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Binary nucleation kinetics. I. Self-consistent size distribution

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Using the principle of detailed balance, we derive a new self-consistency requirement, termed the kinetic product rule, relating the evaporation coefficients and equilibrium cluster distribution for a binary system. We use this result to demonstrate and resolve an inconsistency for an idealized Kelvin model of nucleation in a simple binary mixture. We next examine several common forms for the equilibrium distribution of binary clusters based on the capillarity approximation and ideal vapor behavior. We point out fundamental deficiencies for each expression. We also show that each distribution yields evaporation coefficients that formally satisfy the new kinetic product rule but are physically unsatisfactory because they depend on the monomer vapor concentrations. We then propose a new form of the binary distribution function that is free of the deficiencies of the previous functions except for its reliance on the capillarity approximation. This new self-consistent classical (SCC) size distribution for binary clusters has the following properties: It satisfies the law of mass action; it reduces to an SCC unary distribution for clusters of a single component; and it produces physically acceptable evaporation rate coefficients that also satisfy the new kinetic product rule. Since it is possible to construct other examples of similarly well-behaved distributions, our result is not unique in this respect, but it does give reasonable predictions. As an illustrative example, we calculate binary nucleation rates and vapor activities for the ethanol–hexanol system at 260 K using the new SCC distribution and compare them to experimental results. The theoretical rates are uniformly higher than the experimental values over the entire vapor composition range. Although the predicted activities are lower, we find good agreement between the measured and theoretical slope of the critical vapor activity curve at a constant nucleation rate of $10^7 \text{ cm}^{-3} \text{ s}^{-2}$. © 1995 American Institute of Physics.

I. INTRODUCTION

Recent work on the subject of binary and multicomponent nucleation has covered a wide range of topics: numerical^{1–3} and analytical^{4–6} solutions for steady state and transient rates, self-consistent distribution functions,⁷ density functional techniques for determining binary cluster free energies of formation,⁸ models for the cluster composition,^{9,10} accurate measurements of binary nucleation rates covering many orders of magnitude,^{11–13} rigorous means for determining critical cluster compositions from measured rates,^{12–14} and binary condensation measurements in supersonic nozzle expansions.¹⁵ With the availability of high quality experimental results covering a wide range of conditions, it is finally possible to critically assess the accuracy of competing theoretical rate expressions. However, in contrast to most theories of unary nucleation, all theoretical binary rate equations involve significant mathematical approximations in their development. Thus, in order to judge each theoretical rate expression fairly, it is important to understand how the predicted rates are affected by these approximations. At present this can be done only by comparing the predictions of the different rate expressions with exact numerical solutions of the population balance equations governing binary nucleation kinetics.

In our efforts to numerically solve these equations,¹⁶ we found it necessary to resolve several inconsistencies involv-

ing the kinetic and equilibrium aspects of the theory. Both aspects are related by the need to evaluate the evaporation rate coefficients using the principle of detailed balance and the equilibrium cluster size distribution. The difficulties involving the binary equilibrium distribution are related to issues of self-consistency for distributions in unary systems^{17,18} but are more complex. First, an acceptable binary equilibrium distribution should obey the law of mass action. Beyond satisfying this obvious and fundamental requirement, a binary distribution should also display appropriate limiting behavior as one component vanishes. From a purely formal standpoint, this is not an issue, since general statistical mechanical formulas for binary cluster concentrations produce formally consistent results for these limits. Formal results, however, are not very useful for doing calculations. Calculations always involve a model for determining the cluster free energy, so the issue reduces to what limiting behavior should apply to the model. For models treating molecular interactions based either directly or indirectly on statistical mechanics,⁸ the proper limiting behavior is guaranteed to emerge by doing the calculations correctly. Unfortunately, these models are currently impossible to apply to most substances of interest, and the only recourse is to more phenomenological approaches, usually based on the capillarity approximation.

What physical considerations can help define the limiting behavior of these models? Based on the asymptotic behavior of very large clusters, it seems reasonable to expect continuous behavior as one component is eliminated. In this case, the binary distribution should pass smoothly into a

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unary distribution of the same general form. For very small clusters this argument has no physical justification. Imposing this type of limiting behavior on the binary distribution for small cluster sizes is equivalent to making a postulate for mathematical convenience. It is directly analogous to insisting that a unary distribution vary smoothly for the smallest clusters sizes. Lacking a more fundamental alternative, however, it is this procedure that will be followed here.

In constructing a self-consistent binary distribution function, our primary goal is to avoid introducing any unphysical behavior into the reverse (or evaporation) rate coefficients required by the kinetics equations. Since these are determined using the binary distribution function and the principle of detailed balance, the distribution function must satisfy the minimum standards just set forth. For the theory to be kinetically consistent, two other conditions must be satisfied: The evaporation rate coefficients should be uniquely determined for each cluster composition, and they should not exhibit unphysical dependence on the monomer vapor concentrations or total pressure. At present, no binary distribution function based on the capillarity approximation meets all of the above requirements.

In this paper, we propose a new form of the binary equilibrium cluster size distribution that obeys the mass action law, reduces to appropriate forms for the unary distributions, and yields a unique and physically well-behaved evaporation rate coefficient for each cluster composition. Our new function is developed for the vapor-to-liquid transition in an ideal vapor, but the result can be readily generalized to other physical systems. Our new distribution is also based on the classical capillarity approximation because this model still provides the most practical means to make routine rate predictions. Our distribution is an *ad hoc* construction, but, as discussed in Appendix A, it has a form that is acceptable from the standpoint of statistical mechanics. Our other main result, which we call the kinetic product rule, is more general and does not depend on either ideal vapor behavior or the classical capillarity approximation, although it is limited to kinetic mechanisms in which clusters change only by the addition and removal of monomers.

The paper proceeds as follows. In Sec. II, we test several binary distribution functions for adherence to the mass action law and for proper reduction to unary distributions. Using detailed balancing in Sec. III, we develop a general self-consistency requirement, our kinetic product rule, that is a necessary, but not sufficient, condition for ensuring the acceptability of any set of evaporation rate coefficients. We then apply this requirement to an idealized Kelvin model introduced by Temkin and Shevelev¹⁹ and to the classical capillarity model to expose inconsistencies that render these approaches unsatisfactory. Next we propose a modified binary distribution function that overcomes these inconsistencies. Finally, in Sec. IV, we illustrate the quantitative effect of the new function on predicted nucleation behavior by comparing theoretical rates and activities with experimental values for the ethanol–hexanol system.¹²

