN_v, \end{aligned} \quad (1)$$

where the suffices denote liquid and vapour, and $p_{l,v}$ denotes the pressures within the condensate and vapour phases. The important continuum assumption is then made that the internal energy, entropy and volume of each phase are proportional to the numbers of molecules in each. This is the assumption which fails for small systems. Then the equations integrate according to Euler's theorem to

$$\begin{aligned} E_l &= TS_l - p_l V_l + \mu N_l, \\ E_v &= TS_v - p_v V_v + \mu N_v. \end{aligned} \quad (2)$$

The thermodynamic properties of the surface are then assigned using

$$E_s = E - E_v - E_l, \quad (3)$$

and similar expressions for N_s and S_s , with the suffix s denoting surface terms. We can then write a relation similar to Equation (2) for the surface properties:

$$E_s = TS_s + \sigma A + \mu N_s, \quad (4)$$

which can be considered to be a definition of the surface tension σ . It is a function of the dividing surface condition in such a way as to make E etc. independent of this unphysical element of the model.

The work required to form the cluster from a uniform vapour phase is given by the change in internal energy of the system in going from a vapour system (at different T , p_v and μ in general) to the critical droplet plus vapour state just considered, with the total number of molecules, volume and entropy all constant.¹⁶ Equivalently, this can be written as the change in grand potential in going from a bulk vapour state to the droplet plus vapour state at constant T , V and μ :¹

$$\Delta\Omega = \Omega - \Omega_0 = E - TS - \mu N + p_v V, \quad (5)$$

where $\Omega_0 = -p_v V$ is the grand potential for the system containing a uniform vapour phase. Summing Equations (2) and (4), using Equation (3) and its analogues, and using the symbol ϵ to denote the droplet work of formation, we obtain

$$\epsilon = \Delta\Omega = \sigma A - (p_l - p_v)V_l = \sigma A - N_l \Delta\mu, \quad (6)$$

where $\Delta\mu = \mu - \mu_e$ and the last result has been obtained using the Gibbs–Duhem relation for the condensed phase, assuming it to be incompressible. $\mu_e(T)$ is the chemical potential for equilibrium at temperature T between bulk condensed and vapour phases. The critical cluster is the size which is in unstable thermal equilibrium, which means that the work of formation is at a maximum with respect to N_l and N_s .

In Hill's treatment, a similar system containing a cluster of the new phase surrounded by vapour is considered, with total volume V and environmental variables T and μ . However, the internal energy and entropy are not separated into contributions from each phase. The crucial step taken is to consider an ensemble of \mathcal{M} such systems with a total internal energy, entropy and number of molecules labelled by a suffix t . A change in system conditions, which includes varying the number \mathcal{M} of what now may be denoted subsystems in the ensemble, gives a first law in the form

$$dE_t = TdS_t - p_v \mathcal{M} dV + \mu dN_t + X d\mathcal{M}, \quad (7)$$

where p_v is the pressure exerted at the outer surface of the volume V , and $X = (\partial E_t / \partial \mathcal{M})_{S_t, V, N_t}$ is a new generalised pressure associated with the variable \mathcal{M} . It is the subsystem work of formation since it is the change in internal energy required to create an additional subsystem of volume V at constant total entropy S_t and number of molecules N_t . For a large ensemble, E_t and S_t are proportional to \mathcal{M} , X is a constant, and so Equation (7) integrates at constant V , T and μ to give

$$X = \bar{E} - TS - \mu \bar{N}, \quad (8)$$

where $\bar{E} = E_t / \mathcal{M}$, $S = S_t / \mathcal{M}$ and $\bar{N} = N_t / \mathcal{M}$. X is therefore also the grand potential for a single subsystem, written in terms of \bar{E} and \bar{N} which are the *ensemble averaged* values of the internal energy and molecular number in each droplet plus vapour subsystem. They are the analogues of the quantities E and N in the Gibbs treatment. The entropy is not given an overbar since S_t is a property of the entire ensemble: each subsystem has the same entropy S .¹¹ Equation (8) is valid for all states of the subsystem, not just equilibrium states.

We are interested in the work of formation of the cluster alone, and not a subsystem which also contains surrounding vapour. This can be found by considering a state of the subsystem which contains just vapour at the same T , V and μ and with a grand potential denoted X_0 . To be specific, we could take the subsystem volume to be small enough so that to a good approximation the vapour consists entirely of unclustered molecules, although this restriction is not necessary. Recall that X describes the same subsystem when an additional cluster is included, and so the droplet work of formation ϵ is given as before by a difference in grand potentials:

$$\begin{aligned} \epsilon &= X - X_0 = \bar{E} - \bar{E}_0 - T(S - S_0) - \mu(\bar{N} - \bar{N}_0) \\ &= \bar{E}_c - TS_c - \mu\bar{N}_c, \end{aligned} \quad (9)$$

where \bar{E}_0 , S_0 and \bar{N}_0 correspond to the pure vapour system, and \bar{E}_c , S_c and \bar{N}_c are now the thermodynamic variables associated with the cluster. They are the mean thermodynamic properties of the cluster (across the ensemble) minus those of the vapour displaced in forming it. However, the latter are small and can usually be neglected. The critical cluster is identified by requiring ϵ to be at a maximum with respect to \bar{N}_c , i.e. $(\partial\epsilon/\partial\bar{N}_c)_{T,\mu} = 0$.

