Equilibrium and steady-state distributions of vapour clusters in nucleation theory

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Abstract. The relationship between equilibrium properties in nucleation theory and cluster partition functions is explored. A new approach to relating the partition function for a cluster with boundaries fixed in space to that required in nucleation theory, which includes arrangements omitted by other approaches, is described. Fluctuations about equilibrium in cluster size and energy are discussed. The usual way of obtaining the steady-state nucleation rate does not take account of possible differences in cluster energy distributions between equilibrium and steady state. A Fokker–Planck equation for the cluster distribution in size and energy is derived and an analytical approach to obtaining the steady nucleation flux from it is presented. In cases where the vapour molecule's latent heat of vaporization is much greater than its heat capacity, this approach gives the same values as those predicted by a simpler analytical formula derived previously. In other cases, the simpler formula underestimates the flux, although only by modest factors. Extensions of this treatment are discussed.

1. Introduction

The theoretical study of homogeneous nucleation of liquid droplets from vapour has a long history, dating back to the development of the classical theory by Becker and Döring [1], Frenkel [2], and Zeldovich [3], and the literature includes a book by Abraham [4] and two volumes edited by Zettlemoyer [5, 6]. However, a recent review by Oxtoby [7] has highlighted the fact that a complete understanding of all the experimental results is still lacking.

Most nucleation theories assume that a vapour contains groups or 'clusters' of different numbers of molecules. In the classical theory, the equilibrium concentration of vapour clusters containing i molecules is given by

$$c^{eq}(i) = \frac{n_1}{V} \exp\left(\frac{-1}{kT}[i^{2/3}A_1\gamma - ikT\ln S]\right) \tag{1}$$

where n_1/V is the monomer concentration, γ is the liquid surface tension, S is the vapour saturation, and A_1 is the monomer surface area (assuming spherical monomers with volume $v_1 = m_v/\rho_1$, where m_v is the molecule mass and ρ_1 is the liquid density). For $S > 1$, equation (1) has a minimum at the critical cluster size i^*, is given by,

$$i^* = \left(\frac{2A_1\gamma}{3kT\ln S}\right)^3. \tag{2}$$

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Table 1. Various dimensionless parameters for water at 293 K and nonane at 273 K. The thermophysical data are taken from [25] and [26].

Parameter	Water	Nonane
S	4	50
$\gamma A_1/kT$	8.4	13.9
i^*	65.9	13.3
σ_i	11.9	3.2
c_1/k	9.06	34.2
σ_E/kT	24.4	21.3
m_vL/kT	18.14	16.3
c_{vv}/k	3.07	22.7
$(\gamma - Td\gamma/dT)A_1/kT$	13.5	28.1
H/kT	11.8	−15.3
$J_Z/\beta(i^*)c^{eq}(i^*)$	0.033	0.12
J_{ss}/J_Z (equation (43))	0.0151	0.396
J_{ss}/J_Z (equation (44))	0.0151	0.275

Table 1 gives typical values of $A_1\gamma/kT$ and i^* for water and nonane, two liquids that have been studied extensively experimentally. The other parameters in table 1 will be discussed in due course.

The inadequacies of the classical liquid droplet model are well known [7] and much effort has been directed at obtaining an improved characterization of vapour clusters. However, this paper is mainly concerned with two other aspects of nucleation theory. First, consideration is given to how the equilibrium distribution is obtained once a correct characterization of a cluster is available, and secondly, how the steady state nucleation rate can be obtained from this equilibrium distribution. Although the classical liquid droplet model is used to obtain numerical results, the development can be applied to any other cluster model.

In section 2, it is shown how the equilibrium distribution is related to the cluster partition function. The treatment is similar to that of Reiss *et al* [8], and like them, the relationship between the partition function for a cluster stationary in the laboratory and that for a cluster that can be anywhere in the container volume is considered. Section 3 is concerned with fluctuations of cluster properties about their mean values in equilibrium, as a preliminary to considering steady-state distributions in sections 4 to 7. In section 4, the usual way of obtaining the nucleation flux is reviewed and it is pointed out why it is inadequate. Section 5 is concerned with the derivation of a Fokker–Planck equation for the steady-state concentration in size and energy. This section expands on the approach of Feder *et al* [9]. In section 6, a procedure developed by Langer [10] is applied to obtain the steady flux from this Fokker–Planck equation, and in section 7 values for the flux from this procedure are compared with more accurate numerical values obtained previously [11], as well as with the simpler formula derived in [9]. In the concluding section, the results of this study are summarized and some suggestions given for further work.

2. Equilibrium cluster distributions

The law of mass action relates the equilibrium concentration of clusters containing i molecules (hereafter called i-clusters for brevity) to the number of monomers in the volume V:

$$c^{eq}(i) = \left(\frac{n_1}{q_1}\right)^i \frac{q_i}{V} \tag{3}$$

where $q_1 = V/\Lambda^3$ is the partition function for a monomer in a volume V and q_i is the partition function for an i-cluster, given by

$$q_i = \frac{1}{i!\Lambda^{3i}} \int \exp[-U(r_1, r_2, \ldots, r_i)/kT] \, dr_1 \ldots dr_i \tag{4}$$

with $\Lambda = (h^2/2\pi m_v kT)^{1/2}$. Equation (3) can be derived by either a canonical [8] or grand canonical [12] approach.

The free energy, F_i, is defined by

$$F_i = -kT \ln q_i. \tag{5}$$

For $S > 1$, $c^{\text{eq}}(i)$ has a minimum at $i = i^*$ and, from equation (3)

$$\left. \frac{dF_i}{di} \right|_{i=i^*} = \mu_1^{\text{eq}} + kT \ln S = \mu_1 \tag{6}$$

where $\mu_1^{\text{eq}} = kT \ln(n_1^{\text{sat}}/q_1)$ is the chemical potential of the vapour at equilibrium, n_1^{sat} being the number of monomers at saturation. Equation (6) shows that the chemical potential of the critical cluster, μ_1, is equal to that of the vapour with which it is in (unstable) equilibrium. Note incidentally that the chemical potential of the molecules in a cluster is larger than in the bulk liquid. In the classical liquid droplet model this can be understood in terms of the very high pressure inside the cluster. The internal pressure p_{int} is related to the external pressure p by Laplace's equation:

$$p_{\text{int}} - p = \frac{2\gamma}{R} \tag{7}$$

where R is the cluster radius, equal to $(3m_v i/4\pi\rho_1)^{1/3}$ in the liquid drop model. Although it is usual to assume that liquid-like clusters are incompressible, typical pressure differences $p_{\text{int}} - p$ from (7) are about 10^8 N/m^2. Since liquid compressibilities are of the order of 10^{-9} m^3/J, the fractional volume decrease can exceed 10%.