II. MASS ACTION AND LIMITING CONSISTENCY

The law of mass action requires that $N(i, j)$, the equilibrium concentration of clusters containing i monomers of type A and j monomers of type B , be expressible in the form

$$N(i, j) = N_A^i N_B^j K(i, j), \quad (1)$$

where N_ν is the number density of monomers of species ν ($=A$ or B) in the vapor, and the equilibrium “constant” K is, in general, a function of i , j , and temperature, but it does not depend on N_A , N_B , or pressure when the vapor is regarded as ideal. The term “limiting consistency” was recently introduced in discussing the limiting behavior of unary distributions.¹⁷ A unary distribution function satisfies limiting consistency if it equals the monomer concentration when it is evaluated for a single monomer unit. Although there are no fundamental theoretical reasons for requiring this type of limiting consistency, when appropriately implemented it can improve the predicted temperature dependence of the nucleation rate. Here, we shall refer to this requirement as type I limiting consistency, since binary distributions of the sort we are considering should also satisfy a second kind of limiting consistency, which we will call type II. Type II limiting consistency requires that a binary distribution reduce to an appropriate unary distribution function when either $i=0$ or $j=0$, but this can be done without satisfying type I limiting consistency. For example, a binary distribution could reduce to a unary distribution of either the Frenkel²⁰ or Courtney²¹ form, neither of which satisfies type I limiting consistency.¹⁷

From the pioneering work of Reiss²² and as discussed in Appendix A, we know that any binary distribution function based on the capillarity approximation can be written in the form

$$N(i, j) = N_0 \left(\frac{N_A}{N_A^\infty(x_A)} \right)^i \left(\frac{N_B}{N_B^\infty(x_B)} \right)^j \exp \left(\frac{-\Omega^s(i, j)}{k_B T} \right), \quad (2)$$

where $N_\nu^\infty(x_\nu)$ is the equilibrium number density of monomers of species ν in a saturated vapor over a bulk solution whose composition will be denoted by either of the mole fractions x_A or x_B ,

$$x_B = 1 - x_A = j/(i + j), \quad (3)$$

for the average cluster composition. One should keep in mind that the actual composition used to determine the values of $N_A^\infty(x_A)$ and $N_B^\infty(x_B)$ may differ from the average cluster composition because of surface enrichment.^{8,13,23,24} Moreover, we have $\Omega^s(i, j) = \sigma(i, j)s(i, j)$, where $\sigma(i, j)$ and $s(i, j)$ are, respectively, the surface tension and surface area of the cluster, k_B is the Boltzmann constant, T is the absolute temperature, and N_0 is a “normalization” factor. If N_0 were solely a function of i , j , and T , Eq. (2) would clearly satisfy the law of mass action for ideal vapors. However, the most commonly used form for N_0 , developed by Reiss,²² is

$$N_0 = N_A + N_B, \quad (4)$$

which violates the mass action law, as was pointed out some time ago.²⁵ A related difficulty with Eq. (4) is its implication that the concentrations of pure A clusters, $N(i, 0)$, will de-

pend linearly on the concentration of B monomers and vice versa, as was first noted by Katz.²⁶ Thus, the most commonly used form of the binary distribution function does not satisfy either type of limiting consistency.

Kulmala, Laaksonen, and Gershick⁷ recently made the first attempt to impose both types of limiting consistency on the binary distribution, and their proposed distribution function (written in our notation) is

$$N(i, j) = [(1 - \delta_{0,i})N_A + (1 - \delta_{0,j})N_B] \times \left(\frac{N_A}{N_A^\infty(x_A)} \right)^{i-x_A} \left(\frac{N_B}{N_B^\infty(x_B)} \right)^{j-x_B} \times \exp\left(\frac{\Omega^s(i, j)}{k_B T} [1 - (i+j)^{-2/3}] \right). \quad (5)$$

For either pure component, this function does, in fact, reduce to the self-consistent classical (SCC) form^{27,28}

$$N_\nu(g) = N_\nu^\infty (N_\nu / N_\nu^\infty)^g \exp[-\Theta_\nu (g^{2/3} - 1)], \quad (6)$$

where $\Theta_\nu = \sigma_\nu s_\nu / (k_B T)$ and σ_ν and N_ν^∞ are, respectively, the surface tension and equilibrium monomer vapor concentration of a pure liquid of type ν . Nevertheless, Eq. (5) must be considered unacceptable because it violates the law of mass action for binary clusters. Because this distribution function cannot be written in the form of Eq. (1), it is impossible, in principle, to derive it from fundamentally sound statistical mechanics. This point is reinforced by the results in Appendix A.

Suppose we now evaluate Eq. (2) for each pure cluster distribution. We then find

$$N(i, 0) = N_0(i, 0) (N_A / N_A^\infty)^i \exp\left(\frac{-\Omega_A^s(i, 0)}{k_B T} \right), \quad (7)$$

$$N(0, j) = N_0(0, j) (N_B / N_B^\infty)^j \exp\left(\frac{-\Omega_B^s(0, j)}{k_B T} \right), \quad (8)$$

where we have explicitly displayed the dependence of N_0 on i and j but left the T dependence implicit. We have also assumed that the surface tension is independent of size for pure clusters, i.e.,

$$\Omega_A^s(i, 0) = \sigma(i, 0) s(i, 0) = k_B T \Theta_A i^{2/3}, \quad (9)$$

$$\Omega_B^s(0, j) = k_B T \Theta_B j^{2/3}. \quad (10)$$

If we now demand that Eqs. (7) and (8) satisfy type I limiting consistency by equating the SCC form of Eq. (6), we then conclude that

$$N_0(i, 0) = N_A^\infty \exp(\Theta_A), \quad (11)$$

$$N_0(0, j) = N_B^\infty \exp(\Theta_B). \quad (12)$$

The similarity of Eqs. (11) and (12) to the self-consistent correction factor found for the unary case is a deliberate consequence of using Eq. (6). Although the SCC distribution has no more fundamental justification than any other,^{17,18} it yields a better temperature dependence for the nucleation rate than do other forms of classical nucleation theory except for the Kelvin model.^{17,29} By incorporating the form of the unary SCC correction into the binary distribution, we hope to

achieve a similar improvement in the predicted temperature dependence of the binary rate. Equations (11) and (12) serve to outline the form of the general result we seek, but to finish our reasoning we need to consider the binary kinetics equations and address an inconsistency in their formulation. We tackle this in Sec. III.

III. BINARY KINETICS, DETAILED BALANCE, AND SELF-CONSISTENCY

A. General considerations

The binary kinetics equations are generalizations of the one-component equations and were first proposed by Reiss²² for the case in which growth and decay involves only monomer addition or evaporation. The net rates at which binary clusters of composition (i, j) become clusters of composition $(i+1, j)$ or $(i, j+1)$, respectively, are

$$J_A(i, j) = \Gamma_A(i, j) N_A f(i, j) - E_A(i+1, j) f(i+1, j), \quad (13)$$

$$J_B(i, j) = \Gamma_B(i, j) N_B f(i, j) - E_B(i, j+1) f(i, j+1), \quad (14)$$

where f is a nonequilibrium cluster concentration, and $\Gamma_\nu(i, j)$ and $E_\nu(i, j)$ are, respectively, the forward and reverse rate coefficients for the growth and decay of a cluster of composition (i, j) via the addition or evaporation of a monomer of species ν . In this paper, a specific form for $\Gamma_\nu(i, j)$ is not needed, so we defer this choice to our following paper.¹⁶ We only need to remember that $\Gamma_\nu(i, j)$ is determined by collisional cross-sections and mean molecular velocities, so it does not depend on either N_ν or N_ν^∞ . Likewise, for ideal vapor mixtures, the evaporation coefficients will not depend on N_A , N_B , or the total pressure.

