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The Kelvin equation and self-consistent nucleation theory

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Issues of self-consistency are reviewed for several unary equilibrium size distributions based on the capillarity approximation. Some apparent difficulties of interpretation are resolved. In terms of the kinetic approach to nucleation theory, the influence of self-consistency on the nucleation rate is shown to arise entirely from differences in the dimer evaporation rates for nearly all versions of classical theory. The nucleation rate behavior of the Kelvin model is explored. In this model, the Kelvin equation is used to prescribe all cluster evaporation rates. Nucleation rates predicted by the Kelvin model are quantitatively similar to those of the self-consistent classical (SCC) theory, but not to other simple versions of the classical theory. This behavior arises entirely from the relatively close coincidence of the SCC and Kelvin dimer evaporation rates. This means that, for the distribution-based versions of classical theory, the SCC model is the closest analogue of the Kelvin model. Because the Kelvin equation is fundamentally inadequate for very small clusters, the close relationship between the Kelvin and SCC formulations indicates that both are equally lacking in fundamental justification. The Kelvin model may, however, have some pragmatic utility, and a simple analytical rate expression is also derived for it to simplify the calculation of nucleation rates for this model. © 1995 American Institute of Physics.

I. INTRODUCTION

Accurate evaluation of the decay or evaporation rates of small clusters has long stood in the way of a satisfactory treatment of the kinetics of new phase formation. Since the work of Zeldovich¹ and Frenkel,^{2,3} the usual approach has been to rely on the principle of detailed balance to express these decay coefficients as ratios of either true or constrained equilibrium cluster concentrations for adjacent cluster sizes. These equilibrium concentrations are obtained using a blend of statistical and thermodynamic arguments that, almost invariably, rely substantially on the capillarity approximation to express the reversible work of cluster formation as the sum of volume and surface contributions. There have been numerous attempts to improve on the capillarity approximation, and the associated difficulties and controversies are well documented.^{4,5} These will not be addressed here. This paper deals, instead, with vapor phase nucleation theory based on the Kelvin equation^{6,7} and its relationship with recent theoretical developments⁸⁻¹⁰ that use the capillarity approximation in a certain self-consistent form.

The Kelvin equation describes the equilibrium vapor pressure for a curved liquid surface relative to that of a flat interface. It has long held a position of great importance in nucleation theory since, in its most familiar and approximate form,⁶ it relates the radius of the critical nucleus to the supersaturation. The Kelvin equation can also be used to determine evaporation rates for droplets of noncritical size. Katz⁷ has recently done this and has shown numerically that nucleation rates calculated for this Kelvin model are relatively close to those found using the self-consistent classical (SCC) theory.⁸⁻¹⁰ One of the principal aims of this work is to deepen the connection between these two approaches. Another is to make the Kelvin model more computationally

accessible. A final goal is to provide some historical perspective on the use of the Kelvin equation in nucleation theory.

Despite its physical appeal, the Kelvin model has not received much attention in recent years. Besides the work of Katz,⁷ there appear to be only a few papers in the last ten years that are concerned with it. Temkin and Shevelev¹¹ and Kožisek and Demo¹² applied it to nucleation of a highly idealized binary mixture. Yang and Qiu¹³ developed a kinetic approach to nucleation using a parametric form for the cluster evaporation rates suggested by the Kelvin equation. They also reviewed the original Kelvin model, referring to it as the classical result, which is not quite correct since the similar Kelvin (Ref. 7) and SCC (Refs. 9 and 10) results differ greatly from those of the traditional classical rate theory due to Frenkel (Refs. 2 and 3).

This lack of attention to the Kelvin model is somewhat surprising because this model dominated the early thinking of Farkas,¹⁴ Becker and Döring,¹⁵ and Volmer,¹⁶ who all used it to evaluate the droplet evaporation rates without relying on any equilibrium distribution. Actually, Farkas¹⁴ began his paper by using the Kelvin equation for cluster evaporation rates along with the principle of detailed balance to derive an approximate form for the constrained equilibrium distribution, the opposite of what is usually done nowadays. Apparently, he did this so he could interpret his final result for the nucleation rate in support of Volmer and Weber¹⁷ concerning the proportionality of the rate to the equilibrium concentration of critical clusters. In deriving this equilibrium distribution, Farkas introduced the first kinetic mechanism for nucleation, which he attributed to Szilard as cited in Ref. 14. Farkas then used these now-familiar kinetics equations for cluster growth via monomer addition and removal to obtain approximate expressions for the steady state cluster concentrations and nucleation rate. However, all of his final results involve undetermined constants because he was unwilling to use the

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Kelvin equation, or anything else, to determine evaporation rates for the smallest clusters.

