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Energy fluctuations in steady-state binary nucleation

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Abstract. An analytical method to obtain the steady-state nucleation flux of binary liquid droplets is developed. The method is based on the solution of a Fokker–Planck equation for the concentration of clusters where both number (size) and cluster-energy fluctuations are included. The Fokker–Planck equation is solved in the vicinity of the saddle point. The kinetic prefactor is found to depend on the product of the three eigenvalues of a matrix that describes fluctuations about the critical cluster. The explicit, analytical expression for the total steady-state nucleation rate is applied to the water–ethanol binary system. The model predicts a nucleation rate that is slightly higher than the classical nucleation rate.

1. Introduction

Nucleation is the initial stage of a first-order phase transition that takes place in various energetically metastable or unstable systems. The formation of water droplets and ice crystals in the atmosphere, the casting of metals, and bubble formation are just a few examples of nucleation-related phenomena. One- and two-component nucleation have received extensive treatment in the literature, both in experimental and theoretical investigations (the reader is referred to the classic works [1] and [2] or more recent reviews [3] and [4]). Theoretical analyses of nucleation problems have been based on numerous, complementary approaches. The first approach, which is referred to as the classical nucleation model, was formulated by Becker and Döring [5], Volmer [6], and Turnbull and Vonnegut [7]. This theory is based on the phenomenological concept of a droplet that is viewed as a group of molecules which interact strongly among themselves and weakly with the rest of the system. According to the classical theory, the nucleating cluster is treated with equilibrium thermodynamics as a macroscopic droplet whose free energy of formation depends crucially on the bulk surface tension. The kinetics by which small clusters of the new phase gain or lose particles is based on ideas developed in chemical kinetics. It is assumed that clusters grow or shrink via the gain or loss of single molecules, an approximation that is reasonable for condensation at low pressures.

Recent developments within the framework of the classical theory (see, for example, [8, 9]) have been partly successful in explaining experimental data for one-component, homogeneous nucleation. However, results based on the classical theory show significant discrepancies for the temperature dependence of the nucleation rate [10]. Moreover, the classical theory being a phenomenological theory lacks a sound microscopic foundation. Alternative approaches to the classical theory either start from a microscopic point of view or use extensive computer simulations, see, for example [2, 11–13].

Two-component, homogeneous nucleation (binary nucleation) differs in a significant way from one-component (unary) nucleation. Whereas in one-component systems nucleation occurs in supersaturated systems, binary nucleation can occur even when a mixture of vapours is unsaturated with respect to the pure substances. Consequently, binary nucleation is the predominant particle-formation mechanism in the atmosphere, where various condensable vapours exist, which, however, are not present in high supersaturations. The importance of two-component nucleation for atmospheric processes motivated us to develop a steady-state nucleation model for binary mixtures and to apply it to the water–ethanol system. This system was chosen because large discrepancies between theoretical predictions based on the classical theory and experimental results have been reported [14, 15].

The binary nucleation problem was first studied by Flood [16] and then by Reiss [17]. These initial results have been refined and extended by numerous authors, we refer the reader to [18–22]. Heterogeneous binary nucleation has recently been studied in [23].

The present work is concerned with the derivation of an expression for the steady-state total nucleation rate for binary systems where fluctuations in number (size) and cluster energy are included. The analytical expression is based on the derivation and solution of a Fokker–Planck equation for the cluster concentration. The fundamental idea is that the transition to the stable phase is most likely to occur via a passage through the lowest intervening saddle point of the free energy that divides the metastable phase from the stable phase. Consequently, the problem reduces to solving the appropriate Fokker–Planck equation in the vicinity of the saddle point.

Our work was motivated by the pioneering work of Langer [24] to solve multidimensional Fokker–Planck equations that appear in nucleation phenomena, and the more recent work of Barrett [25] where Langer’s ideas are used to derive an expression for one-component nucleation. It may be considered an extension of Barrett’s analysis to two-component systems. Even though we derive an expression for the nucleation rate that is general, we evaluate it using the classical theory Gibbs free energy of formation of a cluster. Numerical results are compared with experimental data for the water–ethanol system. In a future work our results will be compared with Stauffer’s [18] and those of Wilemski and co-authors [22]: the emphasis will be on the effect of energy fluctuations on direction of growth of the nucleating droplet in the saddle-point approximation. Our analysis is easily extended to multicomponent nucleation.

2. Classical theory of binary nucleation

The first treatment of homogeneous, binary nucleation was developed by Reiss [17], and later refined by Stauffer [18]. It is an extension of the usual treatment of nucleation of a single vapour. A droplet fluctuation of the new binary phase is stabilized if its free energy of formation F is large enough to overcome the free energy barrier F^* that separates the two phases. According to the classical treatment the free energy of the formation of the droplet F has a saddle point as a function of n_1 and n_2 where n_i is the total number of molecules (monomers) of species, i , in a droplet. The saddle point defines the critical droplet free energy and the corresponding composition.

Under the capillarity approximation the free energy of formation of a liquid embryo from a binary mixture of vapours is expressed as the sum of a volume and a surface term,

$$F = n_1\delta\mu_1 + n_2\delta\mu_2 + \gamma A(n_1, n_2) \quad (1)$$

where n_i is the number of molecules of species i in the droplet, γ is the surface tension,

$A(n_1, n_2)$ is the surface area of the binary droplet, and

$$\delta\mu_i = \mu_i^l - \mu_i^g \quad (i = 1, 2) \quad (2)$$

where μ_i^l is the liquid-phase chemical potential of species i , and μ_i^g is the gas-phase chemical potential. In the case of the constant temperature process, the change of the Helmholtz free energy from the vapour to the liquid phase (droplet formation) has an extremum, whereas in the case of constant temperature and pressure, the Gibbs free energy difference has an extremum. However, the change of the Gibbs free energy during a phase transition is equivalent to a change of the Helmholtz free energy if the vapour pressure before and after the transition is the same [2]. Consequently, either free energy can be used in the analysis of nucleation rates.

For spherical droplets and under the assumption that the partial molecular volumes v_i are independent of pressure the surface area of the critical droplet may be expressed in terms of the critical droplet radius r_{cr} by

$$A(n_1, n_2) = 4\pi r_{\text{cr}}^2 = (36\pi)^{1/3} (n_1 v_1 + n_2 v_2)^{2/3}. \quad (3)$$

This equation defines the critical droplet radius.

The critical droplet composition is given by the composition at the saddle point. It is defined by the extremal conditions (Gibbs–Thomson equations)

$$\left. \frac{\partial F}{\partial n_1} \right|_{n_2, T, P} = 0 \quad (4)$$

$$\left. \frac{\partial F}{\partial n_2} \right|_{n_1, T, P} = 0 \quad (5)$$

where T is the absolute temperature and P is the pressure. It should be stressed that the derivatives that define the saddle point are taken keeping the gas-phase partial pressures constant [26]. There has been considerable discussion in the literature on whether the compositional derivatives of the surface tension appear in equations (4) and (5). In fact, they are absent because under the capillarity approximation one must distinguish between surface composition and bulk (internal) droplet composition. The use of the Gibbs–Duhem equation for the bulk liquid phase and the Gibbs–Duhem adsorption equation for the surface ensures that the surface tension derivatives do not appear in the equations that define the saddle point. When the surface–bulk decomposition is used the Gibbs–Thomson equation becomes

$$\delta\mu_i + \frac{2\gamma_{\text{cr}} v_i}{r_{\text{cr}}} = 0 \quad (i = 1, 2) \quad (6)$$

where γ_{cr} is the surface tension of the critical droplet. From these two equations it is easy to derive the consistency equation (revised classical theory) that determines the bulk droplet composition [19] at the saddle point

