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The effects of temperature fluctuations in homogeneous nucleation theory

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Abstract. Classical homogeneous nucleation theory assumes a constant temperature for droplets of arbitrary size. However, the temperature of a droplet is bound to fluctuate due to both the release of latent heat upon absorption of further molecules, and the collisions with the surrounding gas molecules. We examine the effects of such fluctuations upon the nucleation rate and conclude that the corrections could be substantial, in contrast to the results of a previous study.

1. Introduction

Experimental methods for measuring the rate of homogeneous nucleation of liquid droplets from a vapour have been improving in recent years [1, 2] whilst theoretical ideas concerning the same process have been slow to develop. It has become increasingly apparent that theoretical predictions for the nucleation rate can disagree with the results of experiment by many orders of magnitude. This has led to an examination of the assumptions underlying each of the various theoretical approaches. The original approach of Volmer and Weber [3] and Becker and Döring [4] represents the nucleation process as a fluctuation phenomenon where small droplets, or clusters, overcome a Gibbs free energy barrier given by volume and surface terms. The droplets are characterised at all sizes by a density and a surface tension. This classical approach is thought to be a poor description of droplets consisting of 100 molecules or fewer, and more careful statistical mechanical treatments of such molecular clusters have been given by Lothe and Pound [5] and Reiss *et al* [6]. The essential difference provided by these approaches is to include translational and rotational terms in the free energy activation barrier. Unfortunately these treatments, which seem to rest upon a more secure theoretical foundation, do not give a better agreement with the experimental data, and have largely been discredited in favour of the classical approach. The situation is not satisfactory, however, since Becker-Döring theory still fails to account for the correct temperature dependence of the nucleation rate. The disagreement can amount to four orders of magnitude, for instance, for *n*-nonane (e.g. figure 1, adapted from [2]).

All of the current versions of nucleation theory assume the clusters have a constant temperature equal to that of the surrounding vapour. It has recently been suggested [7] that fluctuations in cluster temperature may have an important bearing on the nucleation rate. Physically, it is argued that a subcritical droplet which is cooler than average would be more likely to grow past the critical size since it has a reduced tendency to lose molecules by evaporation. Reference [7] indicates that considerable

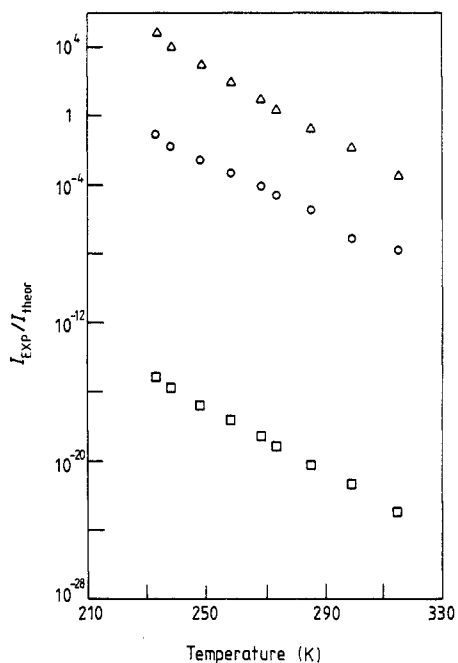


Figure 1. Comparison of experimental results I_{EXP} for the homogeneous nucleation of *n*-nonane with various theoretical predictions I_{theor} taken from [2]. Δ , classical; \circ , [6]; \square , [5].

temperature fluctuations are to be expected solely on the basis of the exchange of latent heat upon transfer of molecules between the droplet and the vapour. In this paper we have sought the consequences of these ideas within the framework of classical nucleation theory. It is shown in § 2 that the concept of nucleation by fluctuations in droplet size to overcome a Gibbs free energy barrier has to be replaced by a two-dimensional picture incorporating droplet temperature. The nucleation path lies over a saddle point on a surface of ‘availability’, which is a thermodynamic property of a droplet in a particular environment. A simple model of the nucleation process which incorporates the temperature fluctuation effect is given in § 3. The work is summarised in § 4, and contrasted with a previously published study of the phenomenon which suggested different conclusions from those reached here.