Returning now to the law of mass action, equation (3), it is pointed out that, since q_i is proportional to Λ^{-3i} and q_1 is proportional to Λ^{-3}, n_i is independent of Λ, or of Planck's constant, h. This is not surprising—by writing the classical partition function (involving integrals over co-ordinates instead of sums over states), all quantum effects have been ignored and h just appears as a scaling parameter which cannot give rise to any measurable effects. However, some nucleation formulae based on classical statistical mechanics appear to include a dependence on h. This is true of the earliest expositions of the Lothe–Pound theory [14, 9], although in their later papers [5, 6, 15] the h-dependence disappears due to the assumed form of the replacement term. The recent result derived by Huang and Seinfeld [16], based on the cell theory of liquids, also includes an h-dependence. It would appear that some modification of their treatment is needed to remove this.

Introducing the monomer and cluster free energies (see equation (5)) and the saturation $S = n_1/n_1^{\text{sat}}$ into (3) gives the equilibrium cluster concentration as

$$c^{\text{eq}}(i) = \frac{Sn_1^{\text{sat}}}{V} \exp\left(\frac{-1}{kT}([F_i - iF_1 - (i-1)kT \ln n_1^{\text{sat}}] - (i-1)kT \ln S) \right). \tag{8}$$

Equation (8) predicts that $c^{\text{eq}}(i)$ is proportional to S^i, in contrast to the classical result, equation (1), which predicts $c^{\text{eq}}(i)$ is proportional to S^{i+1}. It is now widely accepted [7] that the saturation dependence in (8) is correct.

Finally in this section, the range of integration over the molecular coordinates r_j in the cluster partition function, equation (4) is discussed. The question of cluster definition has been considered recently in papers by Reiss and co-workers [17, 18]. We shall follow these authors in assuming that molecules in a cluster move within a spherical shell of radius R and volume $v_c = iv_0$, where v_0 is the molecular volume in the cluster. The partition function for such a cluster with boundaries fixed in the laboratory frame, denoted by q_i^{lab}, is given by

$$q_i^{lab} = \frac{1}{i!\Lambda^{3i}} \int_0^R r_1^2 \, dr_1 \int_{-1}^1 d(\cos\theta_1) \int_0^{2\pi} d\phi_1 \int_0^R r_2^2 \, dr_2 \int_{-1}^1 d(\cos\theta_2) \int_0^{2\pi} d\phi_2 \ldots$$

$$\times \int_0^R r_i^2 \, dr_i \int_{-1}^1 d(\cos\theta_i) \int_0^{2\pi} d\phi_i \exp(-U(r_1, r_2, \ldots, r_i)/kT) \quad (9)$$

where the polar coordinates (r_j, θ_j, ϕ_j) of the vectors r_j have been introduced. Now, q_i^{lab} is independent of system volume V whereas q_i must be proportional to V. Equation (9) cannot simply be multiplied by V to give q_i since q_i^{lab} already involves integrations over all $3i$ molecular coordinates. One alternative is to follow Abraham (Chapter 5 of [4]) and consider a cluster centred on a monomer, labelled 1 in figure 1(a). This monomer is free to move throughout the container volume, but the remaining $(i - 1)$ monomers must lie within a distance R of it. However, this approach does not count all the arrangements which do not have a monomer at their centre (that they do count *some* such arrangements is illustrated in figure 1(a): the arrangement shown can be viewed either as being centred on a monomer (solid circle) or on empty space (dashed circle)). Also, the integrations do not include all arrangements with a monomer other than that labelled 1 at the centre. Note that monomers should be treated as being distinct when evaluating the integrals in q_i, the factor $1/i!$ before the integrals accounts for their actual indistinguishability.
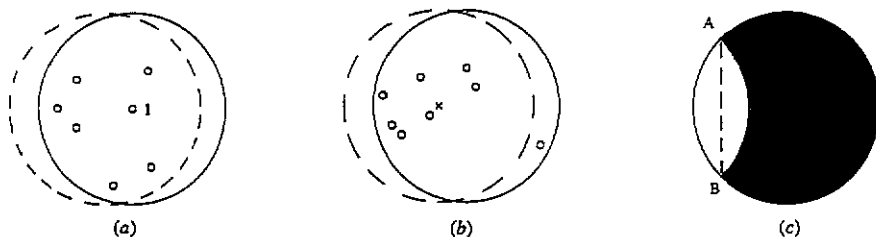

Figure 1. (a) Cluster defined as centred on a molecule. (b) Cluster defined as centred on the centre of mass. (c) Geometric shape used to define cluster containing three molecules.

Reiss and co-workers [17, 18] have argued that a cluster can be defined unambiguously as being centred on the centre of mass of the molecules it contains. The centre of mass (position vector $\bar{r}$) is allowed to move throughout the container volume to give q_i. However, this procedure also omits some arrangements, as illustrated in figure 1(b). The arrangement shown (within the fixed boundary shown as a solid circle) has its centre of mass at X. However, the dashed circle, radius R, centred on X does not include all the molecules in the cluster. Therefore this arrangement is never counted in the Reiss approach. Although diffuse arrangements such as the one shown are likely to have a larger potential energy than arrangements that are included, and therefore yield only a small contribution to the partition function, it would be more satisfactory to include them. We now discuss how this can be

done for a perfect gas cluster (or, more generally, for a cluster model where the interaction potential is independent of molecular positions).