$$v_1 \delta\mu_2 = v_2 \delta\mu_1. \quad (7)$$

The nucleation rate according to the classical theory is expressed as

$$J = J_0 \exp(-\beta F^*) \quad (8)$$

where J_0 is a kinetic prefactor, βF^* is the free energy of formation of the critical droplet, and $\beta = 1/k_B T$ where k_B is the Boltzmann constant. For binary condensation the pre-exponential factor was first calculated by Reiss [17] by considering the contribution of number fluctuations, i.e. by assuming that a droplet could grow or shrink by the condensation or evaporation of a single molecule. Stauffer [18] extended the calculation to non-associated

vapours and in the case where the impingement rate of different molecules was different. He argued that in general the calculation of the nucleation flux should not be performed along the steepest descent path as Reiss originally did. According to Stauffer the final expression for the kinetic prefactor for the binary nucleation may be written in a form similar to the one used in unary nucleation as follows

$$J_0 = \rho_v ABZ \quad (9)$$

where ρ_v is the total density of condensible vapours ($\rho_v = \rho_{1v} + \rho_{2v}$), A is the surface area of the droplet, B is the average growth rate, and Z is the Zeldovich non-equilibrium factor. For non-associated vapour the average growth rate is given as

$$B = \frac{\beta_1 \beta_2}{\beta_1 \sin^2 \phi + \beta_2 \cos^2 \phi} \quad (10)$$

and the impingement rate β_i of species i is

$$\beta_i = p_{iv} / (2\pi m_i k_B T)^{1/2} \quad (11)$$

where m_i is the molecular mass of the i th component. The factor Z may be considered as a generalization of the unary Zeldovich factor because it incorporates the effect of number fluctuations. In the general case where the impingement rates of different components differ it is given by

$$Z = - \frac{D_{11} \cos^2 \phi + 2D_{12} \cos \phi \sin \phi + D_{22} \sin^2 \phi}{(D_{12}^2 - D_{11}D_{22})^{1/2}} \quad (12)$$

where

$$D_{ij} = \frac{1}{2} \frac{\partial^2 F}{\partial n_i \partial n_j} \Big|_{T,P}^* \quad (13)$$

The superscript \star denotes evaluation of the appropriate derivatives at the saddle point. The angle ϕ defines the direction of growth of the critical droplet, and it is given by

$$\tan \phi = s + \left(s^2 + \frac{\beta_2}{\beta_1} \right)^{1/2} \quad (14)$$

where

$$s = \frac{1}{2D_{12}} \left(D_{22} \frac{\beta_2}{\beta_1} - D_{11} \right). \quad (15)$$

If one component is dilute [26] (for example, component 1) the kinetic prefactor of the equation for the nucleation rate reduces the kinetic prefactor of one-component nucleation to become $J_0 = \rho_{v1} A \beta_1 Z$.

An alternative method of calculating the Zeldovich factor in binary systems is based on the concept of a virtual monomer [27]. Accordingly, a virtual monomer is introduced whose volume is $v = (n_1 v_1 + n_2 v_2) / (n_1 + n_2)$. It can then be shown that the nucleation rate may be expressed in terms of properties of the virtual monomer, i.e. the problem reduces to one-component nucleation and the Zeldovich factor becomes [28]

$$Z = (\beta \gamma)^{1/2} \frac{v}{2\pi r_{cr}^2}. \quad (16)$$

In the calculations of section 5 where the results of the classical theory are compared with our results, we use this method to calculate the Zeldovich factor. Moreover, for consistency with the definitions that we will be using in the rest of the paper, we define the Zeldovich

factors as the inverse of the second-order free energy derivatives. For the case of a virtual monomer we define (a result that will be used later in section 4)

$$\sigma_z = \frac{1}{(2\pi)^{1/2}Z}. \quad (17)$$

In the following section we consider number and energy fluctuations, we derive a general expression for the equilibrium distribution that incorporates contributions from these fluctuations, and we evaluate the fluctuation terms according to the classical nucleation theory (in the capillarity approximation and for droplets that are considered to form ideal solutions).

3. Equilibrium cluster distribution

The usual way to calculate the equilibrium distribution of clusters (liquid droplets) for a given degree of supersaturation involves the minimization of the Helmholtz free energy with respect to the concentration of various components subject to the constraints of constant temperature, volume, and total mass. In the present work we extend this treatment to include fluctuations in the energy of the clusters. We are interested in the contribution of energy fluctuations to the nucleation rate, and in particular to the kinetic prefactor. The idea is that a condensing or evaporating monomer not only alters the composition of the droplet, but it also adds or removes the latent heat of condensation. Thereby the energy of the droplet is modified. Hence, in addition to the usual number fluctuations, which give rise to the Zeldovich factor, energy fluctuations will modify the kinetic prefactor.

We consider the effect of energy fluctuations in a cluster containing n_1 molecules of species 1, n_2 molecules of species 2, and whose energy is ϵ on the equilibrium cluster distribution $c_{\text{eq}}(n_1, n_2, \epsilon)$. In accordance with the general theory of fluctuations the cluster distribution becomes

$$c_{\text{eq}}(n_1, n_2, \epsilon) = D \exp\{-\beta F(n_1, n_2)\} \exp\left\{-\frac{[\epsilon - \overline{\epsilon(n_1, n_2)}]^2}{2\sigma_\epsilon^2(n_1, n_2)}\right\} \quad (18)$$

where the average cluster energy is denoted as $\overline{\epsilon(n_1, n_2)}$ and σ_ϵ is the variance of the cluster-energy probability distribution. The normalization coefficient D is determined from the condition

$$\int_{-\infty}^{\infty} c_{\text{eq}}(n_1, n_2, \epsilon) d\epsilon = c_{\text{eq}}(n_1, n_2). \quad (19)$$

Number fluctuations about the critical cluster are calculated in the standard way by performing a second-order Taylor series expansion of the exponents in equation (18). The critical cluster is denoted as $(n_1^*, n_2^*, \bar{\epsilon})$ where $\bar{\epsilon} = \overline{\epsilon(n_1^*, n_2^*)}$ is the average energy of the critical cluster. The expansion of the first exponent yields

$$\beta F(n_1, n_2) = \beta F(n_1^*, n_2^*) + \frac{1}{2} \left. \frac{\partial^2 \beta F}{\partial n_1^2} \right|_* \delta n_1^2 + \frac{1}{2} \left. \frac{\partial^2 \beta F}{\partial n_2^2} \right|_* \delta n_2^2 + \left. \frac{\partial^2 \beta F}{\partial n_1 \partial n_2} \right|_* \delta n_1 \delta n_2 \quad (20)$$

where deviations from the critical cluster values are expressed as

$$\delta n_1 = n_1 - n_1^* \quad (21)$$

$$\delta n_2 = n_2 - n_2^*. \quad (22)$$

As discussed in the previous section, linear terms vanish because the saddle-point configuration is an extremum (it determines the critical cluster parameters). The terms

that arise from number fluctuations may be expressed in terms of the generalized Zeldovich factors as follows

$$\left. \frac{\partial^2 \beta F}{\partial n_1^2} \right|^\star \equiv -\frac{1}{\sigma_1^2} \quad (23)$$

$$\left. \frac{\partial^2 \beta F}{\partial n_2^2} \right|^\star \equiv -\frac{1}{\sigma_2^2} \quad (24)$$

$$\left. \frac{\partial^2 \beta F}{\partial n_1 \partial n_2} \right|^\star \equiv -\frac{1}{\sigma_{12}^2}. \quad (25)$$

Note that in analogy to unary nucleation we introduce an explicit negative sign in the definition of the generalized Zeldovich factors and we define them as the inverse of the second-order free energy derivatives. Moreover, as noted by Stauffer in his analysis of binary nucleation [18], the individual elements of the matrix $\partial^2 \beta F / \partial n_i^2$ that define the generalized Zeldovich factors need not be negative, but the product of the corresponding eigenvalues is.