2. The availability surface and temperature fluctuations

The usual method of estimating the probability that a droplet of a certain size might appear as a fluctuation within a vapour is to evaluate the Gibbs free energy of formation. We use here a more general approach which considers the fluctuations of the droplet and its environment together, in terms of the ‘availability’ of the combined system. In particular, the approach allows for differences in temperature between the droplet and its surroundings.

The development given below is to be found in many textbooks (e.g. [8]), but is repeated for familiarity. Consider a large heat and particle reservoir with an internal energy E_0 , temperature T_0 , pressure p_0 , entropy S_0 , chemical potential μ_0 and particle

number N_0 . The intensive variables T_0 , p_0 and μ_0 are assumed not to vary. Within the reservoir, and able to exchange heat and mass with it, is a subsystem with thermodynamic variables E , T , p , S , μ and N . This is taken to be a liquid droplet lying within a vapour phase. The probability of occurrence of a particular set of values of the droplet variables is related to the total entropy of the whole system at those values. The equilibrium situation is that which maximises the total entropy, and the off-equilibrium variation of the entropy can tell us the likelihood of fluctuations.

Consider the change in total entropy S_{TOT} under a change in the droplet variables:

$$dS_{\text{TOT}} = dS_0 + dS. \quad (1)$$

The reservoir entropy change is given by

$$T_0 dS_0 = dE_0 + p_0 dV_0 - \mu_0 dN_0. \quad (2)$$

Allowing for the conservation of internal energy, volume and particle number of the whole system, we can write

$$\begin{aligned} T_0 dS_{\text{TOT}} &= -dE - p_0 dV + \mu_0 dN - \sigma dA + T_0 dS \\ &= -d\psi \end{aligned} \quad (3)$$

where σ is the surface tension of the liquid (assumed constant), and dA the change in surface area of the drop. The availability ψ is given by

$$\psi = E + p_0 V - \mu_0 N + \sigma A - T_0 S. \quad (4)$$

The probability that the whole system should be found in a state characterised by a droplet variable given generically by x is therefore

$$P(x) \propto \exp\left(\frac{S_{\text{TOT}}(x)}{k}\right) \propto \exp\left(-\frac{\psi(x)}{kT_0}\right) \quad (5)$$

where k is Boltzmann's constant.

The availability minima correspond to the state where no droplet has formed, and the state containing a droplet of infinite radius. An unstable equilibrium exists at a point between the two corresponding to a critical radius a^* . The critical availability is equal to $\frac{4}{3}\pi\sigma a^{*2}$. We now show that, if T is constrained to be equal to T_0 for all size droplets, the classical expression for the nucleation barrier is obtained.

From (4) and a thermodynamic identity for μ we obtain the availability for $T = T_0$ as

$$\psi_T = (\mu - \mu_0)N - (p - p_0)V + \sigma A. \quad (6)$$

The chemical potentials are functions of the temperature and the local pressures and must be related to each other at a reference pressure in order to proceed. The Gibbs-Duhem relation in the absence of temperature change, $V dp = N d\mu$, gives for the vapour phase (assuming ideal gas properties):

$$\mu_0(p_0) - \mu_0(p_\infty) = kT_0 \ln p_0/p_\infty \quad (7)$$

and for the droplet, assuming it to be incompressible, we have

$$\mu(p) - \mu(p_\infty) = v_m(p - p_\infty) \quad (8)$$

where p_∞ is the reference pressure and v_m the volume of droplet per molecule. Thus

$$\psi_T = (p_0 - p_\infty)V + \sigma A - NkT_0 \ln p_0/p_\infty. \quad (9)$$

For very large droplets, or for a planar surface, A is a constant, and for equilibrium with respect to changes in V :