We shall see later on how Equation (9) can be made to correspond more closely to Equation (6) without assuming incompressibility of the condensed phase. It is the starting point of a procedure by which two important theorems can be derived, which is pursued in the next section.

First, it is worth reflecting briefly on some important conceptual points. A bulk vapour phase contains populations of molecular clusters with a range of sizes. The state of thermal equilibrium of such a system in contact with particle and heat reservoirs has a cluster size distribution which minimises the system grand potential. In statistical mechanics, this corresponds to choosing a cluster size distribution which maximises the system partition function.¹⁷ In the present procedure we calculate the change in grand potential ϵ of two systems which differ through the presence of a *single* additional cluster. The formation of the cluster is considered to occur with a probability proportional to $\exp(-\epsilon/kT)$. The two pictures are equivalent, and we can take the cluster populations in the bulk vapour phase in equilibrium to be proportional to the probabilities of the associated fluctuations in grand potential.

It is also worth reflecting on the ensemble of small subsystems. The clusters in the ensemble vary in size and energy

about the mean values \bar{N}_c and \bar{E}_c . This reflects the stochastic nature of properties of clusters of such small size. For larger systems and clusters the variations become negligible, and we pass into continuum thermodynamics. Nevertheless, the procedure clearly indicates that small clusters will exhibit a variation in properties. Fortunately, it is the mean properties which determine the work of formation, the fluctuation probability and hence the cluster populations in equilibrium, which in turn control the rate of nucleation.

III. TWO NUCLEATION THEOREMS

From the theory of small system thermodynamics, we have seen that the work of formation of a droplet in contact with heat and particle reservoirs at temperature T and chemical potential μ is

$$\epsilon = \bar{E}_c - TS_c - \mu\bar{N}_c, \quad (10)$$

where \bar{E}_c , S_c and \bar{N}_c are the internal energy, entropy and number of molecules characterising the droplet. The critical cluster is identified by $(\partial\epsilon/\partial\bar{N}_c)_{T,\mu} = 0$. Hill's formalism also yields the first law of thermodynamics for the droplet variables by the substitution of Equation (8) into Equation (7):

$$d\bar{E}_c = TdS_c + \mu d\bar{N}_c, \quad (11)$$

which leads to the fundamental relation

$$d\epsilon = -S_c dT - \bar{N}_c d\mu. \quad (12)$$

The work of formation of the critical cluster is central to most theories of nucleation. We shall therefore focus on the properties of this cluster, and denote associated properties with an asterisk. We make the usual assumption that the rate of nucleation J is proportional to the population of critical clusters, and is given by

$$J = J_0 \exp(-\epsilon^*/kT), \quad (13)$$

where k is Boltzmann's constant and J_0 is a kinetic prefactor. We can write for the general case

$$\begin{aligned} d\left(\frac{\epsilon}{kT}\right) &= \frac{d\epsilon}{kT} - \frac{\epsilon}{kT^2} dT \\ &= -\frac{\bar{N}_c}{kT} d\mu - \frac{(\bar{E}_c - \mu\bar{N}_c)}{kT^2} dT, \end{aligned} \quad (14)$$

using Equations (10) and (12). The chemical potential μ is related to the properties of the vapour by

$$\mu = \mu_e + kT \ln S_v, \quad (15)$$

with $\mu_e(T)$ the chemical potential of the vapour when in equilibrium with bulk condensate at temperature T , and S_v the vapour supersaturation defined by $S_v = p_v / p_{ve}(T)$ where p_v is the vapour pressure and p_{ve} the vapour pressure at equilibrium with a plane surface of its condensate at temperature T . A suffix v is attached to the usual symbol for supersaturation to avoid any confusion with the droplet entropy.

It is more convenient to use $\ln S_v$ instead of μ as the environmental variable, so with

$$d\mu = (\mu'_e(T) + k \ln S_v) dT + kT d(\ln S_v), \quad (16)$$

where the prime denotes a derivative with respect to T , we obtain

$$d\left(-\frac{\epsilon}{kT}\right) = \bar{N}_c d(\ln S_v) + \frac{1}{kT^2} (\bar{E}_c - (\mu_e - T\mu'_e)\bar{N}_c) dT. \quad (17)$$

Applying this relation to the critical cluster, and using Equation (13), this relation immediately yields the nucleation theorem:^{13,14}

$$\left(\frac{\partial(\ln(J/J_0))}{\partial(\ln S_v)}\right)_T = \bar{N}_c^*, \quad (18)$$

which, once an expression for J_0 has been chosen, allows the number of molecules in the critical cluster to be obtained from the supersaturation dependence of measured nucleation rates J .