The expansion of the second exponent in equation (18) (average cluster energy) in combination with the previous expansion in terms of number fluctuations (cf equation (20)) results in

$$c_{\text{eq}}(n_1, n_2, \epsilon) = D \exp\{-\beta F(n_1^\star, n_2^\star)\} \exp \left\{ \frac{\delta n_1^2}{2\sigma_1^2} + \frac{\delta n_2^2}{2\sigma_2^2} + \frac{\delta n_1 \delta n_2}{\sigma_{12}^2} - \frac{1}{2\sigma_\epsilon^2} \right. \\ \times \left[\delta \epsilon^2 + \left(\frac{\partial \bar{\epsilon}}{\partial n_1} \right)^2 \delta n_1^2 + \left(\frac{\partial \bar{\epsilon}}{\partial n_2} \right)^2 \delta n_2^2 - 2 \frac{\partial \bar{\epsilon}}{\partial n_1} \delta n_1 \delta \epsilon \right. \\ \left. \left. - 2 \frac{\partial \bar{\epsilon}}{\partial n_2} \delta n_2 \delta \epsilon + 2 \frac{\partial \bar{\epsilon}}{\partial n_1} \frac{\partial \bar{\epsilon}}{\partial n_2} \delta n_1 \delta n_2 \right] \right\} \quad (26)$$

where similarly to the previous definition of number fluctuations we have defined the energy difference as

$$\delta \epsilon = \epsilon - \overline{\epsilon(n_1^\star, n_2^\star)} \quad (27)$$

and the average-energy derivatives are evaluated at the critical cluster.

The previous equation may be written in a more transparent form if we use the following definition

$$H_i \equiv - \left. \frac{\partial \bar{\epsilon}}{\partial n_i} \right|^\star \quad (i = 1, 2) \quad (28)$$

and if the normalization constant is determined from the normalization condition shown in equation (19). Therefore, the final expression for the equilibrium cluster distribution that incorporates the combined effects of number and energy fluctuations becomes

$$c_{\text{eq}}(n_1, n_2, \epsilon) = \frac{c_{\text{eq}}(n_1^\star, n_2^\star)}{(2\pi)^{1/2} \sigma_\epsilon} \exp \left\{ -\delta n_1^2 \left[\frac{H_1^2}{2\sigma_\epsilon^2} - \frac{1}{2\sigma_1^2} \right] - \delta n_2^2 \left[\frac{H_2^2}{2\sigma_\epsilon^2} - \frac{1}{2\sigma_2^2} \right] \right. \\ \left. - \delta n_1 \delta n_2 \left[\frac{H_1 H_2}{\sigma_\epsilon^2} - \frac{1}{\sigma_{12}^2} \right] - \frac{\delta \epsilon^2}{2\sigma_\epsilon^2} - \frac{H_1}{\sigma_\epsilon^2} \delta n_1 \delta \epsilon - \frac{H_2}{\sigma_\epsilon^2} \delta n_2 \delta \epsilon \right\}. \quad (29)$$

This general result will be used in the next section to determine the nucleation flux by solving the appropriate Fokker–Planck equation for the cluster concentration. In what follows we evaluate the various derivatives that appear in equation (29) under well-defined approximations.

The generalized Zeldovich factors for binary nucleation may be determined in the capillarity approximation. If the Gibbs–Duhem equation for the bulk phase and the Gibbs adsorption isotherm for the surface are used in the first derivatives of the free energy the surface tension and the liquid-phase chemical potential derivatives are eliminated. The second-order free energy derivatives (which determine the generalized Zeldovich factors according to the definitions of equations (23)–(25)) may be expressed as

$$-\frac{1}{\sigma_i^2} = \frac{\partial \beta \mu_i^l}{\partial n_i} + \frac{2v_i}{r_{\text{cr}}} \frac{\partial \beta \gamma}{\partial n_i} - \frac{\beta \gamma v_i^2}{2\pi r_{\text{cr}}^4} \quad (i = 1, 2) \quad (30)$$

$$-\frac{1}{\sigma_{12}^2} = \frac{\partial \beta \mu_1^l}{\partial n_2} + \frac{2v_2}{r_{\text{cr}}} \frac{\partial \beta \gamma}{\partial n_1} - \frac{\beta \gamma v_1 v_2}{2\pi r_{\text{cr}}^4}. \quad (31)$$

As discussed in the previous section, the free energy derivatives are taken keeping gas-phase activities constant. Moreover, a consistent evaluation of equation (31), namely that the order of differentiation with respect to n_1 and n_2 is not important, requires either that the middle term is zero, i.e. that the surface tension derivatives with respect to n_i is zero an observation that is in agreement with the revised classical theory, or that the surface tension is a function of $n_{\text{total}} = n_1 + n_2$. A more general expression for the generalized Zeldovich factors, where the surface tension derivatives are explicitly calculated, may be found in Mirabel and Katz [29].

For the numerical calculations that are discussed in section 5 we evaluate the previous expressions (equations (30) and (31)) by making the approximation that droplets have properties of macroscopic systems and that they form ideal solutions (see, also, Mirabel and Clavelin [30] and Zeng and Oxtoby [13]). Consequently, the second-order free energy derivatives with respect to particle number become

$$-\frac{1}{\sigma_1^2} = \frac{n_2^*}{n_1^*(n_1^* + n_2^*)} - \frac{\beta \gamma v_1^2}{2\pi r_{\text{cr}}^4} \quad (32)$$

$$-\frac{1}{\sigma_2^2} = \frac{n_1^*}{n_2^*(n_1^* + n_2^*)} - \frac{\beta \gamma v_2^2}{2\pi r_{\text{cr}}^4} \quad (33)$$

$$-\frac{1}{\sigma_{12}^2} = -\frac{1}{n_1^* + n_2^*} - \frac{\beta \gamma v_1 v_2}{2\pi r_{\text{cr}}^4}. \quad (34)$$

It is instructive to note the similarity of these expressions to the expression for the Zeldovich factor in unary nucleation. In classical unary nucleation the Zeldovich factor is

$$\sigma_1^2 = \frac{2\pi r_{\text{cr}}^4}{\beta \gamma v^2} = \frac{9n^{4/3}}{2\beta \gamma A_1} \quad (35)$$

where n is the number of particles and A_1 is the surface area of a monomer. (In deriving equation (35) the usual assumption that the droplet surface tension is independent of composition was used.) This expression should also be compared with equations (16) and (17).

The average energy derivatives and the variance of the energy probability distribution are evaluated under the approximation that the total energy of an (n_1, n_2) cluster is the sum of the energy of its two independent components, i.e. $\epsilon(n_1, n_2) = \epsilon(n_1) + \epsilon(n_2)$. Then, simple arguments from statistical mechanics give the following expression for the mean-square energy fluctuations [31] (see also appendix 2 of [1])

$$\sigma_\epsilon^2 = \sum_{i=1}^2 c_i n_i k_B T^2 \quad (36)$$

where c_i is the bulk specific heat per molecule of species i in the cluster and we have assumed additivity of the specific heat.

The derivatives of the average energy with respect to n_i are re-expressed (under the assumption of independent species) as follows (the derivation closely follows the derivations of Barrett [25] and Feder *et al* [1])

$$H_i = q_i - (c_{iv} + \frac{1}{2}k_B)T \quad (i = 1, 2) \quad (37)$$

where q_i is the energy released upon addition of a monomer of vapour i to a cluster, and c_{iv} is the molecular heat capacity of a monomer in the vapour phase at constant volume. The quantity q_i is given for one-component nucleation in [1]. Similar arguments give the corresponding expression in the two-component case

$$q_i = m_i L_i - \frac{1}{2}k_B T - \gamma \frac{\partial A(n_1, n_2)}{\partial n_i} \quad (38)$$

where m_i is the molecular mass of species i , L_i is the differential latent heat of condensation of species i , and $A(n_1, n_2)$ is the total surface area of the cluster. In the calculations of section 5 we approximate the differential latent heat of condensation with the latent heat of condensation of pure species i . Equation (38) shows that the energy released when a molecule condenses is less than the latent heat of condensation because part of the energy is used to create the new surface area and part to raise the temperature (Feder *et al* [1]). As noted by Barrett [25] this derivation is valid if the temperature derivative of the surface tension can be neglected.