Now apply detailed balancing to Eqs. (13) and (14) to obtain the following relations between successive values of $N(i, j)$:

$$\Gamma_A(i, j) N_A N(i, j) = E_A(i+1, j) N(i+1, j), \quad (15)$$

$$\Gamma_B(i, j) N_B N(i, j) = E_B(i, j+1) N(i, j+1). \quad (16)$$

These equations may be iterated to obtain the following expressions relating the binary equilibrium distribution function to the two unary distributions:

$$N(i, j) = N_A^i N(0, j) \prod_{k=1}^i \frac{\Gamma_A(k-1, j)}{E_A(k, j)}, \quad (17)$$

$$N(i, j) = N_B^j N(i, 0) \prod_{k=1}^j \frac{\Gamma_B(i, k-1)}{E_B(i, k)}. \quad (18)$$

They may also be used to express the unary distributions in similar fashion:

$$N(i, 0) = N_A^i \prod_{l=1}^i \frac{\Gamma_A(l-1, 0)}{E_A(l, 0)}, \quad (19)$$

$$N(0, j) = N_B^j \prod_{l=1}^j \frac{\Gamma_B(0, l-1)}{E_B(0, l)}, \quad (20)$$

provided the following quantities are all understood to equal unity (in their appropriate units): $N(0, 0)$, $\Gamma_A(0, 0)$,

$\Gamma_B(0,0)$, $E_A(1,0)$, and $E_B(0,1)$. Replacing the unary distributions in Eqs. (17) and (18) with the latter two expressions, we find

$$N(i,j) = N_A^i N_B^j \prod_{k=1}^i \frac{\Gamma_A(k-1,j)}{E_A(k,j)} \prod_{l=1}^j \frac{\Gamma_B(0,l-1)}{E_B(0,l)} \quad (21)$$

and

$$N(i,j) = N_B^j N_A^i \prod_{k=1}^j \frac{\Gamma_B(i,k-1)}{E_B(i,k)} \prod_{l=1}^i \frac{\Gamma_A(l-1,0)}{E_A(l,0)}. \quad (22)$$

To avoid confusion, throughout this paper any product with an upper index of 0 should be interpreted as equal to unity.

Since the products of kinetic coefficients are independent of N_A and N_B , these two equations verify that the usual binary rate equations are formally consistent with the law of mass action. However, these results have more than just formal significance since they provide a stringent test of the internal consistency of the theory when specific expressions are substituted for the kinetic coefficients. By equating Eqs. (21) and (22), we can frame this test in the form of a product rule,

$$\prod_{k=1}^i \frac{\Gamma_A(k-1,j)}{E_A(k,j)} \prod_{l=1}^j \frac{\Gamma_B(0,l-1)}{E_B(0,l)} = \prod_{l=1}^i \frac{\Gamma_A(l-1,0)}{E_A(l,0)} \prod_{k=1}^j \frac{\Gamma_B(i,k-1)}{E_B(i,k)}, \quad (23)$$

that must be satisfied by the kinetic coefficients. Alternatively, but perhaps easier to appreciate, the test can be posed in terms of the equivalent pairs of equations, Eqs. (17) and (18) or Eqs. (21) and (22). For a given set of kinetic coefficients, self-consistency demands that each of the paired equations must yield identical results for $N(i,j)$.

From the standpoint of equilibrium thermodynamics this requirement is obvious: $\ln N(i,j)$ is proportional to the free energy of cluster formation, and the free energy is a thermodynamic state function independent of the path. The paths used in formulating Eqs. (17)–(23) are not unique, but they are convenient for evaluating the consistency of the kinetic coefficients used in the theory. This connection with equilibrium thermodynamics can be formally strengthened by realizing that Eqs. (15) and (16) also provide kinetic definitions of equilibrium constants for the exchange of A and B monomers, respectively, between clusters of adjacent compositions. We briefly discuss this point in Appendix B.

We will close this section by considering the special case of the mixed dimer. For the mixed dimer, Eqs. (21) and (22) [or Eqs. (15) and (16)] simplify to the following expressions:

$$N(1,1) = N_A N_B \frac{\Gamma_A(0,1)}{E_A(1,1)}, \quad (24)$$

$$N(1,1) = N_B N_A \frac{\Gamma_B(1,0)}{E_B(1,1)}. \quad (25)$$

To properly assess these expressions, we must appreciate that there is only a single kinetic path for the formation of a mixed dimer. Thus the two, apparently different, rate equations, Eq. (13) with $i=0, j=1$ and Eq. (14) with $i=1, j=0$,

are degenerate, and $E_A(1,1)=E_B(1,1)$ and $\Gamma_A(0,1)=\Gamma_B(1,0)$ for obvious physical reasons: When a mixed dimer breaks up, it loses both an A and a B ; similarly, the collision frequency of an A with a B is the same as that of a B with an A . (We realize that dimer formation is actually a three body process, but this aspect is typically neglected in treating nucleation kinetics.) With these considerations, we see that Eqs. (24) and (25) are formally identical, but we haven't yet specified what $E(1,1)$ is, nor have we established which models for $N(i,j)$ lead to consistent values for E_A and E_B through Eqs. (15) and (16).

We will initially address this issue by reanalyzing an idealized Kelvin model for E_A and E_B first introduced by Temkin and Shevelev,¹⁹ whose results were later employed by Kožišek and Demo² in numerically solving the binary kinetics equations. The simplicity of this model permits us to answer directly the questions we are asking without concern for the complications that arise in treating more realistic cases.

B. Idealized Kelvin model

Temkin and Shevelev¹⁹ originally applied the Kelvin model to an idealized binary system with the following properties: constant surface tension, constant and equal partial molar volumes of the two components, and ideal solution behavior for the equilibrium partial pressures of the mixtures. Use of the Kelvin equation to evaluate the evaporation rate coefficients leads to the following two general expressions:

$$E_A(i,j) = \Gamma_A(i-1,j) N_A^\infty(x_A) \exp\left(\frac{2\sigma(i,j)v_A}{rk_B T}\right), \quad (26)$$

$$E_B(i,j) = \Gamma_B(i,j-1) N_B^\infty(x_B) \exp\left(\frac{2\sigma(i,j)v_B}{rk_B T}\right), \quad (27)$$

where v_A and v_B are the respective partial molecular volumes of species A and B , and r is the droplet radius. With the restrictions of the Temkin–Shevelev model, these equations simplify to

$$E_A(i,j) = \Gamma_A(i-1,j) x_A N_A^\infty \exp[\kappa(i+j)^{-1/3}], \quad (28)$$

$$E_B(i,j) = \Gamma_B(i,j-1) x_B N_B^\infty \exp[\kappa(i+j)^{-1/3}], \quad (29)$$