$$\partial\psi_T/\partial V = p_0 - p_\infty = 0 \quad (10)$$

i.e. p_∞ is the equilibrium pressure of the vapour above a planar surface. The ratio p_0/p_∞ is therefore the supersaturation ratio S_p . The availability for $T = T_0$ can now be written

$$\psi_T = p_0(1 - S_p^{-1})V - NkT_0 \ln S_p + \sigma A \quad (11)$$

$$\approx \sigma A - NkT_0 \ln S_p \quad (12)$$

which is the usual form for the barrier potential. This expression is also obtained if the reservoir contains a mixture of vapour and an inert carrier gas.

We have introduced the availability formalism into the discussion in order to examine the likely temperature fluctuations of a droplet. This we do, finally, by expanding (5) about $T = T_0$:

$$P(T) \propto \exp\left(-\frac{\psi(T_0)}{kT_0}\right) \exp\left[-\frac{(T - T_0)^2}{2kT_0} \left(\frac{\partial^2\psi(T_0)}{\partial T^2}\right)_{v,N}\right]. \quad (13)$$

The expected temperature fluctuation is therefore

$$\Delta T = \left(kT_0 \left(\frac{\partial^2\psi(T_0)}{\partial T^2}\right)_{v,N}^{-1}\right)^{1/2} \quad (14)$$

and

$$\begin{aligned} \left(\frac{\partial^2\psi}{\partial T^2}\right)_{v,N} &= \frac{\partial}{\partial T} \left[\left(\frac{\partial E}{\partial T}\right)_{v,N} - T_0 \left(\frac{\partial S}{\partial T}\right)_{v,N} \right] \\ &= \frac{\partial}{\partial T} [(1 - T_0/T)C_v] = \frac{C_v}{T_0} \end{aligned} \quad (15)$$

so that

$$\Delta T = T_0 \left(\frac{k}{C_v}\right)^{1/2} \quad (16)$$

where C_v is the heat capacity of the droplet at constant volume. For water at room temperature, the maximum of (12) occurs for $S_p \approx 4$ at a cluster size of the order of 100 molecules, and (16) predicts a typical temperature fluctuation of about 10 °C for such a droplet. On a purely combinatoric basis, therefore, a droplet of critical radius a^* at temperature T_0 is clearly not the only state of the system which can conceivably lead to nucleation: a range of temperature is possible without a vanishingly small probability. Figure 2 shows the new situation as an extension into two dimensions of the usual one-dimensional nucleation barrier. Critical states which lead to nucleation lie along the col at the critical size. The usual approach is to assume that the heat

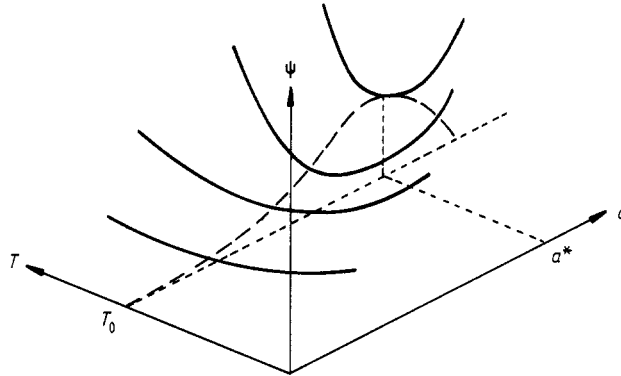


Figure 2. Availability surface as a function of droplet temperature T and radius a . The vapour temperature T_0 and the critical radius a^* are shown. The classical path to nucleation is shown as a broken curve.

capacity of a droplet is infinite so that the rise in availability away from $T = T_0$ at the critical radius is infinitely steep.