As a final remark, in this section we should stress that the evaluation of the various derivatives that appear in the exponent of the equilibrium cluster distribution (equation (29)) were evaluated using the classical expression for the Gibbs free energy for binary mixtures [17] (cf equation (1)). We used an expression for the free energy of the formation of the droplet that can be divided into a volume and a surface part, and the various parameters were obtained from values for macroscopic systems. Alternatively, the droplet free energy may be evaluated by other methods. An attractive choice is to use Monte Carlo simulations to evaluate it, which, however, requires that the form of the interaction potential, U_i , in the cluster be known. This is a severe limitation because in many cases the interaction potential is not known. The classical theory expression for the droplet Gibbs free energy of formation may be derived by approximating the cluster potential.

Another limitation of the classical approach is the use of macroscopic quantities, such as the bulk surface tension, to describe the properties of the critical cluster. Since the clusters under consideration usually consist of only a few hundred molecules, it is doubtful whether macroscopic parameters can be used with impunity. It is clear that a theory which takes into account corrections to the bulk properties of small clusters is required. In the case of one-component systems an approach based on the use of the second virial coefficient [32] has been proposed. For binary mixtures the calculation of the second virial coefficients is more tedious, but a systematic way to evaluate them [33] has also been suggested. The evaluation of second virial coefficients for binary mixtures is beyond the scope of the present work.

4. Fokker–Planck equation for binary droplets

The calculation of the nucleation rate of binary droplets requires information about the mechanism of cluster formation, the effect of fluctuations of relevant variables, and the rate at which these processes occur. The first approach to calculate the nucleation flux of a

single-component droplet was made by Becker and Döring [5]. Zeldovich [34] improved their approach by assuming steady-state concentrations. These approaches are based on the assumption that only the gain or loss of monomers in the clusters are important, and hence they do not take into account other factors that influence the growth of the droplets. Barrett [25] improved these descriptions by incorporating the effect of energy fluctuation in single-component nucleation. In the present work we follow Langer [24] to introduce a general method that considers changes in the cluster concentration in binary nucleation by deriving an appropriate Fokker–Planck equation. Our work is an extension of the work of Barrett [25] to binary nucleation. The extension to multicomponent nucleation is easily derived.

The appropriate Fokker–Planck equation is derived by considering the general form of the master equation for the time evolution of the concentration of binary droplets since the master equation describes gains and losses. The transformation of the master equation to a Fokker–Planck equation is made by performing a second-order Taylor expansion in the size and energy of the clusters. The resulting Fokker–Planck equation is solved via the method presented by Langer [24] to solve multidimensional Fokker–Planck equations which appear in nucleation problems.

We begin by introducing the form of the master equation for binary droplets. Consider a physical system which has N degrees of freedom and, hence, it is described by $2N$ coordinates and canonically conjugate momenta. We denote these coordinates collectively by a_j , where j runs from 1 to $2N$. The time change of the cluster concentration $c(a)$ is described by the master equation

$$\frac{\partial c(a)}{\partial t} = \int da' [P(a, a')c(a') - P(a', a)c(a)] \quad (39)$$

where $P(a, a')$ is the rate (transition probability) at which the concentration c changes from configuration a' to configuration a . Changes due to the dynamical behaviour of the clusters are not included in this form of the master equation.

For binary clusters of species 1 and 2 and energy ϵ the master equation may be explicitly written as

$$\begin{aligned} \frac{\partial}{\partial t} c(n_1, n_2, \epsilon; t) = & \int_{-\infty}^{\infty} d\epsilon' \int_1^{\infty} dn'_1 \int_1^{\infty} dn'_2 \\ & \times [R(n_1 n_2 \epsilon | n'_1 n'_2 \epsilon') c(n'_1 n'_2 \epsilon'; t) - R(n'_1 n'_2 \epsilon' | n_1 n_2 \epsilon) c(n_1, n_2, \epsilon; t)] \end{aligned} \quad (40)$$

where $R(n'_1 n'_2 \epsilon' | n_1 n_2 \epsilon)$ is the transition probability that a cluster rate in state $(n_1 n_2 \epsilon)$ moves to state $(n'_1 n'_2 \epsilon')$.

The transition probability that a cluster moves from one configuration to another may be written as the sum of a condensation rate for clusters with a monomer less than the required cluster size and an evaporation rate for clusters with a monomer more than the required cluster size. We make the usual assumption that condensation and evaporation occur only via the addition or the loss of either a monomer of vapour 1 or vapour 2. These transitions change the number of molecules (n_1, n_2) and the energy of the cluster ϵ . Therefore, the transition rate R may be written as

$$\begin{aligned} R(n'_1 n'_2 \epsilon' | n_1 n_2 \epsilon) = & R_{\text{cond}}^{(1)}(n'_1 n_2 \epsilon' | n_1 n_2 \epsilon) \delta(n'_2 - n_2) + R_{\text{cond}}^{(2)}(n_1 n'_2 \epsilon' | n_1 n_2 \epsilon) \delta(n'_1 - n_1) \\ & + R_{\text{evap}}^{(1)}(n'_1 n_2 \epsilon' | n_1 n_2 \epsilon) \delta(n'_2 - n_2) + R_{\text{evap}}^{(2)}(n_1 n'_2 \epsilon' | n_1 n_2 \epsilon) \delta(n'_1 - n_1) \end{aligned} \quad (41)$$

where the superscript refers to species number, the subscript ‘cond’ refers to condensation ($n' = n + 1$), and ‘evap’ refers to evaporation ($n' = n - 1$). Specifically, $R_{\text{cond}}^{(2)}(n_1 n'_2 \epsilon' | n_1 n_2 \epsilon)$ is the transition rate at which a cluster (n_1, n_2, ϵ) moves to the required cluster size $(n_1, n'_2 \epsilon')$

via the condensation of a species 2 monomer with energy $\epsilon' - \epsilon$, and $R_{\text{evap}}^{(2)}(n_1 n_2' \epsilon' | n_1 n_2 \epsilon)$ is the transition rate at which a cluster (n_1, n_2, ϵ) moves to the required cluster size $(n_1, n_2' \epsilon')$ via the evaporation of a species 2 monomer of energy $\epsilon' - \epsilon$. In equation (41) we have introduced the Dirac delta function, $\delta(x)$ and we are using a continuous description.

The condensation and the evaporation rates can be written as (see, also [1])

$$R_{\text{cond}}^{(1)}(n_1' n_2 \epsilon' | n_1 n_2 \epsilon) = \int_{-\infty}^{\infty} A(A(n_1, n_2)) \beta_1(x) \delta(\epsilon' - \{\epsilon + q_1 + x\}) \delta(n_1' - \{n_1 + 1\}) dx \quad (42)$$

$$R_{\text{cond}}^{(2)}(n_1 n_2' \epsilon' | n_1 n_2 \epsilon) = \int_{-\infty}^{\infty} A(A(n_1, n_2)) \beta_2(x) \delta(\epsilon' - \{\epsilon + q_2 + x\}) \delta(n_2' - \{n_2 + 1\}) dx \quad (43)$$

$$R_{\text{evap}}^{(1)}(n_1' n_2 \epsilon' | n_1 n_2 \epsilon) = \int_{-\infty}^{\infty} A(A(n_1, n_2)) \alpha_1(n_1, n_2, \epsilon, x) \delta(\epsilon' - \{\epsilon - q_1 - x\}) \delta(n_1' - \{n_1 - 1\}) dx \quad (44)$$

$$R_{\text{evap}}^{(2)}(n_1 n_2' \epsilon' | n_1 n_2 \epsilon) = \int_{-\infty}^{\infty} A(A(n_1, n_2)) \alpha_2(n_1, n_2, \epsilon, x) \delta(\epsilon' - \{\epsilon - q_2 - x\}) \delta(n_2' - \{n_2 - 1\}) dx \quad (45)$$