where $\kappa=2\Theta/3$, and no subscripts are needed. If we use these two expressions to evaluate Eqs. (17) and (18), and use the following unary distribution function¹⁷ for the Kelvin model,

$$N_\nu(g) = N_\nu^\infty \left(\frac{N_\nu}{N_\nu^\infty}\right)^g \exp\left[-\kappa\left(\sum_{j=1}^g j^{-1/3} - 1\right)\right], \quad (30)$$

to consistently evaluate $N(i,0)$ and $N(0,j)$, we obtain the following results for $N(i,j)$:

$$N(i,j) = N_A^\infty \left(\frac{N_A}{N_A^\infty}\right)^i \left(\frac{N_B}{N_B^\infty}\right)^j \frac{(i+j)!}{i!j!} \times \exp\left[-\kappa\left(\sum_{l=1}^{i+j} l^{-1/3} - 1\right)\right] \quad (31)$$

from Eqs. (17) and (28), and

$$N(i,j) = N_B^\infty \left(\frac{N_A}{N_A^\infty} \right)^i \left(\frac{N_B}{N_B^\infty} \right)^j \frac{(i+j)!}{i!j!} \times \exp \left[-\kappa \left(\sum_{l=1}^{i+j} l^{-1/3} - 1 \right) \right] \quad (32)$$

from Eqs. (18) and (29).

Because N_A^∞ and N_B^∞ are generally different, we have found two conflicting expressions for $N(i,j)$, and this discordance must reflect some fundamental inadequacy in the construction of the evaporation coefficients. Temkin and Shevelev do not indicate in their paper that they were aware of the difficulty that we have just exposed. In fact, their result for $N(i,j)$ differs from either Eq. (31) or (32) and amounts to replacing the leading factor of either N_A^∞ [in Eq. (31)] or N_B^∞ [in Eq. (32)] with $(N_A + N_B) \exp(-\kappa)$, which violates the law of mass action and both types of limiting consistency. However, it does possess some of the symmetry that a fully satisfactory distribution function must have. We also note that the more general analysis of the nucleation rate by Temkin and Shevelev is not invalidated by this deficiency; only their results that depend specifically on the prefactor are affected.

There is one trivial way to reconcile the correct, but inconsistent, solutions for the Temkin–Shevelev model. This possibility is based on the argument that the mixture properties assumed by Temkin and Shevelev are so restrictive that they also imply that $N_A^\infty = N_B^\infty$, thus making Eqs. (31) and (32) identical. However, this expedient clearly fails in every other case, and a more general solution is needed. At the outset it seems fair to point out that we do not have a rigorous derivation of our final result. We can supply only a heuristic argument to generate it, but our final result is at least consistent with the general functional form obtained from statistical mechanics in Appendix A. To illustrate our thinking we first consider the equilibrium concentration of mixed dimers.

From detailed balance for the equilibrium of monomers and mixed dimers we know that

$$\Gamma_{AB} N_A N_B = E(1,1) N(1,1), \quad (33)$$

where $\Gamma_{AB} = \Gamma_A(0,1) = \Gamma_B(1,0)$. Even with this latter equality, we see that Eqs. (28) and (29) yield different results for $E(1,1)$. In order to write a satisfactory expression for $E(1,1)$, it is helpful to recognize that the inequality of $E_A(1,1)$ and $E_B(1,1)$ for this model stems from approximating a mixed dimer as a 50–50 bulk solution. This practically guarantees that the evaporation coefficients will differ since the equilibrium number densities (or vapor pressures) for a 50–50 mixture are almost never equal, even for ideal solutions. Now to correct this deficiency we write an equation that is analogous to Eqs. (28) and (29),

$$E(1,1) = \Gamma_{AB} N_{AB}^\infty \exp(\kappa/2^{1/3}), \quad (34)$$

but where N_{AB}^∞ represents an effective monomer number density that accounts in some symmetric way for the influence of both A and B on the mixed dimer breakup rate. A simple and acceptable expression for N_{AB}^∞ results from taking the harmonic mean of the product of the individual equilibrium number densities of an ideal 50–50 mixture,

$$N_{AB}^\infty = [N_A^\infty(1/2)N_B^\infty(1/2)]^{1/2} = \frac{1}{2}(N_A^\infty N_B^\infty)^{1/2}. \quad (35)$$

From Eqs. (33) and (34), we then find the following result for $N(1,1)$:

$$N(1,1) = 2(N_A^\infty N_B^\infty)^{1/2} \frac{N_A}{N_A^\infty} \frac{N_B}{N_B^\infty} \exp(-\kappa/2^{1/3}), \quad (36)$$

which does not appear to violate any physical or chemical principles. Although, the prefactor $(N_A^\infty N_B^\infty)^{1/2}$ works fine for the mixed dimer, it does not suffice for any other case. However, the form of this term suggests that a general prefactor of the type $(N_A^\infty)^a (N_B^\infty)^b$, where $a + b = 1$ to preserve proper dimensionality, would be satisfactory. To ensure that the unary distributions are properly recovered, the exponents a and b must be functions of composition such that $a = 1$ and $b = 0$ when $j = 0$ and vice versa when $i = 0$. Without further justification, we therefore propose the following expression for $N(i,j)$:

$$N(i,j) = (N_A^\infty)^{x_A} (N_B^\infty)^{x_B} \left(\frac{N_A}{N_A^\infty} \right)^i \left(\frac{N_B}{N_B^\infty} \right)^j \frac{(i+j)!}{i!j!} \times \exp \left[-\kappa \left(\sum_{l=1}^{i+j} l^{-1/3} - 1 \right) \right]. \quad (37)$$

This expression reproduces the results of Eqs. (34) and (36) and reduces properly to Eq. (30) for the unary distribution when either $i = 0$ or $j = 0$. It will not, of course, reproduce exactly the expressions for E_A and E_B in Eqs. (28) and (29), but this is desirable since those expressions were responsible for the inconsistent results in Eqs. (31) and (32). The new self-consistent expressions are

$$E_A(i,j) = \Gamma_A(i-1, j) x_A N_A^\infty \left(\frac{N_B^\infty}{N_A^\infty} \right)^{x_B/(i+j-1)} \times \exp[\kappa(i+j)^{-1/3}] \quad (38)$$

and

$$E_B(i,j) = \Gamma_B(i, j-1) x_B N_B^\infty \left(\frac{N_A^\infty}{N_B^\infty} \right)^{x_A/(i+j-1)} \times \exp[\kappa(i+j)^{-1/3}]. \quad (39)$$

These expressions differ from those of Temkin and Shevelev only by the factors exponentiated with x_B and x_A , but these factors are decisive in providing self-consistency to this model. For small, nonzero values of i and j , the new expressions will differ considerably from the old, but their functional dependence on thermodynamic variables is now presumably sounder, at least qualitatively. For large values of i and j , the new expressions will differ very slightly from the old, but the accumulated product of these small differences is now enough to ensure that the product rules, Eqs. (17)–(23), are satisfied.