3. The kinetics of droplet growth and temperature fluctuation

The arguments in the previous section showed that the probability for occurrence of a droplet within a vapour-filled reservoir was a function of its temperature as well as its size. The probability was assessed purely by a combinatoric evaluation of possible microstates corresponding to a particular macrostate and we did not consider the processes by which the macrostates might appear. The kinetics of fluctuation of droplet size and temperature are dealt with here within a simple model.

The processes which cause the fluctuations are collisions between the droplet and vapour molecules (or molecules of any inert carrier gas present), and capture or release of vapour molecules by the droplet. The timescales for both events are long compared with the interaction time between molecules already in the droplet, so we can assume the droplet temperature to be well defined, but suffering almost instantaneous jumps due to collisions and molecular capture/loss. The temperature fluctuations to be expected for a collision without capture between the droplet and a vapour (or carrier gas) molecule is about $T_0(k/C_v)$ whilst for a vapour molecule capture (condensation) the fluctuation is about L_1/C_v , where L_1 is the molecular latent heat of vaporisation. For water droplets at room temperature these fluctuations are about 0.3 and 5 K, respectively, for a 100 molecule cluster. Collision-type fluctuations occur more rapidly than condensation/evaporation fluctuations, unless there is no carrier gas and the sticking probability is large. We take the view that, within each size range, the fluctuation processes described above produce a range of droplet temperatures which can be described by a Gaussian distribution. Later on, we shall use (16) to describe the width of this distribution. This means that we shall take the cluster populations to have an equilibrium distribution in temperature, in contrast to their distribution in size. This assumption immediately leads to an expression for the nucleation rate by the traditional methods. The coupling between temperature and size fluctuations via evaporation/condensation processes is ignored, leading to the replacement of the difficult two-dimensional kinetic equations by effective one-dimensional expressions.

If the collision timescale is much greater than the capture timescale this should not matter. We are thus describing a limiting case which we discuss further in § 4.

We write the nucleation rate of droplets per unit volume of vapour as

$$I = \int \beta A_n C_n(T_n) dT_n - \int \alpha_{n+1}(T_{n+1}) A_{n+1} C_{n+1}(T_{n+1}) dT_{n+1} \quad (17)$$

where C_n is the volume concentration of clusters of n molecules, assumed to have a distribution in temperature T_n :

$$C_n(T_n) = c_n \frac{1}{(2\pi)^{1/2} \sigma_T} \exp\left(-\frac{(T_n - T_0)^2}{2\sigma_T^2}\right) \quad (18)$$

where c_n are the total concentrations of clusters of size n at any temperature and σ_T is the dispersion in temperature. A_n is the surface area of a droplet of size n . The flux of molecules which hit the surface of a droplet and stick is given by

$$\beta(T_0) = \frac{p_0 q}{(2\pi m k T_0)^{1/2}} \quad (19)$$

where q is the sticking probability and m the vapour molecular mass. The evaporative flux is given by

$$\alpha_n(T_n) = \beta(T_n) \frac{p_{ve}(T_n)}{p_0} \exp\left(\frac{2\sigma v_m}{ak T_n}\right) \quad (20)$$

where p_{ve} is the equilibrium partial pressure of vapour above a plane surface of liquid, v_m is the droplet volume per molecule and a is the radius of the cluster of size n . The evaporation flux has this form so that the evaporative and condensative fluxes are equal for a critical size droplet with temperature T_0 , i.e. $\alpha_{n^*}(T_0) = \beta(T_0)$. This makes use of Kelvin's law, which is a consequence of the classical free energy barrier (12). If it is assumed that the molecular loss rate from a droplet depends only on the internal droplet properties, then (20) must hold for sizes and temperatures away from a^* and T_0 . The justification of (20) is important since it lies at the heart of our subsequent development of the model.