Consider first the case of three molecules lying within a spherical shell of radius R. Molecule 1 (at A, say) can be anywhere in the container volume, however, molecule 2 (at B) must be within a distance $2R$ of A if it is to lie in the shell. Finally, molecule 3 (at C) must lie within the solid of revolution formed by rotating the part of the disc in figure 1(c) to the right of AB about the line AB. Let this volume be $V_1(r)$ and let the volume formed by rotating the part of the disc to the left of AB about AB be $V_2(r)$, where r is the length of AB. The volume $(V_1(r) - V_2(r))$, formed by rotating the shaded part of the disc in figure 1(c) about AB, will be referred to as the 'shaded volume' and the remaining volume, $V_2(r)$, as the 'unshaded volume'. If molecule 3 lies within the shaded volume, then all possible arrangements of the 3 molecules are counted by allowing C to move throughout this volume (while B moves throughout the sphere, radius $2R$, centred on A). However, if molecule 3 lies within the unshaded volume, only $1/3$ of the possible arrangements are counted when C moves through $V_2(r)$, since arrangements that interchange the molecules at A or B with the one at C are distinguishable. The volume available to the three molecules is thus

$$
\int dr_1 \int dr_2 \int dr_3 = 4\pi V \int_0^{2R} r^2 \, dr [V_1(r) + 2V_2(r)]
$$
$$
= 16\pi^2 V \int_0^{2R} r^2 dr \left\{ \int_{-R_{min}}^{R} d\tau (R^2 - \tau^2)^{1/2}(\tau + R_{min}) \right.
$$
$$
\left. + 2 \int_{R_{min}}^{R} d\tau (R^2 - \tau^2)^{1/2}(\tau - R_{min}) \right\}
$$
$$
= V v_c^2 \left(21 + \frac{9}{16}\pi^2 \right) \tag{10}
$$

where $R_{min} = (R^2 - r^2/4)^{1/2}$ and $v_c = 4\pi R^3/3$.

To extend the treatment to i molecules, it is necessary to ensure that a unique sphere is chosen to enclose the molecules (in general, there will be infinitely many spheres enclosing each arrangement). One way to do this is, for each arrangement of molecules within the sphere, freeze the molecules in position and then let the sphere fall 'under gravity' onto the molecules. There are three possible ways in which the sphere may come to rest:

(I) touching one molecule (the 'top' one), which can move throughout V, the remaining $(i - 1)$ molecules moving within v_c. There are i choices of the top molecule, so these arrangements give a contribution to the volume integrations of $i V v_c^{i-1}$.

(II) touching two molecules, the first being anywhere within V and the second lying within the hemisphere of radius $2R$ (and therefore volume $4v_c$) centred on the first and below it. However, arrangements in which the second molecule lies within the sphere resting on the first have already been counted in (I) above, so the volume available to the second molecule that gives rise to new arrangements is $3v_c$. There are i choices of first molecule and $(i - 1)$ choices of second molecule, so the total contribution from these arrangements is $3i(i - 1)V v_c^{i-1}$.

(III) touching 3 molecules. Clearly, this will give rise to a factor proportional to $i(i - 1)(i - 2)V v_c^{i-1}$. The constant of proportionality can be found by comparing the sum of the contributions in (I), (II) and (III) with equation (10) for $i = 3$, giving the value $3\pi^2/32$.

For a perfect gas cluster, $q_i^{\text{lab}} = v_c^i / \Lambda^{3i} i!$ and so the relation between q_i and q_i^{lab} can be written

$$q_i = \frac{V}{v_c} \left(i + 3i(i - 1) + \frac{3\pi^2}{32} i(i - 1)(i - 2) \right) q_i^{\text{lab}}. \tag{11}$$

For such perfect gas clusters, the principle difference between the result (11) and the centre of mass treatment by Reiss *et al* [8] is the approximate dependence of i^3 instead of $i^{3/2}$. For clusters of interacting molecules, the difference may be less since, as already noted, the arrangements omitted from the centre of mass treatment tend to be diffuse (i.e. high energy) ones.

3. Fluctuations

First, consider the cluster concentration for cluster sizes near $i = i^*$. Performing a second-order Taylor series expansion of the exponent in (8) gives

$$c^{\text{eq}}(i) = c^{\text{eq}}(i^*) \exp \left[\frac{(i - i^*)^2}{2\sigma_i^2} \right] \tag{12}$$

where

$$\frac{1}{\sigma_i^2} = \frac{-1}{kT} \frac{d^2 F_i}{di^2} \bigg|_{i=i^*} = \frac{d}{di} \left(\frac{1}{q_i} \frac{dq_i}{di} \right) \bigg|_{i=i^*}. \tag{13}$$

For classical nucleation, $\sigma_i^2 = 9kT(i^*)^{4/3} / 2A_1\gamma$. Values of σ_i are given in table 1.

Equation (12) is similar in form to equations describing fluctuations about equilibrium (see, for example, [13]). An important difference, however, is that the exponent in (12) is positive, in contrast to the usual case of a Gaussian distribution about the mean value. This reflects the fact that $i = i^*$ represents an unstable equilibrium position.

Energy fluctuations in a cluster can be examined in a standard way [13]. The mean energy and its mean square deviation for an i-cluster can be written

$$\overline{E(i)} = kT^2 \frac{\partial}{\partial T} \ln q_i \tag{14}$$

$$\sigma_E^2(i) = \overline{E^2} - \bar{E}^2 = k^2 T^2 \frac{\partial}{\partial T} \left(T^2 \frac{\partial}{\partial T} \ln q_i \right) = i c_1 kT^2. \tag{15}$$

The final equation defines the specific heat per molecule in a cluster, c_1. In numerical calculations, this is taken to be the molecular heat capacity in the liquid state. Values of σ_E / kT are quoted in table 1. The energy distribution for an i-cluster can be written

$$c^{\text{eq}}(i, E) = \frac{c^{\text{eq}}(i)}{(2\pi)^{1/2} \sigma_E(i)} \exp \left[\frac{-(E - \overline{E(i)})^2}{2\sigma_E^2(i)} \right] \tag{16}$$

where the coefficient is chosen so that $\int c^{\text{eq}}(i, E) \, dE = c^{\text{eq}}(i)$.