C. General equilibrium distribution

Now we consider how to generalize these results to less restrictive mixture models. We present our discussion in terms of Eq. (2), the distribution function based on the usual form of the capillarity approximation, since it already con-

tains all of the elements needed to treat realistic solution models. We proceed by temporarily assuming that the normalization factor N_0 is independent of i and j and by pursuing an apparently circular argument that follows closely the steps used in analyzing the idealized Kelvin model.

Thus, we first use Eqs. (2), (15), and (16) for all i and j to obtain the following expressions for the evaporation coefficients:

$$E_A^0(i, j) = \Gamma_A(i-1, j) N_A^\infty(x_A) \left(\frac{N_A^\infty(x_A)}{N_A^\infty(x'_A)} \right)^{i-1} \left(\frac{N_B^\infty(x_B)}{N_B^\infty(x'_B)} \right)^j \times \exp\left(\frac{\Omega^s(i, j) - \Omega^s(i-1, j)}{k_B T} \right), \quad (40)$$

$$E_B^0(i, j) = \Gamma_B(i, j-1) N_B^\infty(x_B) \left(\frac{N_A^\infty(x_A)}{N_A^\infty(x''_A)} \right)^i \left(\frac{N_B^\infty(x_B)}{N_B^\infty(x''_B)} \right)^{j-1} \times \exp\left(\frac{\Omega^s(i, j) - \Omega^s(i, j-1)}{k_B T} \right), \quad (41)$$

where x' and x'' refer to compositions evaluated with one less A and B monomer, respectively, than the unprimed values. We use the superscript zero on E_A and E_B to indicate that these results were derived using a constant N_0 . Note that using the Reiss form for N_0 , Eq. (4), gives identical results.

Although these expressions appear physically reasonable, they do not satisfy the kinetic product rule, Eq. (23). This basic inconsistency results from two deficiencies of Eqs. (40) and (41): They fail to give the correct values (for this model) for the two pure dimer evaporation coefficients and they do not produce a unique result for the mixed dimer evaporation coefficient, even when $\Gamma_A(0,1) = \Gamma_B(1,0) = \Gamma_{AB}$. The reason for these difficulties becomes apparent when we directly examine the detailed balance equations, Eqs. (15) and (16), for the compositions in question. In these cases, the expressions for $E_A(1,1)$, $E_B(1,1)$, $E_A(2,0)$, and $E_B(0,2)$ involve the monomer densities, N_A or N_B , disguised as the factors $N(1,0)$ or $N(0,1)$, respectively. The use of Eq. (2) with constant N_0 for these two monomer concentrations is physically incorrect and leads to the difficulties just noted.

Suppose we now evaluate the evaporation coefficients more carefully using a slightly more general model in which we allow N_0 for each unary distribution to differ from the value used for the binary distribution. Note that this means we are temporarily sacrificing type II limiting consistency. Then Eqs. (40) and (41) still hold for most values of i and j , but several modifications must be noted. First, for $i=1$ and $j>1$ we find

$$E_A^i(1, j) = \frac{N_{0,B}}{N_0} E_A^0(1, j), \quad (42)$$

and for $j=1$ and $i>1$ we also have

$$E_B^i(i, 1) = \frac{N_{0,A}}{N_0} E_B^0(i, 1). \quad (43)$$

Here the new values are denoted by primes, E_A^0 and E_B^0 are still given by Eqs. (40) and (41), and $N_{0,A}$ and $N_{0,B}$ are unary normalizing factors such as, but not necessarily, those in Eqs. (11) and (12). For the special dimeric cases we find

$$E'(1,1) = \frac{1}{N_0} \Gamma_{AB} N_A^\infty(\frac{1}{2}) N_B^\infty(\frac{1}{2}) \exp\left(\frac{\Omega^s(1,1)}{k_B T} \right), \quad (44)$$

$$E'_A(2,0) = \frac{1}{N_{0,A}} \Gamma_A(1,0) (N_A^\infty)^2 \exp\left(\frac{\Omega^s(2,0)}{k_B T} \right), \quad (45)$$

$$E'_B(0,2) = \frac{1}{N_{0,B}} \Gamma_B(0,1) (N_B^\infty)^2 \exp\left(\frac{\Omega^s(0,2)}{k_B T} \right). \quad (46)$$

When these expressions are used to replace the corresponding faulty E^0 values, the kinetic product rule is satisfied. This means that the amended set of evaporation coefficients could be used as a basis for a self-consistent kinetics scheme. Type II limiting consistency can be recovered, if desired, simply by letting $N_0 = N_{0,A} = N_{0,B}$, but not if the Reiss value for N_0 , Eq. (4), is used. This value is unacceptable for use in these coefficients not only for the reasons given in Sec. II, but also because it forces some of the evaporation coefficients given by Eqs. (42)–(46) to depend on N_A and N_B . This is physically incorrect. Thus, the price for using Eqs. (2) and (4) and achieving consistency with the kinetic product rule is a set of evaporation coefficients that is partially unphysical. Although the evaporation coefficients derived from the Kulmala, Laaksonen, and Gershick distribution⁷ formally satisfy the kinetic product rule they also pay the price of being unphysical by depending on N_A and N_B .

It is also important to appreciate that a numerical solution of the full set of binary kinetics equations using Eqs. (40) and (41) at every composition will lead to steady state rates that differ significantly from those predicted using the standard Reiss formula for the nucleation rate. Moreover, this disparity has nothing to do with the saddle point approximation used to derive the formula of Reiss.¹⁶ The reason is that, besides giving a nonunique value for $E(1,1)$, Eqs. (40) and (41) also give the SCC values for the pure dimer evaporation rates, but these are not the correct values to use with the Reiss theory, as seen from Eqs. (45) and (46). In their vapor-to-liquid modeling, Kožiček and Demo² used Eqs. (40) and (41), but there is no indication that they corrected for the problems just noted. Thus, they cannot fairly compare their numerical results with the analytical results using the Reiss distribution, and their conclusions based on such comparisons need to be reevaluated.

The modified set of evaporation coefficients represented by Eqs. (40)–(46) works with any values of the constants N_0 , $N_{0,A}$, and $N_{0,B}$. If we follow the arguments of Weakliem and Reiss,¹⁸ we see that these constants can be interpreted as reference cluster concentrations in any arbitrary standard state. Reimposing type II limiting consistency in this case is equivalent to using the same standard state for each type of cluster, which is perfectly acceptable, even desirable. Beyond this we have no fundamental guidelines to help us evaluate these constants. Moreover, even if we somehow select “reasonable” values for them, we do not expect to find much, if any, improvement in the predicted temperature dependence of the binary nucleation rate. This is because the rates will only differ by the factor $N_0/(N_A + N_B)$ from those of the standard Reiss theory. Thus, we will adopt a different *ad hoc* approach and invent an expression for N_0 that is an

analogue of the unary SCC result. We have two motives for doing this. One is formal: to illustrate some sort of dependence on i and j as demonstrated in Appendix A. The other is pragmatic: the unary SCC model appears, along with the Kelvin model, to predict a better temperature dependence for the nucleation rate than other versions of classical theory based on the simple capillarity approximation.^{17,29} We hope and expect that an appropriate binary SCC model will show a comparable degree of improvement.