We first perform the temperature integrals in (17). The temperature dependence of the equilibrium vapour pressure is written

$$p_{ve} \propto \exp(-K/T) \quad (21)$$

where K is given by L_1/k according to the Clausius-Clapeyron equation ($K \approx 5000$ K for water). The evaporative contribution to I can be written as

$$- \int \alpha_{n+1} A_{n+1} C_{n+1} dT_{n+1} = -\alpha_{n+1}(T_0) A_{n+1} c_{n+1} [1 + B_{n+1}(\sigma_T, K', T_0)] \quad (22)$$

where the correction term B_{n+1} is given by

$$\begin{aligned} & \frac{1}{(2\pi)^{1/2} \sigma_T} \int_{-\infty}^{\infty} \exp\left(-\frac{K'}{T} - \frac{(T - T_0)^2}{2\sigma_T^2}\right) \frac{1}{T^{1/2}} dT \\ & = \frac{1}{T_0^{1/2}} \exp\left(-\frac{K'}{T_0}\right) [1 + B_{n+1}(\sigma_T, K', T_0)] \end{aligned} \quad (23)$$

and

$$K' = K - 2\sigma v_m / ak = K - R / n^{1/3} \tag{24}$$

with $R = 1642$ for water.

Expanding the factors depending on T^{-1} in the integrand to order $(T - T_0)^2$, we obtain

$$1 + B_{n+1}(K', \sigma_T, T_0) = \frac{1}{[1 + 2\sigma_T^2(K'/T_0 - \frac{1}{4})/T_0^2]^{1/2}} \times \exp\left(\frac{\sigma_T^2(K'/T_0 - \frac{1}{2})^2}{2T_0^2[1 + 2\sigma_T^2(K'/T_0 - \frac{1}{4})/T_0^2]}\right). \tag{25}$$

The first approximation for B_{n+1} from expanding the exponential is

$$B_{n+1}(K', \sigma_T, T_0) \approx K'^2 \sigma_T^2 / 2T_0^4 \tag{26}$$

which is reasonably accurate for the water vapour at room temperature data ($B_{n+1} \approx \frac{1}{6}$).

Consider a steady state nucleation current given by

$$\begin{aligned} I &= \xi_1 c_1 - \gamma_2 c_2 \\ &= \xi_2 c_2 - \gamma_3 c_3 \\ &= \xi_{n_m-1} c_{n_m-1} - \gamma_{n_m} c_{n_m} \end{aligned} \tag{27}$$

where

$$\xi_n = \beta A_n \quad \gamma_n = \alpha_n A_n (1 + B_n). \tag{28}$$

We follow closely the procedure given in [9]. Droplets with size up to n_m are considered in these kinetic equations, well above the critical size. A repeated process of elimination yields

$$I \left(1 + \sum_{n=2}^{n_m-1} \prod_{j=2}^n \frac{\gamma_j}{\xi_j} \right) = \xi_1 c_1 - \gamma_{n_m} \prod_{j=2}^{n_m-1} \frac{\gamma_j}{\xi_j} c_{n_m} \tag{29}$$

which is well approximated by

$$I \approx \xi_1 c_1 \left(\sum_{n=2}^{n_m-1} \prod_{j=2}^n \frac{\gamma_j}{\xi_j} \right)^{-1}. \tag{30}$$

Now

$$\ln \left(\prod_{j=2}^n \frac{\gamma_j}{\xi_j} \right) = \ln \left[\prod_{j=2}^n S_p^{-1} \exp \left(\frac{2\sigma v_m}{akT_0} \right) (1 + B_j) \right] \tag{31}$$

where $S_p = p_0/p_{ve}(T_0)$ is the supersaturation ratio of the vapour. This can be reduced to a more familiar form by substituting for a in terms of n :

$$\begin{aligned} \ln \left(\prod_{j=2}^n \frac{\gamma_j}{\xi_j} \right) &\approx -(n-1) \ln S_p + \frac{2\sigma v_m}{kT_0} \left(\frac{4\pi}{3v_m} \right)^{1/3} \int_2^n \frac{dn}{n^{1/3}} + \sum_{j=2}^n \ln(1 + B_j) \\ &= -(n-1) \ln S_p + \sigma A_n / kT_0 + \eta_n \end{aligned} \tag{32}$$