Furthermore, Equation (17) yields a second nucleation theorem which concerns the temperature dependence of J at constant supersaturation. This is the main result of this paper, and is believed to be new. In order to obtain this result in the most useful form, we need to simplify Equation (17) further. Since μ_e characterises a bulk vapour phase, we can use the continuum Gibbs–Duhem relation $s_v dT - v_v dp_v + d\mu = 0$, where s_v and v_v are the molecular entropy and volume in the vapour phase. This leads to

$$\mu'_e = v_v p'_{ve} - s_v = \frac{v_v(h_v - h_l)}{T(v_v - v_l)} - s_v, \quad (19)$$

after using the Clausius–Clapeyron equation. h_v and h_l are the molecular enthalpies of bulk vapour and liquid at the temperature T and pressure p_v , and v_l is the molecular volume of bulk liquid. Noting that $\mu_e = h_v - Ts_v$, these results lead to

$$\mu_e - T\mu'_e = h_l + O(v_l/v_v) \approx e_l, \quad (20)$$

where e_l is the molecular internal energy in the bulk liquid at equilibrium with saturated vapour at temperature T , and terms of order v_l/v_v have been dropped. Hence we obtain a second nucleation theorem:

$$\left(\frac{\partial(\ln(J/J_0))}{\partial T}\right)_{\ln S_v} = \frac{1}{kT^2} (\bar{E}_c^* - e_l \bar{N}_c^*) = \frac{E_x^*}{kT^2}, \quad (21)$$

where E_x^* is the excess internal energy of the critical cluster: the amount by which its internal energy differs from the internal energy of \bar{N}_c^* molecules of a bulk condensed phase. Once a form for J_0 has been chosen, this relation allows the internal energy of the critical cluster to be determined from the temperature dependence of the nucleation rate. An equivalent, but more compact expression of this theorem is

$$\left(\frac{\partial(\beta\epsilon^*)}{\partial\beta}\right)_{\ln S_v} = E_x^*, \quad (22)$$

where $\beta = 1/kT$.

It is also possible to simplify Equation (10) using some of the results so far obtained. Defining the excess entropy of the cluster by $S_x = S_c - s_l \bar{N}_c$, and using Equation (15) (once again neglecting terms of order v_l/v_v), we can write

$$\epsilon = E_x - TS_x - \bar{N}_c kT \ln S_v = F_x - \bar{N}_c kT \ln S_v, \quad (23)$$

which now defines the cluster excess Helmholtz free energy F_x . This is the result which corresponds most closely to the usual Gibbs treatment result, given in Equation (6), and indeed the two are identical, if the Gibbs equimolecular dividing surface is chosen such that $N_l = \bar{N}_c$ and F_x is identified with σA . The excess quantities are precisely those which are associated with the surface of the droplet in the Gibbs treatment of droplet thermodynamics. In Hill's treatment, they arise more naturally without the introduction of a surface phase, without modelling the condensate and vapour using bulk thermodynamic phases, and without the assumption that the condensate is incompressible.

Apart from the assumption of Equation (13) as the form taken for the nucleation rate, the results obtained so far are model independent. In order to make use of experimental data for J to determine \bar{N}_c^* and \bar{E}_c^* for the critical cluster, a model for the temperature and supersaturation dependence of J_0 has to be introduced. Since ϵ^*/kT dominates the T and $\ln S_v$ dependence of J defined in Equation (13), the expression chosen will not have a major influence on our conclusions, except perhaps for extremely small clusters. For the nucleation of single component condensed phases from the vapour phase, we take the classical kinetic prefactor for a spherical droplet,^{1,2} corrected by a factor of $1/S_v$ for consistency with the law of mass action:¹⁸

$$J_0 = \left(\frac{2\sigma}{\pi m}\right)^{1/2} \frac{S_v p_{ve}^2 v_l}{(kT)^2}, \quad (24)$$

where σ is the bulk liquid surface tension and m the molecular mass. The derivative of $\ln J_0$ with respect to $\ln S_v$ is unity, and the T derivative is well approximated by

$$\left(\frac{\partial(\ln(J_0))}{\partial T}\right)_{\ln S_v} \approx \frac{2}{T} \left(\frac{L}{kT} - 1\right), \quad (25)$$

where $L = h_v - h_l$ is the latent heat of evaporation.