where $\beta_1(x)$ is the impingement rate of a vapour monomer 1 with energy $q_1 + x$, x being the corresponding energy fluctuation with respect to the mean energy of the impinging molecule, and $\alpha_1(n_1, n_2, \epsilon, x)$ is the vapourization coefficient of the cluster of interest. Terms with subscripts 2 have the same meaning as those described except they refer to a vapour monomer of species 2. The vapourization coefficient is related to the impingement rate via the principle of detailed balance

$$A(n_1, n_2) \alpha_1(n_1, n_2, \epsilon; x) c_{\text{eq}}(n_1, n_2, \epsilon) = A(n_1 - 1, n_2) \beta_1(x) c_{\text{eq}}(n_1 - 1, n_2, \epsilon - q_1 - x) \quad (46)$$

$$A(n_1, n_2) \alpha_2(n_1, n_2, \epsilon; x) c_{\text{eq}}(n_1, n_2, \epsilon) = A(n_2 - 1, n_1) \beta_2(x) c_{\text{eq}}(n_2 - 1, n_1, \epsilon - q_1 - x) \quad (47)$$

where, as before, c_{eq} is the equilibrium cluster distribution. Hence, a detailed balance can be used to eliminate the dependence of the evaporation transition rates on the vapourization coefficients to obtain

$$R_{\text{evap}}^{(1)}(n_1' n_2 \epsilon' | n_1 n_2 \epsilon) = \int_{-\infty}^{\infty} A(A(n_1 - 1, n_2)) \beta_1(x) \frac{c_{\text{eq}}(n_1 - 1, n_2, \epsilon - q_1 - x)}{c_{\text{eq}}(n_1 - 1, n_2, \epsilon)} \times \delta(\epsilon' - \{\epsilon - q_1 - x\}) \delta(n_1' - \{n_1 - 1\}) dx. \quad (48)$$

A similar result is obtained for $R_{\text{evap}}^{(2)}(n_1 n_2' \epsilon' | n_1 n_2 \epsilon)$.

The substitution of equations (46), (47) into equation (41), and their subsequent substitution into equation (40), followed by second-order Taylor expansion about (n_1, n_2, ϵ) yields

$$\begin{aligned} \frac{\partial}{\partial t} c(n_1, n_2, \epsilon; t) &= \int_{-\infty}^{\infty} dx \sum_{i=1}^2 \beta_i(x) \left\{ \left(\frac{\partial}{\partial n_i} + \delta\epsilon_i \frac{\partial}{\partial \epsilon} \right) [c_{\text{eq}}(n_1, n_2, \epsilon) A(n_1, n_2)] \right. \\ &\quad \times \left(\frac{\partial}{\partial n_i} + \delta\epsilon_i \frac{\partial}{\partial \epsilon} \right) \left[\frac{c(n_1, n_2, \epsilon; t)}{c_{\text{eq}}(n_1, n_2, \epsilon)} \right] + c_{\text{eq}}(n_1, n_2, \epsilon) A(n_1, n_2) \\ &\quad \left. \times \left(\frac{\partial^2}{\partial n_i^2} + 2\delta\epsilon_i \frac{\partial^2}{\partial n_i \partial \epsilon_i} + \delta\epsilon_i^2 \frac{\partial^2}{\partial \epsilon^2} \right) \left[\frac{c(n_1, n_2, \epsilon; t)}{c_{\text{eq}}(n_1, n_2, \epsilon)} \right] \right\} \quad (49) \end{aligned}$$

where we have defined the fluctuation terms as

$$\delta\epsilon_i = q_i + x \quad (i = 1, 2). \quad (50)$$

Integration over the energy fluctuations x involves the following integrals

$$\int_{-\infty}^{\infty} dx \beta_i(x) = \beta_i = p_{iv}/(2\pi m_i k_B T)^{1/2} \quad (i = 1, 2) \quad (51)$$

$$\frac{1}{\beta_i} \int_{-\infty}^{\infty} dx x \beta_i(x) dx = \bar{x} = 0 \quad (i = 1, 2) \quad (52)$$

$$\frac{1}{\beta_i} \int_{-\infty}^{\infty} dx \beta_i(x) (q_i + x)^2 = q_i^2 + \bar{x}^2 \quad (i = 1, 2). \quad (53)$$

The first equation, (51), is the impingement rate of species i (cf equation (11) in the first section), whereas the second equation (equation (52)) is zero by symmetry. The quantity q_i , the energy released upon addition of a monomer of vapour i to a cluster, has been discussed in the previous section. The mean-square energy fluctuations (equation (53)) of the impinging monomers is given by [1]

$$\bar{x}^2 = b^2 = \sum_{i=1,2} \left\{ \left(c_{iv} + \frac{1}{2} k_B \right) k_B T^2 + \frac{\beta_c}{\beta_i} \left(c_{iv,c} + \frac{1}{2} k_B \right) k_B T^2 \right\} \quad (54)$$

where β_c is the carrier-gas impingement frequency and $c_{iv,c}$ the specific heat of the carrier gas. The second term in equation (54) arises from the contribution of impinging carrier-gas molecules to the mean-square energy fluctuations. In the present work we do not consider carrier-gas contributions to the nucleation rate, and hence it is omitted in the calculations that are presented in the following section. An extensive treatment of carrier-gas effects is given in [35, 36].

After the evaluation of the integrals over the energy fluctuations we obtain the final expression for the time evolution of the concentration of clusters c , which, expressed in compact form, becomes

$$\begin{aligned} \frac{\partial}{\partial t} c(n_1, n_2, \epsilon; t) &= \left(\frac{\partial}{\partial n_1}, \frac{\partial}{\partial n_2}, \frac{\partial}{\partial \epsilon} \right) \\ &\times \left[c_{\text{eq}}(n_1, n_2, \epsilon) A(n_1, n_2) \beta_1 \Theta \begin{pmatrix} \partial/\partial n_1 \\ \partial/\partial n_2 \\ \partial/\partial \epsilon \end{pmatrix} \frac{c(n_1, n_2, \epsilon; t)}{c_{\text{eq}}(n_1, n_2, \epsilon)} \right]. \end{aligned} \quad (55)$$

The matrix Θ is given by

$$\Theta = \begin{pmatrix} 1 & 0 & q_1 \\ 0 & \beta_2/\beta_1 & \beta_2 q_2/\beta_1 \\ q_1 & \beta_2 q_2/\beta_1 & (q_1^2 + \bar{x}^2) + \beta_2 (q_2^2 + \bar{x}^2)/\beta_1 \end{pmatrix}. \quad (56)$$

Langer [24], in his statistical analysis of the decay of metastable states, developed a general method to obtain the steady-state solution of equations that arise in nucleation problems (which are similar to equation (55)). In the following we follow Langer's approach (which has also been used by Barrett in his analysis of unary nucleation [25]) to obtain the steady-state solution. In essence, the approach to obtaining the steady-state nucleation flux is based on the following observation. The phase transition from vapour to liquid is interpreted as a passage from one minimum (local) of the free energy of the system to the vicinity of another minimum (absolute) with lower free energy. The passage from one minimum to another is most likely to happen across the lowest intervening saddle point of the free energy. Therefore, the most important contribution to the nucleation flux arises from the solution of equation (55) in the immediate neighbourhood of the saddle point.