It is also possible to consider fluctuations in vector properties. For example, the centre of mass momentum of an i-cluster, $P = \sum_{j=1}^{i} p_j$, has the following distribution:

$$c^{eq}(i, P) = \frac{c^{eq}(i)}{(2\pi i m_v)^{1/2}} \exp\left[\frac{-P^2}{2im_v}\right].$$ (17)

Consider now fluctuations in both i and E. The distribution can be found by performing a Taylor series expansion of (16) about $i = i^*$ to obtain

$$c^{eq}(i, E) = \frac{c^{eq}(i^*)}{(2\pi)^{1/2}\sigma_E} \exp\left[-(i - i^*)^2\left(\frac{H^2}{2\sigma_E^2} - \frac{1}{2\sigma_i^2}\right) - \frac{(E - \bar{E})^2}{2\sigma_E^2} - H\frac{(i - i^*)(E - \bar{E})}{\sigma_E^2}\right]$$ (18)

where $\bar{E} = \overline{E(i^*)}$, $\sigma_E = \sigma_E(i^*)$ and

$$H = -\frac{d\overline{E(i)}}{di}\bigg|_{i=i^*} = -kT^2\frac{\partial^2}{\partial i \partial T}\ln q_i\bigg|_{i=i^*}.$$ (19)

From (5) and (6) it follows that

$$H = kT^2\frac{\partial}{\partial T}\left(\ln\frac{n_1^{sat}}{q_1} + \ln S\right)$$

$$= m_v L - kT - c_{vv}T + \left(kT^2\frac{\partial \ln S}{\partial T}\right)_i$$

$$= m_v L - kT - c_{vv}T - \frac{2}{3(i^*)^{1/3}}A_1\left[\gamma - T\frac{d\gamma}{dT}\right]$$ (20)

where the second form follows by using the Clausius Clapeyron equation for $n_1^{sat}(\sim \exp(-m_v L/kT)/kT$, where L is the latent heat of vaporization). The final form is appropriate for classical nucleation with $\ln S = 2\gamma A_1/(3(i^*)^{1/3}kT)$. We have also used $kT\partial(\ln q_1)/\partial T = c_{vv}$, the molecular heat capacity of the monomer in the vapour phase at constant volume $(= 3k/2$ for monatomic monomers). As can be seen from the values in table 1, H may be positive or negative.

If the temperature dependence of γ is ignored, the final form of H in (23) is related to the q used by Feder *et al* [9] by $H = q - c_{bv}T$ where $c_{bv} = c_{vv} + \frac{1}{2}k$. Equation (18) can then be shown to be identical to equation (32) of [9]. In fact, however, for many substances, $d\gamma/dT$ is comparable to γ/T (see table 1).

4. Steady-state distributions

To obtain a nucleation rate it is necessary to consider the mechanisms that form clusters and introduce an appropriate rate. The usual picture is that an i-cluster grows by gaining single monomers at a rate $\beta(i)$ given by the product of the monomer–cluster sticking probability, s_A, the cluster surface area, $A_1 i^{2/3}$, and the collision rate of the monomer with a plane surface of unit area, $\frac{1}{4}n_1\bar{c}/V$ (where $\bar{c} = (8kT/\pi m_v)^{1/2}$ is the mean monomer molecular speed). Clusters may also evaporate, losing single molecules at a rate $\alpha(i)$, which is related to $\beta(i)$ by the detailed balance condition in equilibrium: $\beta(i)c^{eq}(i) = \alpha(i + 1)c^{eq}(i + 1)$.

At $i = i^*$, $\alpha(i^*) = \beta(i^*)$. To obtain the nucleation rate, J, the stead-state concentrations $c^{ss}(i)$ are introduced such that:

$$J_Z = \beta(i)c^{ss}(i) - \alpha(i+1)c^{ss}(i+1). \tag{21}$$

By using the detailed balance condition to eliminate the $\alpha(i)$, dividing by $\beta(i)c^{eq}(i)$ and summing over i (with $c^{ss}(1) = c^{eq}(1)$ and $c^{ss}(N+1) = 0$), the following result for the steady-state nucleation rate is obtained:

$$J_Z = \left(\sum_{i=1}^{N} \frac{1}{\beta(i)c^{eq}(i)} \right)^{-1} \simeq \beta(i^*) \left(\int_1^{\infty} \frac{di}{c^{eq}(i)} \right)^{-1}$$
$$\simeq \frac{\beta(i^*)c^{eq}(i^*)}{(2\pi)^{1/2}\sigma_i} \tag{22}$$

where equation (12) has been used to obtain the final form.

For reasons that should become clear, J_Z is referred to as the 'isothermal rate'. The factor $J_Z/\beta(i^*)c^{eq}(i^*)$ is termed the Zeldovich factor and is typically 0.01 to 0.1 (see table 1).

However, the above approach does not take into account any possible dependence of the gain and loss rates on properties of the cluster other than i. Suppose that these rates also depend on a second cluster property, z, say. The nucleation rate should then be written

$$J = \int dz \int dz' \{ \beta(i, z \to z')c^{ss}(i, z) - \alpha(i+1, z \to z')c^{ss}(i+1, z) \}$$
$$= \int dz \{ \bar{\beta}(i, z)c^{ss}(i, z) - \bar{\alpha}(i+1, z)c^{ss}(i+1, z) \} \tag{23}$$

Following the discussion of fluctuations in the previous section, the equilibrium concentration would be expected to have a Gaussian distribution in z (with mean $\bar{z}$ and standard deviation σ_z). If the steady-state concentration has the same z dependence as the equilibrium concentration, then (23) reduces to (21) provided $\alpha(i+1)$ and $\beta(i)$ are equal to integrals over $\bar{\alpha}(i+1, z)$ and $\bar{\beta}(i, z)$, weighted by Guassian factors.

However, $c^{ss}(i, z)$ may not have the same z dependence as $c^{eq}(i, z)$. Such cases are treated in the following sections, but first we comment on the criteria for choosing the variables $\{z\}$ to be represented. A complete treatment would include all the positions and momenta of the molecules in the cluster, and this was the approach originally adopted by Langer [10]. However, this formulation is much too detailed to be of practical use and a more worthwhile approach is to follow Binder and Stauffer [20] and attempt to distinguish between 'relevant' coordinates, that should be considered and 'irrelevant' ones which can be ignored. Binder and Stauffer [20] show that if the cluster concentration is a sharply peaked function of a certain variable then that variable is irrelevant; however, they give no indication how such variables can be identified. Here. it is suggested that the rate of fluctuation also plays a factor in deciding if a variable is relevant or not. Properties that fluctuate on a timescale much shorter than the monomer addition timescale are irrelevant, since they have time to explore virtually the same range of values in the steady state as in the equilibrium case. Variables which fluctuate on timescales comparable to (or longer than) the time for the cluster to gain or lose a monomer, may have different distributions in the two cases and this will affect the nucleation rate. It would seem likely that internal properties of tightly-bound clusters (such as size and shape) would be irrelevant whereas properties which change only by external collisions (such as total cluster energy and momentum) will form the relevant coordinates.