These results can be used with the nucleation theorems to obtain an expression for the temperature dependence of the critical supersaturation S_v^{crit} (the supersaturation required to produce nucleation at a particular rate). We have

$$d(\ln J) = (\bar{N}_c^* + 1) d(\ln S_v) + \frac{1}{T} \left(\frac{\bar{E}_c^* - e_l \bar{N}_c^*}{kT}\right) + 2 \left(\frac{L}{kT} - 1\right) dT. \quad (26)$$

Setting $d(\ln J)$ equal to zero we find that

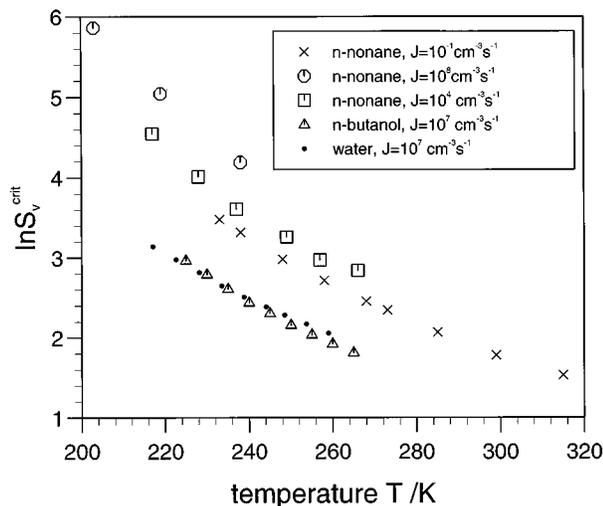


FIG. 1. Experimental critical supersaturations for nucleation of water (Reference 19), *n*-butanol (Reference 20) and *n*-nonane (References 21–23) at the prescribed rates, as a function of temperature.

$$T \frac{d(\ln S_v^{\text{crit}})}{dT} = - \frac{(E_x^* + 2(L - kT))}{kT(\bar{N}_c^* + 1)}. \quad (27)$$

If measurements of the supersaturation dependence of the nucleation rate at constant temperature are available, this result offers the most practical method for extracting information on the cluster internal energy from experimental data. It is used in the next section to study homogeneous nucleation data for water, *n*-butanol and *n*-nonane.

IV. ANALYSIS OF EXPERIMENTAL DATA

A large body of homogeneous nucleation measurements has been accumulated recently, principally using expansion chambers which can study steady state droplet nucleation under carefully controlled conditions. In several cases, data have been gathered for a range of vapour supersaturations at a constant temperature in order to make use of the first nucleation theorem¹⁴ to determine the number of molecules in the critical cluster. The second nucleation theorem can be used to analyse of the temperature dependence of the critical supersaturation through Equation (27).

Critical supersaturation curves have been plotted in Figure 1 from data for water,¹⁹ *n*-butanol²⁰ and *n*-nonane,^{21–23} and for different choices of the constant nucleation rate: $J=10^7 \text{ cm}^{-3}\text{s}^{-1}$ for water and *n*-butanol; and $J=10^4 \text{ cm}^{-3}\text{s}^{-1}$,²¹ $J=10^8 \text{ cm}^{-3}\text{s}^{-1}$,²² and $J=10^{-1} \text{ cm}^{-3}\text{s}^{-1}$ ²³ for *n*-nonane. (The whole *n*-nonane data set is actually taken from Figure 5 in the paper by Hung *et al.*²³) The data are of high quality, with one possible question mark. In the Hung *et al.* data set,²³ which was taken using a diffusion chamber, an unexplained dependence upon the total system pressure was noted. This has not been reproduced in other experiments. Although there is therefore some suspicion attached to this data set, we have nevertheless proceeded to analyse it using the nucleation theorems. Conclusions based on this data set alone should perhaps be accepted with caution. Of

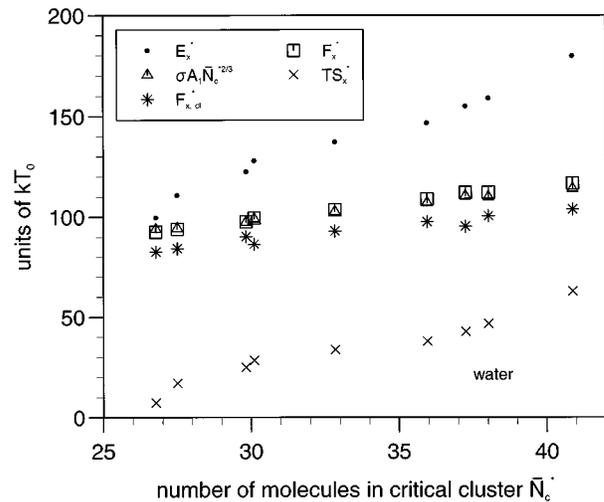


FIG. 2. Various thermodynamic properties of critical clusters of water derived from nucleation rate measurements (Reference 19) against size of the critical cluster \bar{N}_c^* . E_x^* is the excess internal energy, F_x^* is the excess Helmholtz free energy and S_x^* the excess entropy.

course, if the pressure effect is real, then the nucleation theorems would provide us with some information about the pressure dependence of the cluster thermodynamic quantities.