The equation is easier to solve in a coordinate system where the exponent of the equilibrium distribution is diagonal. We change coordinate systems from (n_1, n_2, ϵ) to a new coordinate system (x, y, z) such that the exponent of the equilibrium cluster distribution (equation (29)) is diagonal. Clearly, this coordinate transformation is a rotation whose matrix representation is an orthogonal matrix: the new variables (x, y, z) are related to the old ones (n_1, n_2, ϵ) by an orthogonal transformation which is represented by a matrix \mathbf{M} whose columns are the eigenvectors of the matrix

$$\begin{pmatrix} H_1^2/\sigma_\epsilon^2 - 1/\sigma_1^2 & H_1 H_2/\sigma_\epsilon^2 - 1/\sigma_{12}^2 & H_1/\sigma_\epsilon^2 \\ H_1 H_2/\sigma_\epsilon^2 - 1/\sigma_{12}^2 & H_2^2/\sigma_\epsilon^2 - 1/\sigma_2^2 & H_2/\sigma_\epsilon^2 \\ H_1/\sigma_\epsilon^2 & H_2/\sigma_\epsilon^2 & 1/\sigma_\epsilon^2 \end{pmatrix}. \quad (57)$$

The eigenvalues of this matrix are denoted by $\lambda_i, i = 1, 2, 3$. Since the free energy decreases in one direction of the saddle point (the direction of the stable phase) one eigenvalue (which is chosen to be λ_1) must be negative. In general, we expect that a number of eigenvalues will be identically zero corresponding to broken symmetries (for example, translational modes should have vanishing eigenvalues). We will return to this point in section 5 where the eigenvalues are numerically evaluated.

Under this rotation matrix Θ transforms as

$$\mathbf{M}^T \Theta \mathbf{M} = \Theta_{\text{new}} \quad (58)$$

and its elements are

$$\Theta_{\text{new}} = \begin{pmatrix} \theta_{11} & \theta_{12} & \theta_{13} \\ \theta_{12} & \theta_{22} & \theta_{23} \\ \theta_{13} & \theta_{23} & \theta_{33} \end{pmatrix}. \quad (59)$$

Note that Θ_{new} is symmetric since Θ was symmetric.

In the new coordinate system the steady-state equation for the cluster concentration in vector representation becomes

$$\nabla [c_{\text{eq}} A(n_1, n_2) \beta_1 \Theta_{\text{new}} \nabla F(x, y, z)] = 0 \quad (60)$$

where we have defined $F(x, y, z) = c/c_{\text{eq}}$. The explicit form of the steady-state equation in the new coordinate system is

$$\nabla \left\{ \frac{c_{\text{eq}}(n_1^*, n_2^*)}{(2\pi)^{1/2} \sigma_\epsilon} \exp[-\frac{1}{2}(\lambda_1 x^2 + \lambda_2 y^2 + \lambda_3 z^2)] A(n_1^*, n_2^*) \beta_1 \Theta_{\text{new}} \nabla F(x, y, z) \right\} = 0. \quad (61)$$

Following Langer [24] (and Barrett [25]) we make the ansatz that the solution $F(x, y, z)$ is a function of a linear combination of x, y and z according to the following definition

$$F(x, y, z) = f(v_1 x + v_2 y + v_3 z) \equiv f(u). \quad (62)$$

This ansatz can be justified *a posteriori* because it will be shown that it gives a solution of equation (60) with all the required properties, [25, 37]. Moreover, it can be justified by solving the time-dependent problem [24]. The substitution of equation (62) in equation (61) yields the following ordinary differential equation for the single-variable function $f(u)$

$$\begin{aligned} & (\theta_{11} v_1^2 + \theta_{12} v_1 v_2 + \theta_{13} v_1 v_3 + \theta_{22} v_2^2 + \theta_{23} v_2 v_3 + \theta_{33} v_3^2) \\ & \times f''(u) - [\lambda_1(\theta_{11} v_1 + \theta_{12} v_2 + \theta_{13} v_3)x + \lambda_2(\theta_{12} v_1 + \theta_{22} v_2 + \theta_{23} v_3)y \\ & + \lambda_3(\theta_{13} v_1 + \theta_{23} v_2 + \theta_{33} v_3)z] f'(u) = 0. \end{aligned} \quad (63)$$

Primes denote differentiation of f with respect to the variable u . According to the ansatz for the form of the solution of the steady-state equation the previous equation must contain

only functions of $u = v_1x + v_2y + v_3z$. Hence, the term in the curly brackets must be proportional to u

$$\begin{pmatrix} \lambda_1\theta_{11} & \lambda_1\theta_{12} & \lambda_1\theta_{13} \\ \lambda_2\theta_{12} & \lambda_2\theta_{22} & \lambda_2\theta_{23} \\ \lambda_3\theta_{13} & \lambda_3\theta_{23} & \lambda_3\theta_{33} \end{pmatrix} \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} = \kappa \begin{pmatrix} v_1 \\ v_2 \\ v_3 \end{pmatrix} \tag{64}$$

where κ is an eigenvalue of the matrix on the left-hand side of the previous equation.

From (64) it is easy to derive an important relation that will be used in the calculation of the total nucleation rate

$$\frac{v_1^2}{\lambda_1} + \frac{v_2^2}{\lambda_2} + \frac{v_3^2}{\lambda_3} = \Gamma \tag{65}$$

$$\Gamma = \frac{\theta_{11}v_1^2 + \theta_{22}v_2^2 + \theta_{33}v_3^2 + 2\theta_{12}v_1v_2 + 2\theta_{13}v_1v_3 + 2\theta_{23}v_2v_3}{\kappa} < 0. \tag{66}$$

When writing the expression for Γ we have assumed that κ is the negative eigenvalue of the matrix equation (64). This result is confirmed by our numerical calculations and it is consistent with the general analysis of the Fokker–Planck equation given by Langer [24], and the results of Barrett [25] for one-component nucleation. Physically, κ corresponds to the growth rate of the unstable mode at the saddle point (see [24]).

The solution of equation (63) that satisfies the condition $f(u) \rightarrow 1$ for $u \rightarrow -\infty$ is the function

$$f(u) = \frac{1}{2} \left[1 - \operatorname{erf} \left(\frac{u}{(2|\Gamma|)^{1/2}} \right) \right]. \tag{67}$$

When this solution is substituted into equation (61) the nucleation flux is determined if the components of the steady-state solution are identified with the steady-state components of nucleation flux, J_x , J_y and J_z . Under this identification we obtain

$$\begin{pmatrix} J_x \\ J_y \\ J_z \end{pmatrix} = -\frac{c_{\text{eq}}(n_1^*, n_2^*)}{2\pi\sigma_\epsilon|\Gamma|^{1/2}} A(n_1^*, n_2^*)\beta_1\kappa \begin{pmatrix} v_1/\lambda_1 \\ v_2/\lambda_2 \\ v_3/\lambda_3 \end{pmatrix} \times \exp \left\{ -\frac{1}{2} \left[\lambda_1x^2 + \lambda_2y^2 + \lambda_3z^2 + \frac{(v_1x + v_2y + v_3z)^2}{|\Gamma|} \right] \right\}. \tag{68}$$

The total nucleation rate is determined by integrating the flux \mathbf{J} across any surface not parallel to it [24]. For convenience we chose to integrate across the surface $x = 0$. The integration yields

$$J = \int_{-\infty}^{\infty} dy \int_{-\infty}^{\infty} dz J_x(0) = \frac{c_{\text{eq}}(n_1^*, n_2^*)}{(2\pi|\lambda_1|\lambda_2\lambda_3)^{1/2}\sigma_\epsilon} A(n_1^*, n_2^*)\beta_1|\kappa|. \tag{69}$$

In deriving the previous equation we used equations (65), (66) in the following form

$$1 + \frac{v_2^2}{\lambda_2|\Gamma|} + \frac{v_3^2}{\lambda_3|\Gamma|} = \frac{v_1^2}{|\lambda_1\Gamma|} \tag{70}$$

since λ_1 has been assumed to be the negative eigenvalue of the matrix shown in equation (57). The product of eigenvalues that appears in equation (69) is a general result, first derived in its full generality by Langer [24].