5. Derivation of the Fokker–Planck equation

For simplicity, only two relevant coordinates are considered: the number of monomers in the cluster, i, and the total cluster energy, E. The rate of change in concentration $C(i, E)$ of clusters containing i molecules and having energy E is

$$\frac{\partial C}{\partial t}(i, E) = \int \beta(i-1, \epsilon, E - \epsilon)C(i-1, E-\epsilon)\,d\epsilon + \int \alpha(i+1, \epsilon, E+\epsilon)C(i+1, E+\epsilon)\,d\epsilon$$
$$- C(i, E) \int [\beta(i, \epsilon, E) + \alpha(i, \epsilon, E)]\,d\epsilon + \left(\frac{\partial C}{\partial t}\right)_{\text{gas}}. \tag{24}$$

The first term on the right represents the increase in $C(i, E)$ from sticking collisions between monomers with energy ϵ and $(i-1)$-clusters of energy $E - \epsilon$ (the rate for this process being $\beta(i-1, \epsilon, E - \epsilon)$). Similarly, the second term represents the increase in $C(i, E)$ due to $(i+1)$-clusters losing monomers. The rate at which an $(i+1)$-cluster with energy E loses a monomer with energy ϵ, $\alpha(i+1, \epsilon, E)$, is related to the gain rate $\beta(i, \epsilon, E - \epsilon)$ by the detailed balance condition,

$$\beta(i, \epsilon, E - \epsilon)C^{\text{eq}}(i, E - \epsilon) = \alpha(i+1, \epsilon, E)C^{\text{eq}}(i+1, E). \tag{25}$$

The third term in (24) gives the decrease in $C(i, E)$ due to i-clusters gaining or losing a monomer, and the final term represents changes due to collisions which change E but not i. This term is given the subscript 'gas' since contributions to this term arise from collisions with non-condensing gas molecules. However, if s_A is less than 1, there would also be contributions from non-condensing collisions with vapour molecules. Considering only collisions with gas molecules, this final term can be written

$$\left(\frac{\partial C}{\partial t}\right)_{\text{gas}} = \beta_g(i)\left[\int P(E' \to E)C(i, E')\,dE' - C(i, E)\right] \tag{26}$$

where $\beta_g(i)$ is the collision rate of gas molecules with an i-cluster and $P(E' \to E)$ is the probability that an individual collision changes the cluster's energy from E' to E.

The procedure for converting a master equation of the form of (26) to a Fokker–Planck equation is well known (although not without subtlety)—see, for example, Van Kampen [21]. The main assumptions are that only small jumps occur, so $P(E' \to E)$ is a sharply peaked function of $|E' - E|$, and that $P(E' \to E)$ varies only slowly with both E and E' for constant $|E' - E|$. Then, equation (26) can be approximated by

$$\left(\frac{\partial C}{\partial t}\right)_{\text{gas}} = \beta_g i \left[\frac{\partial}{\partial E}\{a_1(E)C(i, E)\} + \frac{1}{2}\frac{\partial^2}{\partial E^2}\{a_2(E)C(i, E)\}\right]$$
$$= \tfrac{1}{2}\beta_g(i)\frac{\partial}{\partial E}\left\{a_2(E)C^{\text{eq}}(i, E)\frac{\partial F}{\partial E}(i, E)\right\} \tag{27}$$

where

$$a_j(E) = \int dE'(E - E')^j P(E \to E')$$

and $F(i, E) = C(i, E)/C^{\text{eq}}(i, E)$ (not to be confused with the Free energy, F_i). The final form in (27) follows because $(\partial C^{\text{eq}}/\partial t)_{\text{gas}}$ equals zero (since, in equilibrium, the amount of non-condensing gas does not affect the cluster concentration in size and energy).

To determine the value of a_2, it is necessary to consider a model for energy transfer by gas molecules. A model used previously [11] considered gas molecules colliding with clusters to form microcanonical systems which then decayed according to the density of states of the possible final states. The mean energy transfer from a cluster with energy E for this model is $a_1(E) = [c_{bg}/(ic_1 + c_{bv})][E - \overline{E(i)}]$, where $c_{bg} = c_{vg} + 1/2k$, c_{vg} being the heat capacity at constant volume of a gas molecule. A relationship between a_2 and a_1 can be found by substituting C^{eq} in the first form of (27) and using the fact that $(\partial C^{eq}/\partial t)_{gas} = 0$. The resulting value of a_2, assuming $ic_1 \gg c_{bv}$, is a $a_2 = 2c_{bg}kT^2$.

The transformation of the remaining terms in (24) to Fokker–Planck form has been performed by Feder *et al* [9] and involves eliminating the α using the detailed balance condition and carrying out a second-order Taylor series expansion in both i and E. The integrals over ϵ then just involve moments of the energy distribution of incoming monomers, which is taken to be a Maxwellian weighted by an extra $\epsilon^{1/2}$ to take account of the increased monomer–cluster collision rate for faster monomers. Thus, the mean energy of colliding monomers, $\langle \epsilon \rangle = c_{bv}T$, and their mean square energy, $\langle \epsilon^2 \rangle = c_{bv}(c_{bv} + k)T^2$. For more details, see [9, 11]. The resulting equation can be written in tensor form,

$$\frac{\partial C}{\partial t}(i, E) = \left(\frac{\partial}{\partial i}, \frac{\partial}{\partial E} \right) D \left(\begin{array}{c} \partial/\partial i \\ \partial/\partial E \end{array} \right) F(i, E) \tag{28}$$

where

$$D = \beta(i)C^{eq}(i, E) \begin{pmatrix} 1 & c_{bv}T \\ c_{bv}T & W^2(E) \end{pmatrix} \tag{29}$$

with

$$W^2(E) = c_{bv}(c_{bv} + k)T^2 + \frac{1}{2}a_2(E)\frac{\beta_g(i)}{\beta(i)} \tag{30}$$

where any dependence of $\beta(i)$ on the cluster's energy E has been ignored. For $s_A < 1$, there is an additional term in $W^2(E)$ to take account of the heat transfer by non-condensing vapour molecules.

Equation (28) is identical to the equation derived by Feder *et al* (equation (35) of [9], since $q = H + c_{bv}T$ and $b^2 = W^2 - c_{bv}^2T^2$ where b^2 is defined on p 44 of [9]). The above discussion has concentrated on the form of the term arising from the non-condensable gas, since no detailed derivation of this term is given in [9]. Note that different models for gas molecule energy transfer will give different forms of a_2.