We proceed by naively using Eqs. (40) and (41) to evaluate the kinetic product rule, Eq. (23). Note that this is equivalent to evaluating the intermediate formulas, Eqs. (17) and (18), with the unary SCC distribution functions, defined by Eq. (6), because the unary SCC evaporation coefficients are given precisely by Eqs. (40) and (41). Moreover, we already know that the unary SCC distribution function and evaporation coefficients are fully consistent. The result of this procedure is that the kinetic product rule can only be satisfied if

$$N_0(i,0) = N_0(0,j), \quad (47)$$

but the latter two normalizing factors were previously defined in Eqs. (11) and (12), and they are obviously different from each other.

This contradiction resembles the situation previously encountered for the idealized Kelvin model. By reasoning analogously to that case, we resolve this difficulty by proposing the following composition dependence for N_0 :

$$N_0(i,j) = [N_0(i,0)]^{x_A} [N_0(0,j)]^{x_B}. \quad (48)$$

Thus, the final form of our proposed equilibrium distribution follows from Eqs. (2) and (48),

$$N(i,j) = (N_A^\infty)^{x_A} (N_B^\infty)^{x_B} \exp(x_A \Theta_A + x_B \Theta_B) \times \left(\frac{N_A}{N_A^\infty(x_A)} \right)^i \left(\frac{N_B}{N_B^\infty(x_B)} \right)^j \exp\left(\frac{-\Omega^s(i,j)}{k_B T} \right). \quad (49)$$

This form preserves the proper dimensionality of $N(i,j)$, satisfies the law of mass action, and yields proper expressions for $N(i,j)$ in all appropriate limiting cases. Moreover, when the evaporation coefficients are evaluated from Eqs. (15) and (16), the following expressions are found:

$$E_A(i,j) = \left(\frac{N_B^\infty}{N_A^\infty} \right)^{x_B/(i+j-1)} \exp\left[\frac{x_B}{i+j-1} (\Theta_B - \Theta_A) \right] E_A^0(i,j), \quad (50)$$

$$E_B(i,j) = \left(\frac{N_A^\infty}{N_B^\infty} \right)^{x_A/(i+j-1)} \exp\left[\frac{x_A}{i+j-1} (\Theta_A - \Theta_B) \right] E_B^0(i,j). \quad (51)$$

These expressions appear to be physically well behaved, are fully self-consistent, and are now valid for all values of i and j in contrast with Eqs. (40) and (41). The factors exponentiated with x_A or x_B account for these improvements. The first factor is responsible for ensuring type II limiting consistency while the second factor, involving the Θ factors, provides type I limiting consistency. As for the Kelvin model, these factors deviate significantly from unity for small, nonzero values of i and j , they approach unity for large values of i and j , and they are always essential if the product rules, Eqs.

(17)–(23), are to be satisfied. For large i and j , either the new or old evaporation coefficients revert to a close approximation to the Kelvin forms, Eqs. (26) and (27), but in contrast to Eqs. (40) and (41) the new expressions yield a unique result for $E(1,1)$:

$$E(1,1) = \Gamma_{AB} \frac{N_A^\infty(\frac{1}{2}) N_B^\infty(\frac{1}{2})}{(N_A^\infty N_B^\infty)^{1/2}} \exp\left(\frac{\Omega^s(1,1)}{k_B T} - \frac{(\Theta_A + \Theta_B)}{2} \right). \quad (52)$$

The idealized Kelvin model, which we treated earlier in Sec. III B, has little practical value, but there is pedagogic interest in comparing our Kelvin results with those derived from our general expressions for the same idealized solution model. Thus, if we specialize Eq. (52) to this case, we obtain an expression that closely resembles the results we proposed earlier in Eqs. (34) and (35). If we similarly evaluate $N(1,1)$ by specializing Eq. (49), we find an expression that is closely related to our earlier result in Eq. (36). The general formula for $N(i,j)$ obtained from Eq. (49) for this idealized solution model is very similar to our earlier result in Eq. (37): Numerical factors in the prefactor differ slightly due to differences between factorials and power laws; numerical differences in the argument of the exponential term also occur, and these are identical to those found between the SCC and Kelvin results in the unary case.¹⁷

Finally, by neglecting the monomeric surface free energy terms, we obtain a binary distribution function that is analogous to the Courtney²¹ distribution for unary systems:

$$N(i,j) = (N_A^\infty)^{x_A} (N_B^\infty)^{x_B} \left(\frac{N_A}{N_A^\infty(x_A)} \right)^i \left(\frac{N_B}{N_B^\infty(x_B)} \right)^j \times \exp\left(\frac{-\Omega^s(i,j)}{k_B T} \right). \quad (53)$$

This distribution will not yield the correct monomer limiting values, and so it should not be used for the compositions (1,0) and (0,1), but it is fully consistent in all other respects. The evaporation coefficients corresponding to this distribution can be obtained from Eqs. (50) and (51) by neglecting the factors containing Θ_A and Θ_B , provided care is taken to eliminate additional Θ factors that occur in $E_A(1,1)$, $E_A(2,0)$, $E_B(1,1)$, and $E_B(0,2)$.

These are just two examples of many possible binary distribution functions that agree in form with the general result obtained in Appendix A. As demonstrated by Weakliem and Reiss¹⁸ for the case of unary distributions, each of these binary distributions is the product of treating the translational degrees of freedom of the cluster in an uncontrolled, and presumably deficient, manner. Until a correct molecular theory is available to provide better guidance, we will have to rely on pragmatic considerations to provide some empirical justification for these treatments.

IV. ILLUSTRATIVE NUMERICAL RESULTS

Changes to the equilibrium distribution will directly affect the numerical values of theoretically predicted nucleation rates in both binary and unary nucleation. To illustrate the magnitude of this effect we compared various theoretical

predictions with the recent experimental results of Strey and Viisanen¹² for binary nucleation at 260 K in the ethanol–hexanol system. Although binary nucleation rate measurements exist for more complex mixtures, for example, alcohol–water systems,¹¹ we chose the ethanol–hexanol data for the following reasons: (1) Ethanol and hexanol form ideal liquid mixtures; (2) the surface tensions of the pure components are nearly identical, thus, surface enrichment effects are negligible; (3) all of the experiments were conducted using essentially ideal, dilute gas mixtures; (4) the nucleation rates were measured at constant temperature. Within the framework of classical nucleation theory, comparisons with these rate data are straightforward and are not complicated by the effects of surface enrichment on the structure of the cluster. Please note, however, that these simplifications are a matter of convenience, not necessity. Rate calculations with our SCC binary cluster distribution are not precluded for nonideal mixtures, since the formalism does not rely on liquid mixture ideality, and the effects of cluster structure could be handled as in Refs. 9 and 10, for example. Eliminating these two effects from our illustrative calculations focuses attention solely on the new factors present in our SCC distribution function.