where η_n is the correction term arising from the temperature fluctuations:

$$\eta_n = \sum_{j=2}^n \ln(1 + B_j). \tag{33}$$

Thus

$$I = \xi_1 c_1 \left[\sum_{n=2}^{n_m-1} \exp\left(\frac{G_n + kT_0 \eta_n}{kT_0}\right) \right]^{-1} \quad (34)$$

where $G_n = \sigma A_n - (n-1)kT_0 \ln S_p$ is the classical Gibbs free energy of a droplet of size n . We replace the sum by an integral, expand G_n about its maximum at n^* and produce

$$I \approx \xi_1 c_1 Z \exp(-\eta^* - G^*/kT_0) \quad (35)$$

where $\eta^* = \eta_{n^*}$ and $G^* = G_{n^*}$. Z is the Zeldovich factor given by

$$Z = \left(-\frac{1}{2\pi kT_0} \frac{\partial^2 G_n}{\partial n^2} \Big|_{n^*} \right)^{1/2} = \frac{(\ln S)^2}{8\pi v_m} \left(\frac{kT_0}{\sigma} \right)^{3/2}. \quad (36)$$

A more accurate treatment would involve absorbing $\eta_n kT_0$ into G_n before finding the maximum but this we have not done, so as to demonstrate explicitly how the temperature fluctuation term corrects the classical result, which is obtained by setting $\eta^* = 0$ in (35). As we shall see shortly, η_n depends logarithmically on n , compared with the power terms in G_n , so this should not matter much.

The critical size is

$$n^* = \left(\frac{3v_m}{4\pi} \right)^2 \left(\frac{8\pi\sigma}{3kT_0 \ln S_p} \right)^3 \quad (37)$$

so that

$$G^* = \frac{16\pi\sigma^3 v_m^2}{3(kT_0 \ln S_p)^2}. \quad (38)$$

Let us consider the qualitative dependence of (35) upon temperature T_0 . It is well known that the expression for I without the correction factor increases too quickly with temperature to account for the experimental data. Better results would be obtained if η^* increased with T_0 .

Using (25) and (33) we write

$$\eta^* = \int_2^{n^*} \left(\frac{\sigma_T^2 (K'/T_0 - \frac{1}{2})^2}{2T_0^2 [1 + 2\sigma_T^2 (K'/T_0 - \frac{1}{4})/T_0^2]} - \frac{1}{2} \ln [1 + 2\sigma_T^2 (K'/T_0 - \frac{1}{4})/T_0^2] \right) dn. \quad (39)$$

For small σ_T and replacing K' by K , this becomes approximately

$$\begin{aligned} \eta^* &\approx \int_2^{n^*} \frac{\sigma_T^2 K^2}{2T_0^4} dn \\ &= \frac{K^2 k}{2T_0^2 c_v m} \ln(n^*/2) \end{aligned} \quad (40)$$

where we have used (16) for σ_T with $C_v = nmc_v$ to evaluate the integral, c_v being the specific heat at constant volume of the liquid and m the molecular mass.

Using data appropriate to a 100 molecule critical cluster of water at room temperature, this expression produces an estimate $\eta^* \sim 60$. The correction factor to the isothermal nucleation rate is of the order of 10^{-26} ! This calculation can serve only as an indication of the magnitude of η^* since we have neglected a number of terms in (39) which can become important for small n . The assumed proportionality of C_v to n for small clusters, even for $n=2$, is also likely to introduce inaccuracies. Better