The previous equation may also be written in terms of the free energy of formation of a critical cluster as

$$J = \frac{\rho_v}{(2\pi|\lambda_1|\lambda_2\lambda_3)^{1/2}\sigma_\epsilon} A(n_1^*, n_2^*)\beta_1|\kappa| \exp(-\beta F^*) \tag{71}$$

where ρ_v is the total density of condensible vapours (cf equation (9)). In a future work we will show how our result compares with previous expressions for the nucleation rate. In particular, the limiting case of our result when energy fluctuations are neglected will be compared with the results of [18, 22].

The ratio between the new steady-state expression for the nucleation rate J and the classical expression is given by

$$\frac{J}{J_{\text{class}}} = \frac{\sigma_z}{\sigma_\epsilon} \frac{|\kappa|}{(|\lambda_1|\lambda_2\lambda_3)^{1/2}} \quad (72)$$

where σ_z is the Zeldovich factor in classical nucleation theory. For the classical nucleation rate J_{class} we have used an expression in terms of virtual monomers (cf section 2). In particular, the binary nucleation rate was evaluated according to the following expression [28]

$$J_{\text{class}} = \frac{\rho_v}{(2\pi)^{1/2}\sigma_z} A(n_1^*, n_2^*)\beta_1 \exp(-\beta F^*). \quad (73)$$

5. Results and discussion

The expression we derived for the total nucleation rate was evaluated for the water–ethanol binary system. The free energy derivatives and the other required quantities were evaluated as described in section 2. The numerical evaluation of eigenvalues and the eigenvectors was performed using routines reproduced in standard textbooks (for example those shown in [38]). The required thermodynamic data were obtained as described in great detail by Lazaridis *et al* [28] and Laaksonen [39].

We present three groups of figures. Figure 1 shows the temperature dependence of the ratio J/J_{class} and of the eigenvalues λ_i ($i = 1, 2, 3$), figure 2 shows their dependence on water activity, and figure 3 shows their dependence on ethanol activity. We show explicitly the dependence of the eigenvalues on the various parameters because the product of the eigenvalues is the new aspect of our result. All the eigenvalue figures show that there is a positive and a negative eigenvalue and one that is almost zero. As discussed in the text, the negative eigenvalue corresponds to fluctuations that stabilize the droplet, namely fluctuations in the direction of the stable, absolute free energy minimum. Inspection of the numerical values shows that the almost-zero eigenvalue is two to three orders of magnitude lower than the largest eigenvalue. It is important to remark that this eigenvalue is not identically zero (i.e. it does not correspond to a broken symmetry of the system) but it arises from the choice of binary system we are analysing. For the water–ethanol system the thermodynamic properties of water and ethanol we used are very similar and this almost numerical symmetry is reflected in the existence of an almost-zero eigenvalue.

Figure 1(b) shows the temperature dependence of the ratio J/J_{class} (water activity $A_{\text{water},v} = 0.8$ and ethanol activity $A_{\text{ethanol},v} = 1.2$). The results show that the ratio increases with increasing temperature. The maximum reported value occurs in the temperature range of interest (≈ 310 K) and its value is approximately 28. Figure 2(b) shows the dependence of the ratio on water activity (at 293 K and for ethanol activity 1.2). The ratio decreases with increasing water activity. The dependence of the ratio on water activity is more pronounced for water activities less than 1, an effect that is in agreement with experimental results [40]. The dependence of the ratio on ethanol activity is shown in figure 3(b) (at 220 K and for water activity 1.0). The results presented in the figure show that higher ethanol activities lead to lower values of the ratio. As in the case of unary nucleation [25] the effect of

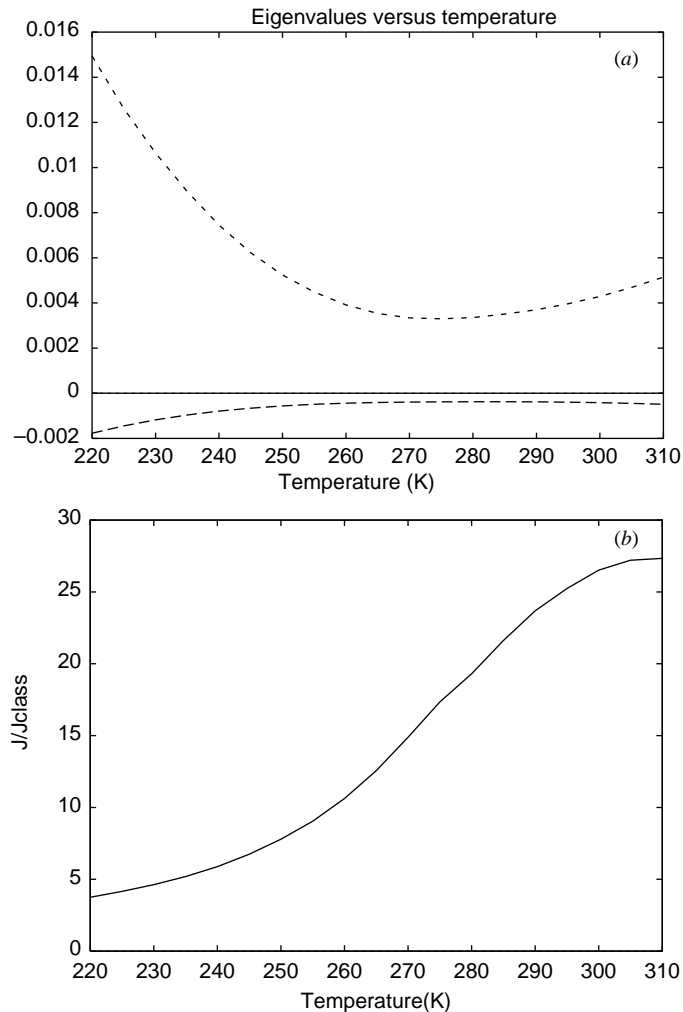


Figure 1. Numerical evaluations for the water–ethanol system at different temperatures. (a) Eigenvalues $\lambda_1, \lambda_2, \lambda_3$ versus temperature. (b) J/J_{class} versus temperature ($A_{\text{water},v} = 0.8, A_{\text{ethanol},v} = 1.2$).

energy fluctuations does not modify the classical result significantly, even though the trend, namely higher nucleation rates, improves the comparison with experimental data.

We also compare explicitly the predictions of our model with experimental data [40] as a function of temperature, water, and ethanol activity. These results are shown in table 1. We note (in conjunction with the results shown in the figures) that the predictions of our expression are in better agreement with the experimental data than the predictions of the classical theory. Nevertheless, the improvements made by the introduction cluster-energy fluctuations in the steady-state nucleation rate are not sufficient to explain in a satisfactory manner the experimental results for the water–ethanol system. A possible explanation of the disagreement of our results with experimental data is the neglect of surface enrichment of the alcohol at the surface of the binary droplet [39, 41].