The number of molecules in the critical cluster \bar{N}_c^* at each temperature is found using Equation (18). Equation (27) is then used to extract the excess internal energy for the critical cluster E_x^* using values of the latent heat L found from the Clausius–Clapeyron equation and expressions for the equilibrium vapour pressure for each substance taken from Reference 8. At the same time, the work of formation of the critical cluster ϵ^* is obtained using Equation (13) with the classical prefactor J_0 given by Equation (24), again using previously compiled physical data.⁸ The excess free energy of the critical droplet F_x^* is then obtained from Equation (23), and the excess entropy S_x^* (times T) found by subtracting F_x^* from E_x^* . Each of these quantities is plotted in Figures 2–5 for water, *n*-butanol and the three data sets for *n*-nonane respectively, in convenient units of kT_0 with $T_0=273.15 \text{ K}$, against the measured size of the critical cluster \bar{N}_c^* . Each thermodynamic quantity is a function of T and $\ln S_v$, and so is \bar{N}_c^* . Uncertainty in these plots arises from statistical errors in the data, in addition to errors in measuring the slopes of the critical supersaturation curves. It is estimated that these sources introduce an uncertainty of about 5% in the values of E_x^*/kT , and the same order of magnitude for \bar{N}_c^* . For the two oldest and smallest data sets,^{21,22} the uncertainties are higher.

According to classical theory, the excess free energy of a cluster at T and $\ln S_v$ is $\sigma A_1 \bar{N}_c^{*2/3}$ where $A_1=(36\pi v_l^2)^{1/3}$. Putting this into Equation (23) and imposing $(\partial \epsilon / \partial \bar{N}_c)_{T, \ln S_v} = 0$ we obtain the classical critical size given by $N_{c,cl}^* = (2\sigma A_1 / 3kT \ln S_v)^3$ with excess free energy $F_{x,cl}^* = \sigma A_1 (N_{c,cl}^*)^{2/3}$. This excess free energy is also plotted in the figures, against values of \bar{N}_c^* corresponding to the

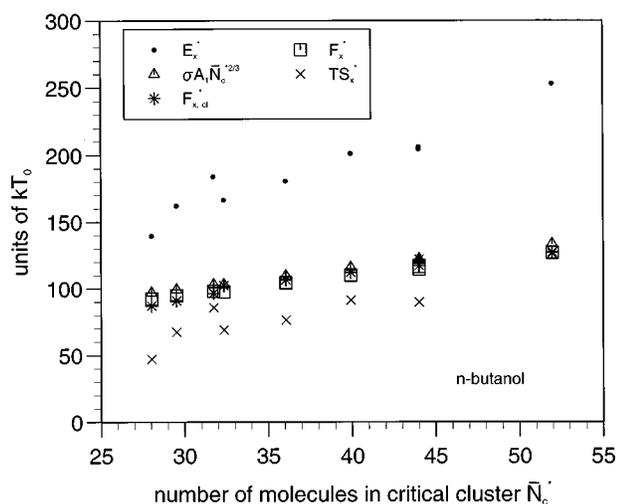


FIG. 3. Various thermodynamic properties of critical clusters of *n*-butanol derived from nucleation rate measurements (Reference 20) against size of the critical cluster \bar{N}_c^* .

same T and $\ln S_v$. There are often large discrepancies between this quantity and the actual excess free energy F_x^* which lead to errors in the predictions of classical theory. However, it is interesting to note that the quantity $\sigma A_1 (\bar{N}_c^*)^{2/3}$ is often in better agreement with F_x^* . This comparison is illustrated for all the data in Figure 6: the values of $\sigma A_1 (\bar{N}_c^*)^{2/3}$ shown previously as points are now shown as slightly smoothed curves. (The curves are jagged since σA_1 is a function of T which varies across the range of \bar{N}_c^* .) This shows that the classical excess free energy for the true number of molecules in the cluster (rather than the classical cluster size) provides a good first order approximation to F_x . Differences between F_x and $\sigma A_1 \bar{N}_c^{2/3}$ correspond to corrections to the classical free energy such as the $\ln \bar{N}_c$,

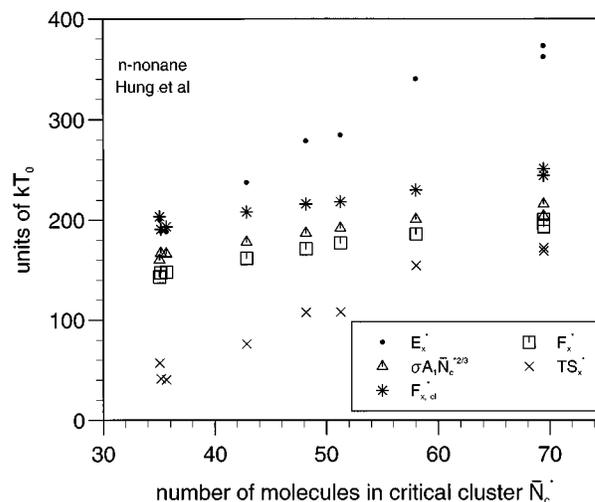


FIG. 5. As Figure 4, for *n*-nonane data taken from Reference 23.

$\bar{N}_c^{1/3}$ and constant terms which have sometimes been suggested.⁸ These terms would also ensure that the critical size satisfying $(\partial \epsilon / \partial \bar{N}_c)_{T, \ln S_v} = 0$ differs from the classical result $N_{c,cl}$.