Theoretical nucleation rates or activities were calculated from rate expressions due to Stauffer³⁰ and Reiss.²² Saddle point compositions and free energies were computed using the corrected classical theory as described in Refs. 12 and 23 with values of the physical constants from Ref. 12. The transition to unary nucleation was handled similarly to earlier work,²⁵ with a modified definition of the rate that is fully described elsewhere.¹⁶ Figures 1(a) and 1(b) compare the experimental data with nucleation rates predicted using Stauffer's rate formula with our SCC distribution, Eq. (49), and the Reiss distribution. The rates are plotted versus the mean value a of the individual vapor species activities, a_E and a_H , where $a = (a_E^2 + a_H^2)^{1/2}$, and the separate data sets correspond to constant values of the activity fraction $y = a_H/(a_E + a_H)$. We have plotted only half of the experimental data to avoid confusion. Although the Reiss distribution gives a better fit to the experimental data for $y < 0.9$, it severely underpredicts the rates for $y \rightarrow 1$. Our proposed distribution, on the other hand, consistently overpredicts the rates somewhat, but it does a better job as $y \rightarrow 1$.

Figure 2 presents the same data as an activity plot for the constant rate of $J = 10^7 \text{ cm}^{-3} \text{ s}^{-1}$. The activities predicted using our SCC distribution parallel the experimental points quite well, although they are somewhat lower. The results calculated using the Reiss distribution do not follow the trend of the data as well, although the absolute fit is better at the higher ethanol activities. We do not expect our SCC distribution to always improve the agreement between binary nucleation experiments and theory because it still relies on the capillarity approximation rather than on a more realistic cluster model. Nevertheless, for cases where SCC theory does a better job of predicting the unary rates, this distribution provides a reasonable binary analogue. Our distribution should also do a better job of predicting the temperature dependence of binary nucleation rates in the same way that the SCC theory does for unary systems.²⁹

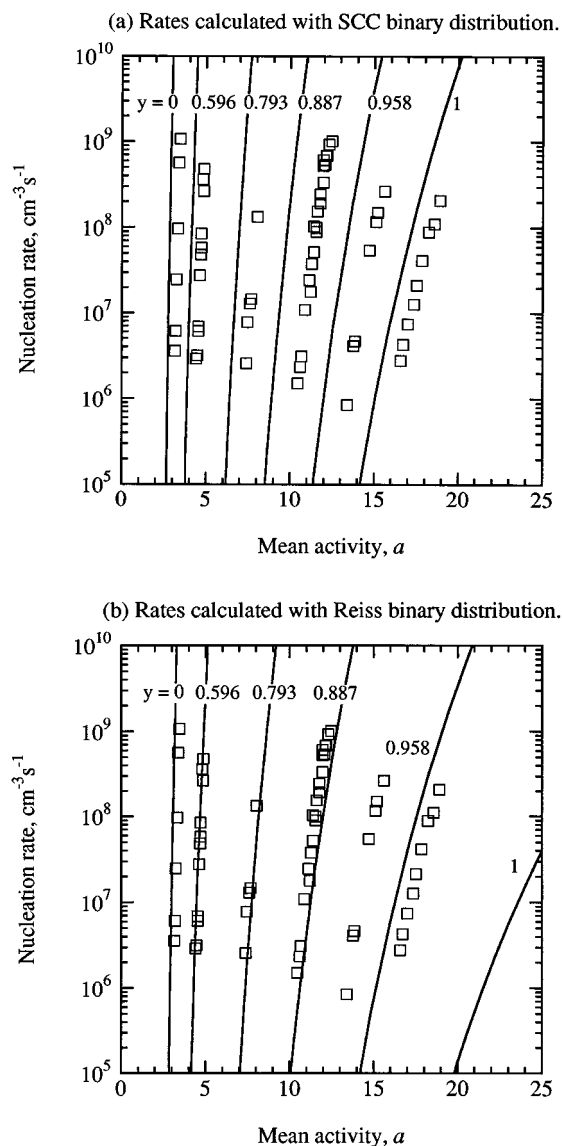


FIG. 1. Nucleation rates at 260 K in the ethanol–hexanol system plotted vs a mean value a of the individual species activities, a_E and a_H , where $a = (a_E^2 + a_H^2)^{1/2}$. The open squares are the data of Strey and Viisanen (Ref. 12). The solid lines are the nucleation rates calculated at the indicated activity fractions, $y = a_H/(a_E + a_H)$, using Stauffer's nucleation rate expression and (a) our SCC binary distribution function or (b) the Reiss binary distribution function.

V. SUMMARY AND CONCLUSIONS

Using the principle of detailed balance, we derived a new kinetic self-consistency requirement relating the evaporation coefficients and equilibrium cluster distribution for a binary system. We first used this result to demonstrate and resolve an inconsistency in the results for an idealized Kelvin model of a simple binary mixture. We then examined several forms of the binary equilibrium distribution based on the capillarity approximation. We showed that although each distribution yields sets of evaporation coefficients that are formally consistent with the kinetic product rules, Eqs. (17)–(23), all or some of these coefficients are physically

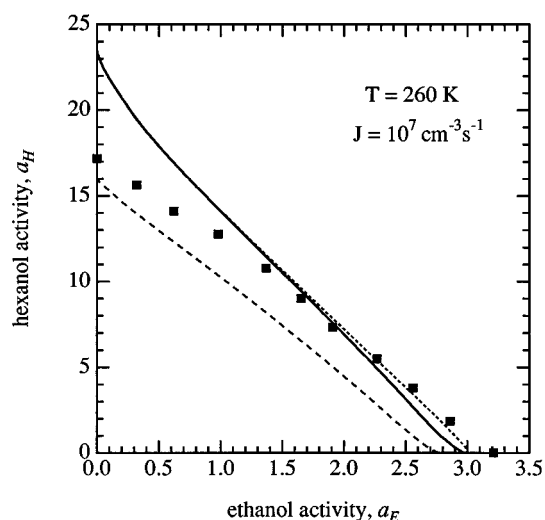


FIG. 2. Activities of ethanol and hexanol required to produce a nucleation rate of $J=10^7 \text{ cm}^{-3} \text{ s}^{-1}$ at 260 K. The solid squares are logarithmically interpolated from the tabulated data of Strey and Viisanen (Ref. 12). The bottom line (long dashes) was calculated using the Stauffer rate expression and our SCC binary cluster distribution. The upper lines use the Reiss binary cluster distribution and either the Stauffer (solid) or the Reiss (short dashes) expressions for the nucleation rate.

unacceptable because they are functions of the monomer vapor concentrations. As examples of acceptable results, we then proposed several new forms for the binary distribution function and evaporation coefficients based on the capillarity approximation that satisfy the degrees of self-consistency investigated here. Finally, we compared experimental binary nucleation rates and vapor activities with theoretical values predicted using our binary SCC distribution in combination with Stauffer's rate formula. While we neither expected nor found perfect agreement, we did note improvement in the predicted slope of the critical vapor activity curve at constant nucleation rate, and we anticipate that the predicted temperature dependence of the rate will also improve.