expressions for η^* may be found but let us first examine (40) more closely. The result is disappointing in that η^* falls with increasing T_0 . Thus, although the nucleation rate I contains a factor which changes by orders of magnitude under small temperature variations, this change is *opposite* to what is required to provide a closer description of the temperature dependence of experimental results, e.g. in figure 1. Thus not only does our model, as it stands, hugely suppress the classical nucleation rate, it does not provide a better qualitative behaviour under temperature change. This observation does not seem to depend upon the approximations used to estimate η^* : a slightly more careful calculation starting from the first term in the integrand of (39), but still putting $K' = K$, gives the result

$$\eta^* \approx \frac{K^2 k}{2c_v m T_0^2} \ln \left(\frac{n^*}{2[1 + kK/(c_v T_0 m)]} \right) \quad (41)$$

which still decreases with T_0 . In the next section we discuss the significance of these results.

4. Discussion

The model we have described here is a natural extension of classical Becker-Döring homogeneous nucleation theory, allowing for the effects of temperature variation within populations of subcritical droplets. According to an analysis of the availability of a reservoir-droplet system, appreciable fluctuations in droplet temperature are possible. If these fluctuations are fully realised, then the effect upon the theoretical prediction for the nucleation rate can be a suppression by many orders of magnitude.

These conclusions are not in accord with a previous study of non-isothermal homogeneous nucleation theory by Feder *et al* [10] which concluded that the isothermal nucleation rate was altered by a factor approximately equal to

$$\frac{b^2}{b^2 + L_1^2} \quad (42)$$

where b is the dispersion in energy of monomers of vapour impinging onto the surface of a droplet and L_1 is the molecular latent heat of vaporisation. This factor cannot be made to deviate very far from unity and it was concluded that the effects of temperature fluctuation are minimal. We have to determine why this approach differs in its conclusions so much from ours.

The essential difference between the approaches lies in the evaluation of the expression for the nucleation rate given in (17). The authors of [10] eliminate the evaporative term in favour of a growth term by reference to an equilibrium size concentration $C_n^0(T)$. In our notation the procedure would amount to using

$$\beta A_n C_n^0(T_n) = \alpha_{n+1}(T_n + L_1/c_v m) A_{n+1} C_{n+1}^0(T_n + L_1/c_v m) \quad (43)$$

which is a detailed balance condition. The kinetic equations can then be formulated as a two-dimensional diffusion equation in size and temperature and the nucleation current can be easily found. This approach is a straightforward extension of the procedure used for the one-dimensional case.

By contrast, in our approach we make no reference to an equilibrium cluster distribution in size and simply make direct use of the evaporation rate given in (20). As [9] and our work here shows, such a direct approach will, in one dimension,

reproduce the standard results based on an equilibrium concentration and the diffusion equation. It has been generally recognised [11] that the equilibrium distribution presents some technical problems in its evaluation. It is usually taken to be proportional to $\exp(-G_n/kT_0)$ and neglected for $n \geq n^*$. For the non-isothermal case the correct approach would be the availability method with the equilibrium distribution proportional to the RHS of (13). This, however, still presents problems in evaluating a nucleation rate, since the detailed balance condition embodied in (43) may be invalidated by currents with vortices in (n, T) space. The discussion in [9] showed that it is an unnecessary device, however, for the solution of the one-dimensional case. We consider it preferable to avoid its use.

The real root of the disparity between our results and those of [10] lies in our choice of the nucleation path. The mean temperature of all droplet size populations is T_0 , whilst in [10] the mean temperature increases with size as a consequence of the explicit inclusion of latent heat transfer in (43). The passage of the nucleation current through subcritical regions at a warmer temperature, in our model where the evaporation rate is greater, provides the suppression. We believe, however, our model represents a real physical situation, examined in more detail below, which is missed by the approach of [10] with its reliance on the equilibrium distribution and (43).