The construction of nucleation models, particularly using statistical mechanics, could be greatly aided by using such thermodynamic information derived from experimental data. For example, the simple model suggested by Ford *et al.*³ makes use of a square well potential to describe the confinement of non-interacting point-like molecules within a cluster volume of a prescribed size. The depth of the well U is designed to reproduce the classical excess free energy, and in the simplest model considered it is equal to $\sigma A_1 \bar{N}_c^{2/3} - 3 \bar{N}_c kT/2$. The excess cluster internal energy is then found from the partition function of the model, which is proportional to $(kT)^{3 \bar{N}_c/2} \exp -U/kT$. By the usual proce-

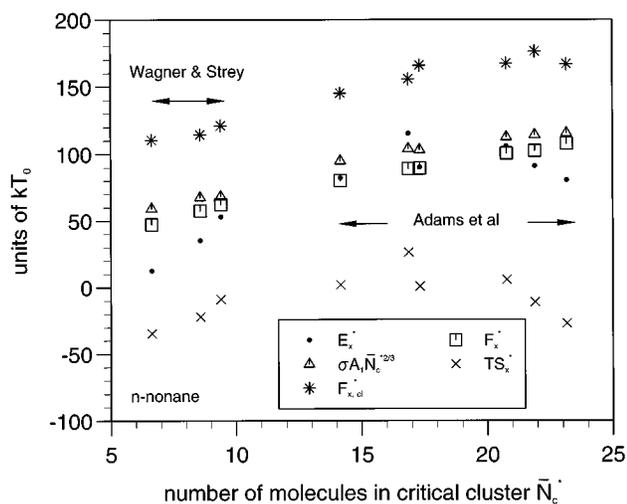


FIG. 4. Various thermodynamic properties of critical clusters of *n*-nonane derived from nucleation rate measurements (References 21 and 22), against size of the critical cluster \bar{N}_c^* .

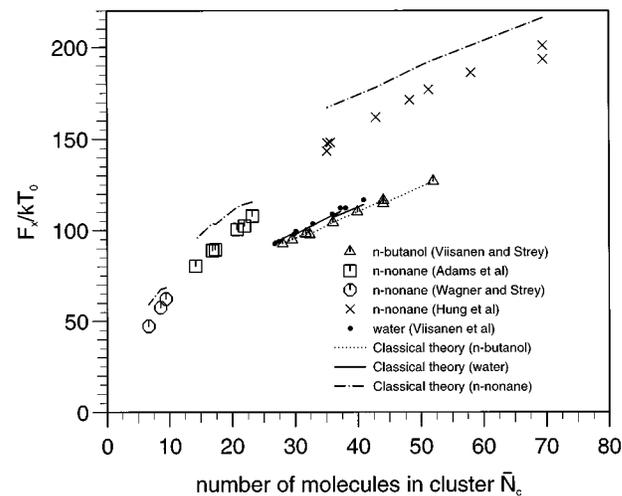


FIG. 6. The excess Helmholtz free energy for all the data sets against cluster size \bar{N}_c . T_0 is equal to 273.15 K. The curves correspond to the classical expression $\sigma A_1 \bar{N}_c^{2/3} / kT_0$.

ture, the excess internal energy is then found to be $\sigma A_1 \bar{N}_c^{2/3} (1 - (T/\sigma)(d\sigma/dT)) + 3\bar{N}_c kT/2$. This result, or others arising from similar statistical mechanics approaches, could be compared with experimental data for E_x^* vs \bar{N}_c^* . A much earlier model due to Abraham²⁴ considers molecules interacting through two-body square well potentials which in combination produce an effective square well for the entire cluster, and leads to similar conclusions.

Another example is the model suggested in Reference 25. Motivated by the reasonable agreement (though inadequate in detail) between the classical critical size and the values of \bar{N}_c^* deduced from Equation (18) it was suggested that the form $\epsilon^* = (1/2)\bar{N}_{c,cl}^* kT \ln S_v - D(T)$ was a possible expression for the critical cluster work of formation, with D a function of temperature only. Clearly the expression must fail for large $\ln S_v$ since ϵ^* should go to zero in this limit, but it could be a reasonable ansatz for smaller $\ln S_v$ and larger critical sizes. Using Equation (21) we derive

$$\begin{aligned} \frac{E_x^*}{kT} &= \frac{3}{2} N_{c,cl}^* \left(1 - \frac{T}{\sigma} \frac{d\sigma}{dT} \right) \ln S_v + T \frac{d(D/(kT))}{dT} \\ &= \frac{\sigma A_1}{kT} (N_{c,cl}^*)^{2/3} \left(1 - \frac{T}{\sigma} \frac{d\sigma}{dT} \right) + T \frac{d(D/(kT))}{dT}. \end{aligned} \quad (28)$$

This result is similar to that obtained from the square well cluster model examined in the previous paragraph. $D(T)$ could be fitted to nucleation rates and so a test of the model against the measured E_x^* is possible.