Although the considerations presented here may appear tedious, they are necessary to make consistent comparisons between analytical and numerical results when evaluating the accuracy of analytical rate expressions.¹⁶ We must be sure that the ingredients used in obtaining numerical solutions are fully compatible with all applicable physical and chemical principles such as detailed balance, symmetry, mass action, and limiting behavior. We must be especially careful to verify that the entire set of evaporation coefficients used in the numerical solution corresponds precisely to the equilibrium distribution on which the analytical results are based, or any comparisons will be meaningless. These considerations will automatically be satisfied when more fundamental theoretical treatments^{8,31,32} are properly employed to evaluate the binary distribution function and evaporation coefficients. However, until these advanced methodologies become routinely applicable, we have to be content with more intuitive, phenomenological models relying on macroscopic thermodynamic concepts. Consequently, we must be vigilant when

using these models because it is easy to overlook or introduce inconsistencies that can markedly affect predicted behavior.

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APPENDIX A: STATISTICAL MECHANICAL DEFINITION OF THE EQUILIBRIUM SIZE DISTRIBUTION

Here, we present the general form of the cluster size distribution expected on the basis of statistical mechanics and show how to relate it to distributions based on the capillarity approximation. The result is not new,²⁵ but we repeat it using more explicit notation to emphasize its important features and to make some connections with the recent work of Weakliem and Reiss¹⁸ on unary systems.

As usual, we regard clusters of different composition as components of an ideal gas. Then the chemical potential of a cluster of composition (i, j) can formally be written as

$$\mu(i, j) = k_B T \ln[\Lambda(i, j)^3 N(i, j) / q(i, j)], \quad (\text{A1})$$

where $\Lambda(i, j)$ is the thermal de Broglie wavelength of the cluster, determined by the cluster mass and temperature, and $q(i, j)$ is the internal partition function of the cluster. The entire contribution of the cluster's translational motion to $\mu(i, j)$ is accounted for by the term $k_B T \ln[\Lambda(i, j)^3 N(i, j)]$. Thus, $q(i, j)$ involves only degrees of freedom relative to the center of mass of the cluster.³³ The equilibrium condition between the vapor phase molecules and the clusters is

$$\mu(i, j) = i\mu_A + j\mu_B, \quad (\text{A2})$$

where μ_ν is the chemical potential of species ν in the vapor phase. If the vapor is an ideal gas mixture, so that the chemical potentials have the form $\mu_\nu = \mu_\nu^0 + k_B T \ln N_\nu$, Eqs. (A1) and (A2) give

$$N(i, j) = (N_A)^i (N_B)^j \frac{q(i, j)}{\Lambda(i, j)^3} \exp\left(\frac{i\mu_A^0 + j\mu_B^0}{k_B T}\right), \quad (\text{A3})$$

where the standard states have been taken as one per unit volume.

The essence of the capillarity approximation in this formalism is to write

$$-k_B T \ln q(i, j) = i\mu_A^m(i, j) + j\mu_B^m(i, j) + \Omega^s(i, j) - k_B T \ln q_{\text{rep}}(i, j), \quad (\text{A4})$$

where $\mu_\nu^m(i, j) = \mu_\nu^0 + k_B T \ln N_\nu^\infty(x_\nu)$ is the chemical potential of species ν in a mixture of composition (i, j) , and $q_{\text{rep}}(i, j)$ is the formal replacement partition function that accounts for any misapportionment of translational and internal free energy among the other terms of Eq. (A4). After substituting Eq. (A4) into Eq. (A3) and using the definitions for

$\mu_v^m(i, j)$, one can write the cluster concentration in a form that does not depend on any choice of standard state:

$$N(i, j) = \frac{q_{\text{rep}}(i, j)}{\Lambda(i, j)^3} \left(\frac{N_A}{N_A^\infty(x_A)} \right)^i \left(\frac{N_B}{N_B^\infty(x_B)} \right)^j \exp\left(-\frac{\Omega^s(i, j)}{k_B T} \right). \quad (\text{A5})$$

If we compare this result with Eq. (2), we see that N_0 can be identified as

$$N_0 = \frac{q_{\text{rep}}(i, j)}{\Lambda(i, j)^3}. \quad (\text{A6})$$

Because of the nature of q_{rep} (Ref. 33) and Λ , we see that N_0 can, in general, depend on i , j , T , and other molecular parameters but not on pressure or actual vapor species concentrations. If we had simply mimicked the argument used by Weakliem and Reiss,¹⁸ instead of Eq. (A6) we could have found $N_0 = N_{\text{ref}}$, where N_{ref} is a gas phase number density arbitrarily chosen as the standard state for the cluster chemical potential. The latter result is acceptable, but it does not give us the general form of the result proposed for N_0 in Sec. III C. It should be clear, however, that we are not claiming to have evaluated $q_{\text{rep}}(i, j)$; we have merely replaced it.

APPENDIX B: KINETIC DEFINITION OF EQUILIBRIUM CONSTANTS

Equations (15) and (16) provide kinetic definitions of the equilibrium constants, $K_A(i, j)$ and $K_B(i, j)$, for the exchange of A and B monomers, respectively, between clusters of adjacent compositions:

$$K_A(i, j) = \frac{N(i, j)}{N_A N(i-1, j)} = \frac{\Gamma_A(i-1, j)}{E_A(i, j)}, \quad (\text{B1})$$

$$K_B(i, j) = \frac{N(i, j)}{N_B N(i, j-1)} = \frac{\Gamma_B(i, j-1)}{E_B(i, j)}. \quad (\text{B2})$$

In terms of these equilibrium constants and with the special values $K_A(1, 0) = K_B(0, 1) = 1$, Eqs. (21) and (22) can be rewritten as

$$N(i, j) = N_A^i N_B^j \prod_{k=1}^i K_A(k, j) \prod_{l=1}^j K_B(0, l) \quad (\text{B3})$$

and

$$N(i, j) = N_B^j N_A^i \prod_{k=1}^j K_B(i, k) \prod_{l=1}^i K_A(l, 0), \quad (\text{B4})$$

where products with an upper index equal to zero are again defined as unity.

Equations (B3) and (B4) merely reformulate the information already expressed in Eqs. (21) and (22). Both sets of

equations provide several different but equivalent definitions of $K(i, j)$. Neither set of equations is likely to be of much practical use at present. *A priori* knowledge of the evaporation coefficients is usually lacking, and the usual procedure is to work with $N(i, j)$ based on the capillarity approximation and evaluate E_A and E_B using Eqs. (15) and (16). The standard state free energy differences needed to evaluate K_A and K_B or $K(i, j)$ are also generally unavailable, although they can, in principle, be determined from statistical mechanics. If they were available, one could work “backwards” to determine the evaporation coefficients directly without ever bothering to determine $N(i, j)$, although this would obviously be possible too. All of this should be well known, and we mention it mainly to reemphasize this connection between thermodynamics and kinetics in the near-equilibrium limit.

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