6. Expression for the steady-state nucleation flux

Langer [10] has given a procedure for solving multidimensional Fokker–Planck equations of the form which arise in nucleation theory. In this section, Langer's procedure is applied to obtain a solution of equation (28). To simplify the notation somewhat, all quantities are made dimensionless by measuring energies (E, σ_E, H, W) in units of kT and specific heats (c_{bv}, c_{bg}) in units of k.

The first step is to transform variables from i and E to ones which diagonalize the exponent in $C^{eq}(i, E)$. The new variables, x and y, say, are related to the old ones by an

orthogonal transformation with matrix M, the columns of which are the eigenvectors of the matrix

$$\begin{bmatrix} (H^2/\sigma_E^2 - 1/\sigma_i^2) & H/\sigma_E^2 \\ H/\sigma_E^2 & 1/\sigma_E^2 \end{bmatrix}.$$

The corresponding eigenvalues $\frac{1}{2}\lambda_1$ and $\frac{1}{2}\lambda_2$ are given by,

$$\frac{1}{2}\lambda_j = \frac{H^2+1}{2\sigma_E^2} - \frac{1}{2\sigma_i^2} + (-1)^j \left[\left(\frac{H^2+1}{2\sigma_E^2} - \frac{1}{2\sigma_i^2} \right)^2 + \frac{1}{\sigma_E^2\sigma_i^2} \right]^{1/2}. \tag{31}$$

The factor $\frac{1}{2}$ is included in the definition of the eigenvalues to correspond with Langer's treatment and the signs are chosen so that λ_1 is negative.

The equilibrium distribution in terms of x and y is

$$C^{eq}(x, y) = \frac{c^{eq}(i^*)}{(2\pi)^{1/2}\sigma_E} \exp(-\tfrac{1}{2}\lambda_1 x^2 - \tfrac{1}{2}\lambda_2 y^2). \tag{32}$$

The equation to be solved becomes

$$\nabla^T[\tilde{D}\nabla F(x, y)] = 0 \tag{33}$$

where

$$\nabla = (\partial/\partial x, \partial/\partial y)^T$$

$$\tilde{D} = M^T D M = \beta(i^*)C^{eq}(x, y) \begin{pmatrix} d_{11} & d_{12} \\ d_{21} & d_{22} \end{pmatrix} \tag{34}$$

with

$$d_{11} = \tfrac{1}{2}[W^2 + 1] + \tfrac{1}{2}[W^2 - 1]\cos\psi - c_{bv}\sin\psi$$

$$d_{12} = d_{21} = -\tfrac{1}{2}[W^2 - 1]\sin\psi - c_{bv}\cos\psi$$

$$d_{22} = \tfrac{1}{2}[W^2 + 1] - \tfrac{1}{2}[W^2 - 1]\cos\psi + c_{bv}\sin\psi$$

$$\tan\psi = 2H/[H^2 - \sigma_E^2/\sigma_i^2 - 1]$$

$$W^2 \equiv W^2(\bar{E}) = c_{bv}(c_{bv} + 1) + c_{bg}\frac{p_g}{p_v}\left(\frac{m_v}{m_g}\right)^{1/2}.$$

In the expression for W^2, it is assumed that β_g is proportional to $p_g/\sqrt{m_g}$ (the gas pressure divided by the square root of the gas molecule mass), and β is proportional to $p_v/\sqrt{m_v}$. Also, in going from (29) to (34) the variation of β and W with i and E near the saddle point $i = i^*$, $E = \bar{E}$, has been ignored.

Since $|H|$ is generally large compared to 1, $\tan\psi$ is small. The angle ψ is chosen so that λ_1 is the negative eigenvalue. Note, however, that M represents a rotation through $\frac{1}{2}(\pi - \psi)$ radians.

The next step is to assume that the required steady-state solution $F(x, y)$ is a function of a linear combination of x and y, that is

$$F(x, y) = f(\nu_1 x + \nu_2 y) \equiv f(u). \tag{35}$$

Langer [10] states that this assumption can be justified by solving the time-dependent problem, but does not reproduce the analysis. Alternatively, following Landauer and Swanson [21], this assumption can be justified *a posteriori* since it leads to a solution of (33) which has all the properties required. Substituting (35) in (33) gives

$$(d_{11}\nu_1^2 + 2d_{12}\nu_1\nu_2 + d_{22}\nu_2^2)f''(u) - \{\lambda_1[d_{11}\nu_1 + d_{12}\nu_2]x + \lambda_2[d_{12}\nu_1 + d_{22}\nu_2]y\}f'(u) = 0 \tag{36}$$

where the primes denote differentiation with respect to the argument of f. If this equation is only to contain functions of $u = \nu_1 x + \nu_2 y$, the term in curly brackets must be proportional to u, that is

$$\begin{pmatrix} \lambda_1 d_{11} & \lambda_1 d_{12} \\ \lambda_2 d_{12} & \lambda_2 d_{22} \end{pmatrix} \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix} = \kappa \begin{pmatrix} \nu_1 \\ \nu_2 \end{pmatrix}. \tag{37}$$

From (37), it is possible to show that

$$\frac{\nu_1^2}{\lambda_1} + \frac{\nu_2^2}{\lambda_2} = \frac{d_{11}\nu_1^2 + 2d_{12}\nu_1\nu_2 + d_{22}\nu_2^2}{\kappa} \tag{38}$$

a result that will be used later.

The negative value of κ (which turns out to be the one of interest) is,

$$\kappa = \tfrac{1}{2}(\lambda_1 d_{11} + \lambda_2 d_{22} - [(\lambda_1 d_{11} - \lambda_2 d_{22})^2 + 4\lambda_1\lambda_2 d_{12}^2]^{1/2}). \tag{39}$$

The solution of (36), satisfying $f(u) \rightarrow 1$ for $u \rightarrow -\infty$, is then $f(u) = \tfrac{1}{2}(1 - \text{erf}[u/(2|\Gamma|)^{1/2}])$ where

$$\Gamma = \frac{d_{11}\nu_1^2 + 2d_{12}\nu_1\nu_2 + d_{22}\nu_2^2}{\kappa} < 0. \tag{40}$$

Using this solution in (33), the term in square brackets, which can be identified with the components of the steady-state flux, J_x and J_y, can be written

$$\begin{pmatrix} J_x \\ J_y \end{pmatrix} = \frac{-c^{\text{eq}}(i^*)\kappa}{2\pi\sigma_E|\Gamma|^{1/2}} \begin{pmatrix} \nu_1/\lambda_1 \\ \nu_2/\lambda_2 \end{pmatrix} \exp\left[-\tfrac{1}{2}\lambda_1 x^2 - \tfrac{1}{2}\lambda_2 y^2 - \frac{(\nu_1^2 x^2 + \nu_2^2 y^2 + 2\nu_1\nu_2 xy)}{2|\Gamma|} \right] \tag{41}$$

where equation (37) have been used.