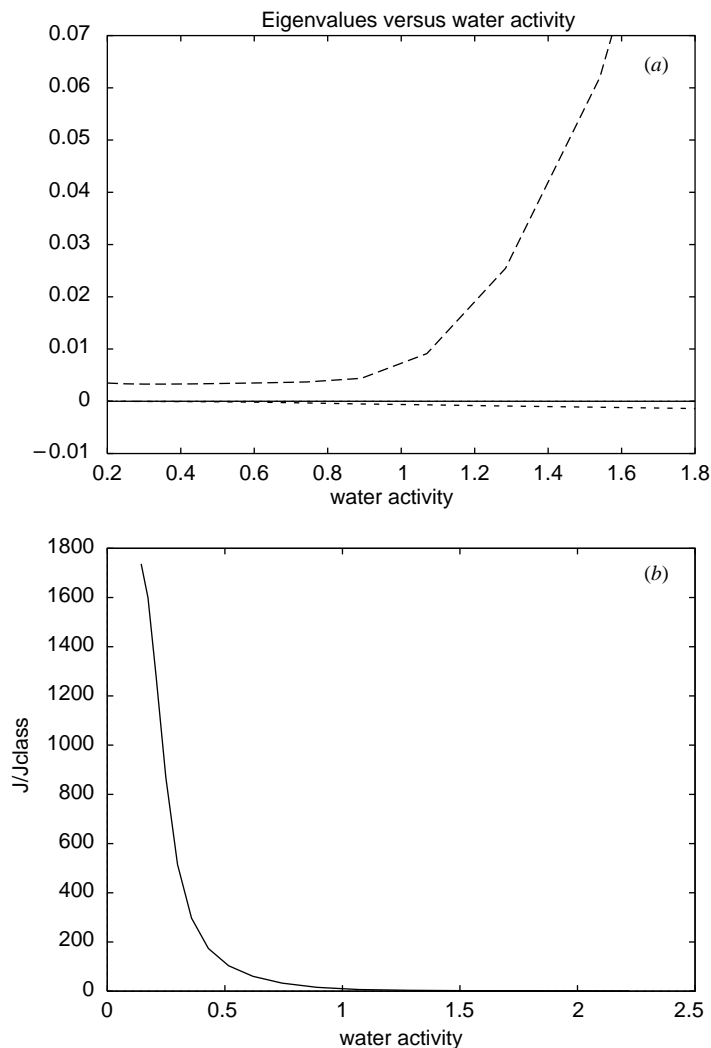


Figure 2. Numerical calculations for the water–ethanol system at different water activities. (a) Eigenvalues $\lambda_1, \lambda_2, \lambda_3$ versus water activity. (b) J/J_{class} versus water activity ($A_{\text{ethanol},v} = 1.2, T = 293.15 \text{ K}$).

6. Conclusions

We have derived an analytical expression for the total nucleation rate in a binary system that incorporates the combined effects of number and cluster-energy fluctuations. Whereas previous theories considered solely the effect of number fluctuations on the pre-exponential factor in the expression for the total nucleation rate we argue that the gain or loss of a monomer will also induce energy fluctuations. Our result is based on the derivation and steady-state solution of a Fokker–Planck equation for the cluster distribution in size and energy. The resulting equation is solved in the immediate neighbourhood of the saddle point since the main contribution to the nucleation rate arises from that region. The derivation and the solution of the Fokker–Planck equation follow the analysis of Langer [24] and

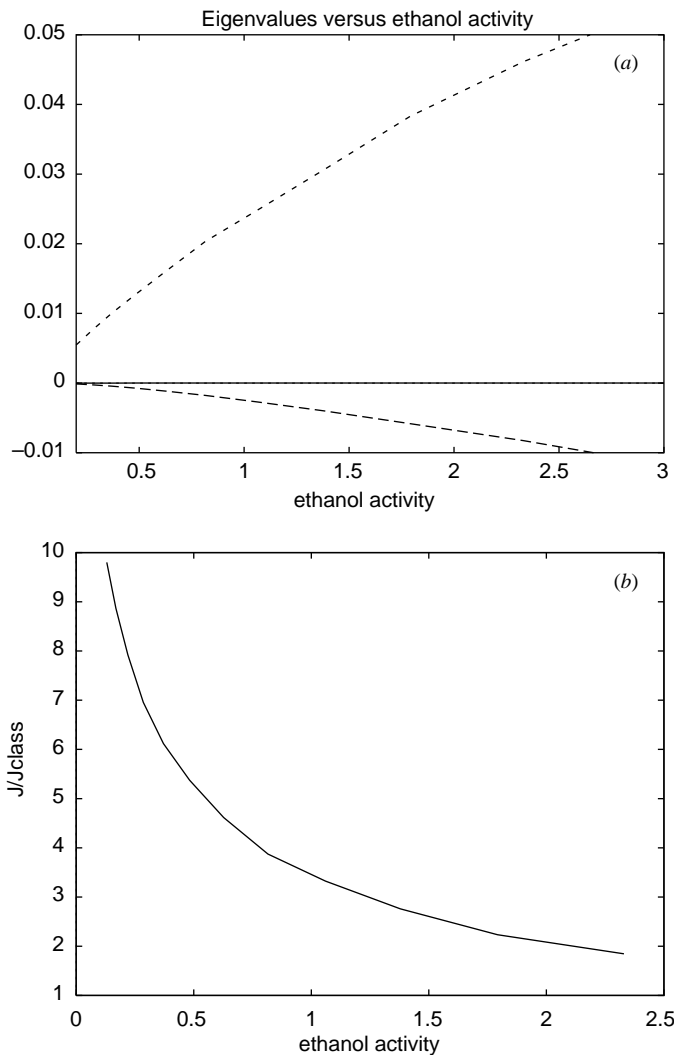


Figure 3. Numerical calculations for the water–ethanol system at different ethanol activities. (a) Eigenvalues $\lambda_1, \lambda_2, \lambda_3$ versus ethanol activity. (b) J/J_{class} versus ethanol activity ($A_{\text{water},v} = 1.0$, $T = 220.15$ K).

they may be considered as a generalization of Barrett's [25] analysis to two-component, homogeneous nucleation.

We show that a consistent treatment of fluctuations of three relevant variables (particle number of each species and cluster energy) renders the pre-exponential factor (kinetic prefactor) of the expression for the nucleation rate dependent on the product of three eigenvalues. These eigenvalues are determined from the matrix that describes the effect of fluctuations on the equilibrium cluster distribution. One of the eigenvalues is numerically shown to be negative, a result that is in agreement with general arguments about the decay of metastable states.

The general expression of the nucleation rate is numerically evaluated in the capillarity approximation and for droplets that form ideal solutions. Theoretical predictions are

Table 1. Comparison of theoretical predictions based on the expression that incorporates cluster-energy fluctuations, J_{theory} , with the experimental results, J_{exp} , of Schmitt *et al* [40] for the water–ethanol system. The nucleation rates are expressed in particles/cm³/s.

T	$A_{\text{water,g}}$	$A_{\text{ethanol,g}}$	J_{theory}	J_{exp}
263	0.459	2.111	7.4×10^{-2}	10^5
263	0.897	1.799	4.2×10^{-3}	10^3
263	0.923	1.847	1.6×10^{-1}	10^4
263	0.949	1.895	4.4×10^0	10^5
263	4.843	0.160	1.4×10^{-3}	10^4
263	5.957	0.0260	1.7×10^1	10^3
263	6.618	0.0233	2.0×10^3	10^5
273	0.434	1.947	5.8×10^{-2}	10^4
273	0.89	1.743	2.2×10^{-1}	10^3
273	0.938	1.827	8.8×10^1	10^5
273	4.074	0.148	1.2×10^{-4}	10^3
273	5.087	0.0197	2.0×10^1	10^3
273	5.609	0.0222	3.4×10^3	10^5
283	0.434	1.899	1.5×10^2	10^5
283	0.897	1.705	1.6×10^2	10^4
283	0.917	1.739	1.8×10^3	10^5
283	3.706	0.153	5.6×10^{-4}	10^4
283	4.468	0.0202	5.2×10^1	10^4
293	0.416	1.778	5.4×10^2	10^3
293	0.434	1.848	2.0×10^5	10^5
293	0.871	1.606	1.2×10^3	10^4
293	3.386	0.152	4.2×10^{-3}	10^4
293	4.064	0.0183	4.8×10^2	10^3

compared with experimental data for the water–ethanol binary system, and they are compared with predictions of the classical binary nucleation rate expressed in terms of virtual monomers. It is shown that the agreement between theoretical predictions and experimental results improves; nevertheless the agreement is not satisfactory. It is argued that a possible reason for the discrepancy is the neglect of surface enrichment.

In a future work our results will be compared with previous expressions for the binary nucleation rate [18,22] with an emphasis on the saddle-point evaluation of the nucleation rate and the effect of cluster-energy fluctuations on the direction of growth of the nucleating droplet. Another possible use of our work is its application to other binary systems, for example the water–sulphuric acid system [42]. The extension of our results to multicomponent nucleation is easily obtained.

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