The main result of our work is that there is scope for a substantial effect due to droplet temperature fluctuation in nucleation theory. The nucleation rate suppression factor we have obtained is rather large (although not extraordinarily large for this field) and has an undesirable dependence on temperature if it is to be applied as a correction to the classical Becker-Döring expression. It has been evaluated using macroscopic parameters, such as the surface tension and heat capacity, even for very small molecular clusters. But a more important limitation is that conductive heat transfer has been assumed to dominate over condensative transfer (to ensure an equilibrium droplet temperature distribution within each size range) and this limits the theory to conditions characterised by

$$Cn_k \gg 1 \quad (44)$$

where Cn_k is the kinetic condensation number (a ratio of conductive to condensative heat transfers) [12], defined in the appendix. At 1 °C this quantity lies between unity and about 25 for water vapour in air at one atmosphere pressure, but falls rapidly with increasing temperature. It should be possible, however, to choose experimental conditions for which the theory described in this paper ought to be a good description. At the very least one ought to be able to observe a crossover between this theory and another, applicable to values of Cn_k of about unity, which would be manifested in a dependence of the nucleation rate upon the carrier gas pressure. As Cn_k is temperature dependent, a similar crossover might be observed as the vapour temperature is changed.

There are several directions in which to develop this work. Firstly, one should re-examine Lothe-Pound theory and similar statistical mechanical approaches [6, 13] in the light of the above discussion. A suppression of the nucleation rate would be most welcome in these cases as they generally overestimate the experimental results. Secondly, one should relax the condition on Cn_k and examine the effects of an off-equilibrium temperature distribution at each droplet size. This would tend to cool the distributions in the subcritical size range and would reduce the suppression of the nucleation rate. It is tempting to speculate that, in the small Cn_k limit, the result of Feder *et al* is reached, and that many physical situations correspond to a description somewhere between the two extremes.

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Appendix

We define here the kinetic condensation number which is the ratio of heat transfer by conduction to that for condensation for very small droplets. It is

$$Cn_k(T_0, S_p) = \frac{HT_0}{qm\beta(T_0)L_m(K/T_0 - S_p/2)} \quad (\text{A1})$$

where

$$H = \alpha_g c_{bg} m_g \beta_g(T_0) + \alpha_v c_{bv} S_p m \beta(T_0) \quad (\text{A2})$$

$$L_m = L(T) - kT/2m \quad (\text{A3})$$

$$c_{bv} = c_{vv} + k/2m \quad (\text{A4})$$

$$c_{bg} = c_{vg} + k/2m_g \quad (\text{A5})$$

and

$$\beta_g(T_0) = p_g / (2\pi m_g k T_0)^{1/2}. \quad (\text{A6})$$

In these equations we have generalised the heat transfer to include the effects of carrier gas molecules, denoted by the subscript g. Most of the parameters have been defined in the main text. Additional ones are α_g and α_v , the accommodation coefficients for the carrier gas and vapour respectively, and c_{vv} and c_{vg} which are specific heat capacities at constant volume for the vapour and gas. L is the specific latent heat of vaporisation, p_g the carrier gas partial pressure, m_g the mass of a gas molecule, q the sticking probability, S_p the supersaturation and K a parameter in p_{ve} (21).

In order to achieve a high value of Cn_k one should use a substance with a low sticking probability, or greatly dilute the condensible vapour with a carrier gas. For pure n -nonane at 273 K and $S_p = 4$ we have

$$Cn_k \approx 0.25\alpha_v/q \quad (\text{A7})$$

so it seems that the experimental results of [1] are outside the range of the model described in the main text unless q is very small. An experiment conducted at 0 °C with n -nonane in a mixture with air at atmospheric pressure would have a value of Cn_k in the region of 10 even with a sticking probability and gas accommodation coefficient of one. A number of interesting experimental effects are possible, since for a pure vapour, Cn_k rises slowly with temperature, whilst for a vapour-gas mixture it falls quickly. This leads us to speculate that the data in figure 1 may be understood via an increasing suppression of the classical result as T_0 and Cn_k rise.

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