If i and j are unit vectors in the directions of the x and y axes, it follows from (41) that J is in the direction $(\nu_1/\lambda_1)i + (\nu_2/\lambda_2)j$. It is also possible to show, using (38) and (40), that the exponent in (41) is constant in this direction. The nucleation flux is the integrated intensity of J across any surface not parallel to J. Choosing the surface $x = 0$ for convenience gives

$$\begin{aligned} J_{ss} &= \int_{-\infty}^{\infty} \mathrm{d}y\, J_x(0) = \frac{c^{\text{eq}}(i^*)\kappa}{2\pi\sigma_E|\Gamma|^{1/2}} \frac{\nu_1}{\lambda_1} \left(\frac{2\pi}{\lambda_2 + \nu_2^2/|\Gamma|} \right)^{1/2} \\ &= \frac{\beta(i^*)c^{\text{eq}}(i^*)|\kappa|}{(2\pi|\lambda_1\lambda_2|)^{1/2}\sigma_E} \end{aligned} \tag{42}$$
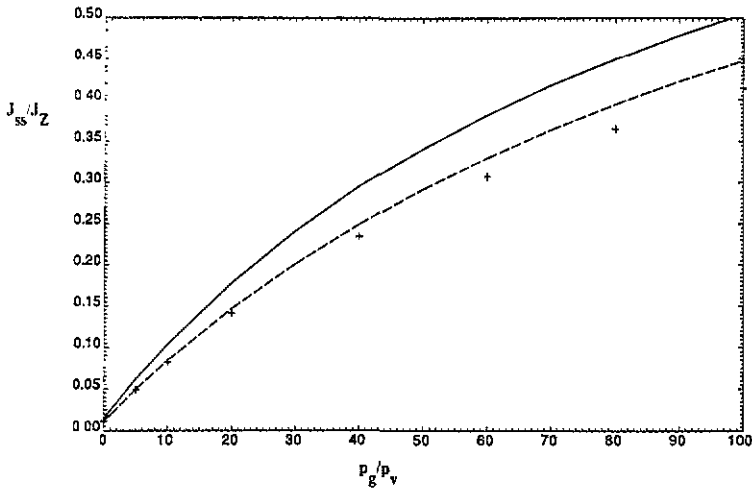
Figure 2. J_{ss}/J_Z versus p_g/p_v for the model system (dashed line) and for water using the parameters in table 1 (solid line). Also shown (crosses) are the numerical results for the model system, from [11].

where (38) has been used to eliminate $\nu_2^2/|\Gamma|$, remembering that Γ is negative.

In terms of the usual expression for the nucleation rate, equation (22), this flux can be written

$$J_{ss} = \frac{\sigma_i}{\sigma_E} \frac{|\kappa|}{(|\lambda_1|\lambda_2|)^{1/2}} J_Z. \tag{43}$$

The numerical evaluation of the quantities in (43) is straightforward; however, some simplification is possible when the magnitude of H is large (specifically, when $H^2 \gg 1$ and $H^2 \gg \sigma_E^2/\sigma_i^2$). Then it is possible to show that

$$\frac{J_{ss}}{J_Z} = \frac{1}{1 + \frac{q^2}{W^2 - c_{bv}^2}} \tag{44}$$

where $q = H + c_{bv}$. Since $W^2 - c_{bv}^2 = c_{bv} + c_{bg} p_g \sqrt{m_v}/(p_v \sqrt{m_g})$, this result is the same as the formula derived in [9], if the temperature variation of γ is ignored.

7. Numerical results

Table 1 gives values for J_{ss}/J_Z with no gas present (i.e. $p_g = 0$) calculated from (43) and (44). For water, the values agree to three significant figures, whereas for nonane the approximate formula, equation (44), gives a value about 30% less than equation (43).

To investigate the accuracy of both the Fokker–Planck approximation and the solution procedure used in the previous section, the values predicted by (43) for a model system are compared with those calculated in [11] by solving the integral equation for $C(i, E)$, equation (24), numerically. The results are shown in figure 2. The 'exact' numerical values from [11] are indicated by crosses and those calculated using (43) by the dashed line (for the model parameters used, values from (43) and (44) are virtually identical). Agreement with the exact results is very good at low gas pressures, although at higher pressures (44) overestimates the flux slightly. This may be due to an inadequate representation of the gas transition probability $P_g(E \to E')$ in the Fokker–Planck treatment.

The model uses a square-well cluster potential with parameters characteristic of the molecular latent heat and surface tension of water. Values for 'real' water, calculated from (43) using the parameters in table 1, are shown by the solid line in figure 2. The differences between the solid and dashed lines arise because the model results do not take into account the temperature variation of γ and they also assume that the vapour and liquid heat capacities are the same.
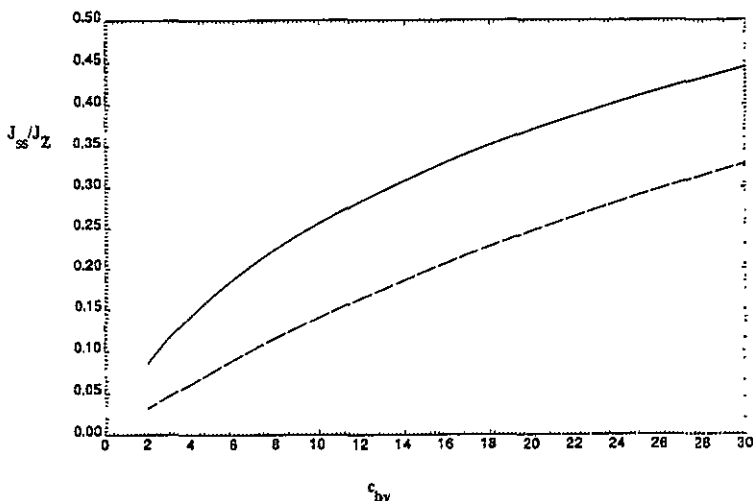

Figure 3. J_{ss}/J_Z versus c_{bv}, in units of k, with $p_g = 0$ calculated from equation (43) (solid line) and from the approximation of it, equation (44) (dashed line).