Finally, we examine the classical excess internal energy for a cluster of \bar{N}_c molecules:

$$E_{x,cl} = \left(\sigma - T \frac{d\sigma}{dT} \right) A_1 \bar{N}_c^{2/3}, \quad (29)$$

which is simply Equation (28) with $D=0$, and using \bar{N}_c instead of $N_{c,cl}^*$. As we found with F_x , we might expect this to be a reasonable first approximation to the cluster excess internal energy deduced from the second nucleation theorem. In Figure 7 the values of E_x^*/kT_0 from Figures 2–5 are once again plotted against \bar{N}_c^* . The curves correspond to Equation (29) for water, *n*-butanol and *n*-nonane. The figure is analogous to the comparison between F_x^*/kT_0 and the classically motivated expression $\sigma A_1 (\bar{N}_c^*)^{2/3}/kT_0$ in Figure 6. Each curve, which is slightly smoothed, illustrates the classical prediction $E_x \propto \bar{N}_c^{2/3}$. For *n*-butanol, the slope and magnitude of the classical curve are in reasonable agreement with the data. For water, the magnitude of the classical prediction is good, but the slope seems wrong. For *n*-nonane, the correlation is poorer still. In fact for all the datasets, including *n*-butanol, $E_x \propto \bar{N}_c$ seems a much better description. Such a fit goes through the origin, as it must.

It would therefore appear that for these substances and cluster sizes, the excess internal energy is, in continuum parlance, a volume effect rather than a surface effect. However, this is inappropriate terminology for clusters as small as this; a better conclusion is that the energies of the clustered molecules are affected more or less equally by the clustering, and so the excess internal energy is proportional to their

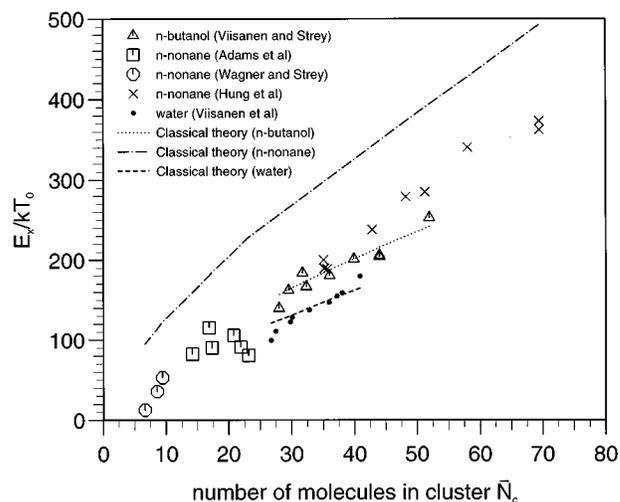


FIG. 7. The excess internal energies of water, *n*-butanol and *n*-nonane clusters against cluster size \bar{N}_c . The curves correspond to classical predictions for each substance, according to Equation (29).

number. The excess internal energies per molecule according to this description for water, *n*-butanol and *n*-nonane are about 0.096, 0.12 and 0.132 eV, respectively.

V. CONCLUSIONS

Droplet thermodynamics is usually developed using the Gibbs formalism,¹⁶ a basic assumption of which is that the cluster surrounded by vapour can be represented by continuum phases separated by a sharp interface which carries an excess free energy. This is a good approximation for large droplets, where the deviations from continuum properties are physically associated with the interfacial region. Results such as the Tolman equation for the radial dependence of the surface tension,¹⁵ and indeed classical nucleation theory, should hold in this limit.

For small critical clusters of only a few tens of molecules, the similarity between the real structure and notional bulk phases is weaker, and the deviations away from such a model are not spatially associated with the interface: for example the density even at the centre of the cluster can fail to reach the bulk condensed phase density. These difficulties in developing the thermodynamics of small clusters can be overcome if Hill's formalism is used.^{11,12} Instead of treating a single cluster surrounded by vapour, this approach considers an ensemble of such systems. Thermodynamic relationships are then derived in terms of the mean thermodynamic quantities over the ensemble of individual clusters.

Hill has proved that his approach is equivalent to the Gibbs treatment for large systems.¹¹ However, the formalism is really designed to describe small systems, and in particular to make contact with statistical mechanical models of clusters. An expression for the work of formation of a cluster, Equation (23), emerges easily from Hill's formalism. The excess Helmholtz free energy of the cluster is simply the difference between the actual free energy of the cluster, which could be derived from statistical mechanics or from

simulation, for example, and the free energy of the same number of molecules in a bulk condensed phase at the same temperature and pressure. It is not necessarily associated with the surface area, which suffers from difficulties of definition. The approach also provides thermodynamic relations which do not involve the ill-defined cluster volume.

The work of formation of the critical cluster is related to the nucleation rate, according to Equation (13), and so we can derive two nucleation theorems, Equations (18) and (21), by which the number of molecules in the critical cluster and its excess internal energy are given by derivatives of the nucleation rate with respect to supersaturation and temperature respectively. The first has been derived previously, using different methods, but the second appears to be new. The critical cluster excess Helmholtz free energy and entropy can also be obtained. Nucleation rate data therefore provide a rather complete thermodynamic characterisation of the small clusters of molecules controlling the process.

The excess internal energy, entropy and free energy at different temperatures and vapour supersaturations can be plotted against measured critical cluster size. These relationships are proposed as stringent tests of theoretical models of clusters. While it may be possible to construct a model which is consistent with the measured excess free energy, it may be more difficult to achieve the same for the measured excess internal energy and entropy separately. This is equivalent to requiring that the nucleation rate should have the observed dependence on temperature and supersaturation, but we have demonstrated that the correct behaviour is linked to the thermodynamic properties of the critical cluster.

In addition, in molecular dynamics or Monte Carlo simulations it is often easier to calculate the excess internal energy rather than the excess Helmholtz free energy. It would be straightforward to test a molecular cluster model by relating this quantity for a critical cluster to values obtained via Equation (27) from the experimental temperature dependence of the critical supersaturation.

Experimental nucleation rates for water, *n*-butanol and *n*-nonane have been analysed. The excess Helmholtz free energy of the critical cluster F_x^* is often quite well approximated by the classical excess free energy associated with the number of molecules in the cluster (compare F_x^* with $\sigma A_1(\bar{N}_c^*)^{2/3}$ in Figures 2–6), even for clusters as small as seven molecules. The classical excess free energy $F_{x,cl}^* = \sigma A_1(N_{c,cl}^*)^{2/3}$, associated with the classical critical size $N_{c,cl}^*$ is in most cases a much poorer representation. It would appear that the classical dependence of F_x^* on the number of molecules is a reasonable first order approximation but that additional terms in the excess free energy shift the critical size away from $N_{c,cl}^*$. These terms are often a feature of semi-empirical models of the droplet free energy.^{8–10} The differences between F_x^* and the classical expression ought to suggest the form that should be taken by these extra terms, although uncertainties in the data might make this difficult.

The excess internal energy of the critical clusters seems to show a linear dependence on the number of molecules, rather than the classical 2/3 power law, although in the case

of *n*-butanol both the classical and linear fits seem possible. It would appear that it is this failure of classical theory which underlies the poor temperature dependence of classical nucleation rates. The excess entropy, however, adds a contribution such that the excess free energy is well approximated by the classical behaviour, as we have seen.

Finally, the analysis of nucleation rate data to study the properties of small clusters is not restricted to vapour-gas systems: the nucleation of clusters growing on surfaces or within materials could also be addressed, as long as the process is controlled by a single critical cluster size, and that the kinetic prefactor can be estimated.

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APPENDIX

Equation (12) can also be proved using a Gibbs treatment of a critical cluster, and therefore the two nucleation theorems given in Section III can be derived from continuum arguments. This is in fact how Equation (18) was derived previously.¹⁴ However, the procedure involves some conceptual difficulties, largely due to the need to take account of the defining condition for the position of the dividing surface. The starting point is an expression for an incremental change in grand potential of the droplet plus vapour system.¹⁶

$$d\Omega = -p_l dV_l - p_v dV_v - SdT + \sigma dA + \left[\frac{\partial \sigma}{\partial a} \right] A da - Nd\mu, \quad (\text{A1})$$

in the notation used in the main text. This expression is formally valid for a system in thermodynamic equilibrium. The bar over N has been dropped since this is a continuum approach; a is the radius of the dividing surface; and the derivative in square brackets represents the change in σ caused by a change in the dividing surface condition. It is given by the generalised Laplace equation:

$$\left[\frac{\partial \sigma}{\partial a} \right] = p_l - p_v - \frac{2\sigma}{a}. \quad (\text{A2})$$

Now consider the change in Ω brought about by a change in temperature with an associated change in droplet volume with μ held constant:

$$\left(\frac{\partial \Omega}{\partial T} \right)_\mu = -(p_l - p_v) \left(\frac{\partial V_l}{\partial T} \right)_\mu - S + \sigma \left(\frac{\partial A}{\partial T} \right)_\mu + \left[\frac{\partial \sigma}{\partial a} \right] A \left(\frac{\partial a}{\partial T} \right)_\mu. \quad (\text{A3})$$

Most of the right hand side cancels using Equation (A2) and $dV_l = A da$, leaving

$$\left(\frac{\partial \Omega}{\partial T}\right)_{\mu} = -S. \quad (\text{A4})$$

Using a similar expression for the system without a droplet we find that

$$\left(\frac{\partial \Delta \Omega}{\partial T}\right)_{\mu} = \left(\frac{\partial \epsilon}{\partial T}\right)_{\mu} = -S + S_0 = -S_c. \quad (\text{A5})$$

Similarly,

$$\left(\frac{\partial \epsilon}{\partial \mu}\right)_T = -N + N_0 = -N_c, \quad (\text{A6})$$

and so with these last two results Equation (12) is proved. The nucleation theorems then follow by the same procedure as in Section III.

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