The accuracy of the approximation equation (44) to equation (43) is now investigated when $p_g = 0$ (which gives the maximum reduction from the isothermal rate, J_Z). Figure 3 shows the variation of J_{ss}/J_Z with c_{bv} (measured in units of k), calculated from (43) and (44). Apart from c_{bv}, all parameters are for nonane at $S = 50$, as listed in table 1. Since $H/kT \simeq (7.9 - c_{bv}/k)$, the results in figure 3 cover a range of positive and negative values, both large and small, for H. The accurate and approximate values often differ by a factor of about 2, however, this is not significant in nucleation theory (where measurements are typically accurate only to within a factor of about 10, and differences between theory and experiment may exceed factors of 10^6). The effect of varying c_1 while keeping the other parameters fixed is also considered. Once again, the accurate values exceed the approximate ones from (44) (which predicts that the nucleation rate is independent of c_1) but the difference, which increases with increasing c_1, involves only modest factors.

8. Conclusions

The way in which the equilibrium cluster distribution, the cluster free energy, and the chemical potential of the critical cluster are related to the partition function for a cluster anywhere within the container volume, q_i have been discussed. However, most theories (not just the classical theory) give the partition function (or some related quantity) for a cluster stationary in the laboratory frame, q_i^{lab}. A new approach to relating these two quantities has been proposed which leads to equation (11). This result suggests that nucleation rates for

such models should be enhanced by a factor of approximately $0.93i^2 v_{\text{g}}/v_1$ (where v_{g} is the volume per molecule in the vapour and it is assumed that $v_{\text{c}} = iv_1$) instead of the factor proportional to $i^{1/2} v_{\text{g}}/v_1$ suggested in [8]. Since, in nucleation, i is typically about 100 and v_{g} is roughly 1000 times v_1, this factor is about 10^7. It should be stressed, however, that (12) is valid only for a cluster model in which the interaction is independent of molecular positions. A significant extension of this work would be to include the effects of finite molecular size (which could be done along the lines followed in [8]) and intermolecular forces.

The fluctuations of the equilibrium distribution in energy, and also coupled fluctuations in size and energy have been considered. These introduce a quantity H defined by (19) and given in the classical liquid droplet model by (20). However, the value of H is fairly insensitive to the model used. The extension of this approach to treat coupled fluctuations in other variables should be straightforward.

In the steady state, properties other than the number of monomers in the cluster may be important in determining the nucleation rate and a way of identifying such properties has been proposed. One such variable is the cluster energy and a Fokker–Planck equation for the steady cluster distribution in size and energy variables has been derived. A procedure developed by Langer [10] was then applied to obtain the nucleation flux from this equation. This procedure is more versatile and more general than that used by Feder *et al* [9], which is justifiable only when $H \gg c_{\text{bv}}$ (i.e. large molecular latent heat compared to vapour molecule heat capacity). However, this is just the case that leads to the largest *reduction in nucleation rate from the isothermal value (by a factor of 100 or more in the* absence of background gas). In other circumstances the approximate formula, equation (44), underestimates the nucleation rate, although the differences (typically a factor 2) are not experimentally detectable at present. It should also be noted that Langer's procedure cannot be applied directly to the Fokker–Planck equation in fluctuation energy units (equation (35) of [9]).

The extension to more than two relevant variables is not difficult and Langer [10] has given the full multidimensional treatment. The problem is to decide which other variables should be considered. Ellerby *et al* [17] have suggested that cluster volume fluctuations (at fixed i) may be important. However, here it is argued that for liquid-like clusters the volume fluctuates on a very short timescale (compared to that for monomer addition) and so it is likely to be an irrelevant variable. This viewpoint seems to be supported by the work of Langer and Turski [23] who considered a field-theoretical model of a vapour near its critical point and did not find significant non-equilibrium effects.

The higher-dimensional result could also be used to treat centre-of-mass momentum fluctuations. However, the following argument suggests that these will have a negligible effect on the steady state nucleation rate. First, note that the equilibrium cluster distribution in i and P (found by using (12) in (17)) is already quadratic with no cross-term, so no rotation is needed and $D = \tilde{D}$. Thus, the off-diagonal elements of $\tilde{D}$ are found from the mean momentum transfer when a monomer hits a cluster with $i = i^*$ and $P = \tilde{P} = 0$. But this is zero (the cluster is stationary and the monomers have an equilibrium Maxwellian distribution) so $\tilde{D}$ is diagonal. In other words there is no coupling between the momentum variables and i. Of course, taking into account the variation of the elements of D with P near $P = 0$ introduces some coupling, as does the fact that P and E are not independent. However, these effects are likely to be very small.

One system where a multidimensional approach would be useful is binary nucleation of sulphuric acid and water. The large heat of hydration means that three cluster variables

should be considered (number of acid molecules, number of water molecules, and total energy).

Experimental nucleation rates for water and nonane are generally higher than the predictions of classical theory at low temperatures and lower at high temperatures. The proposed relationship equation (11) between q_i and q_i^{lab} leads to an enhancement of the classical predictions and therefore better agreement with experiments at very low temperatures but worse agreement at high temperatures. However, as only small changes in surface free energy are needed to produce large changes in nucleation rates, agreement with experiment could be restored with a better characterization of clusters. Indeed, current theories that claim to obtain good agreement with experiment without taking account of the difference between q_i and q_i^{lab} should be treated with suspicion.

The results presented in section 6 predict that the presence of a non-condensable carrier gas will increase the nucleation rate by a factor of up to 100 over the case of nucleation of the pure vapour. This effect has not yet been observed experimentally, with most experiments showing no detectable effect of carrier gas on nucleation rate. One exception is the work of Katz *et al* [24] who find that the nucleation rate decreases by a very large factor as the carrier gas pressure increases (about 10^4 for a gas pressure increase of 2 bar). This interesting observation has yet to be corroborated or explained.

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