Starting with Farkas' kinetics equations and following a purely kinetic approach, Becker and Döring¹⁵ elegantly expressed the steady state nucleation rate solely in terms of impingement and evaporation rates. Perhaps feeling less inhibited than Farkas, they used the Kelvin equation to evaluate the evaporation rates for all cluster sizes to obtain the first predictive rate expression. Volmer¹⁶ also used the kinetic approach of Becker and Döring with a slightly modified definition of the evaporation rate. Although Volmer's method for evaluating the rate expression differed from Becker's and Döring's, his final result was very close to theirs. An amazing aspect of these results is that neither of them is the correct answer for the Kelvin model, as we shall see later. Today, although they still offer rich insights, these early developments are largely forgotten and ignored. This is probably due to the work of Zeldovich¹ and Frenkel³ in the 1940s which induced a shift in emphasis to an approach based on equilibrium statistical mechanics. Aside from brief expositions by Kuhrt,¹⁸ Barnard,¹⁹ Dunning,^{20,21} and Frank and Tosi,²² the kinetic approach of Becker, Döring, and Volmer received little further attention until 1977 when it was independently reinvented by Katz and Wiedersich²³ and subsequently generalized by Katz and Spaepen²⁴ and Katz and Donohue.²⁵

In the course of this presentation, both the kinetic and constrained equilibrium formulations of nucleation theory will be employed. The latter approach will be introduced first in reviewing the most familiar constrained equilibrium distribution functions based on the capillarity approximation. To keep terminology manageable, these functions will be referred to as equilibrium distributions or simply as distributions. These distributions vary in their degree of self-consistency, and the terms "mass action consistency" and "limiting consistency" will be used to classify their behavior. Mass action consistency obviously characterizes distribution functions satisfying the law of mass action. Limiting consistency is satisfied if a g -mer distribution function reduces to the monomer concentration when it is evaluated for $g=1$. In general, a distribution may satisfy either type of consistency, both types, or neither. Some issues of self-consistency have already received prior attention,^{5,7,10,26-28} but the brief review given here will highlight some previously unappreciated points that can be understood better from the kinetic viewpoint. Weakliem and Reiss²⁸ have recently given a thorough critique of the status of mass action consistency and its effect on the classical nucleation rate, but they did not explicitly address the effects of limiting consistency. The latter are explored in this paper, not to provide support for them, but rather because they are involved in understanding how the Kelvin model relates to the other classical models. Because limiting consistency is not a fundamental property, its justification, if any, derives from pragmatic considerations.⁵

Following a review of consistency issues and equilibrium distributions, the principal effects of self-consistency on the nucleation kinetics are discussed from the kinetic approach. This leads naturally to a discussion of the Kelvin

model and its relationship to the SCC approach. After a brief comparison of numerical results for the Kelvin and SCC approaches and some historical comments, the paper closes with a summary of the main conclusions reached here.

II. CONSISTENCY OF EQUILIBRIUM DISTRIBUTIONS

A. Mass action consistency

The most familiar expression for the equilibrium concentration N_g of clusters containing g monomers is due to Frenkel.^{2,3} The Frenkel (F) distribution employs the capillarity approximation and takes the form

$$N_g^F = N_1 \exp(-\Theta g^{2/3} + g \ln S). \quad (1)$$

Here the supersaturation ratio S is defined as N_1/N_1^s , N_1 is the monomer concentration in the vapor, N_1^s is the monomer concentration in a saturated vapor at equilibrium, $\Theta = (\sigma s_1)/(k_B T)$, where σ is the surface tension, s_1 the surface area of a monomer, k_B is the Boltzmann constant, and T is the temperature. This expression clearly fails to satisfy the law of mass action which requires that

$$N_g = (N_1)^g K_g(T), \quad (2)$$

where $K_g(T)$ can depend on g and T but not on N_1 or the total pressure p if the gas phase behaves ideally.

The failure of the Frenkel distribution to satisfy mass action appears to have been first noted and corrected by Courtney.²⁹ Subsequently, Dufour and Defay³⁰ and Blander and Katz³¹ independently addressed this issue. While the arguments of these authors differ, the final corrected result is the same and will be referred to here as the Courtney (C) distribution. It can be written as

$$N_g^C = N_1^s \exp(-\Theta g^{2/3} + g \ln S). \quad (3)$$

Comparing Eqs. (2) and (3), we see that

$$K_g(T) = (N_1^s)^{1-g} \exp(-\Theta g^{2/3}) \quad (4)$$

which is only a function of g and T and, therefore, is an acceptable expression.

Weakliem and Reiss²⁸ have recently shown that Courtney's result is only one of many that can be written and, thus, does not provide a unique correction for the result of Frenkel even in the restricted framework of classical nucleation theory. The particular form one obtains depends on the standard state pressure (or concentration) one uses for the cluster chemical potential and on how one mistreats the contribution of the translational degrees of freedom to the cluster free energy. Thus, although mass action consistency is fundamentally necessary, it alone is not a sufficient basis for deciding which distribution is fundamentally superior to the others.

B. Limiting consistency

While the Courtney distribution satisfies the law of mass action, several authors have noted, either explicitly or implicitly, that it does not return the identity $N_1 = N_1$ for $g=1$. This failure to achieve limiting consistency is obviously a consequence of the capillarity approximation and the specific form, $\Theta g^{2/3}$, chosen for the surface free energy of the g -mer. Unlike mass action consistency, however, limiting consis-

tency is not a fundamental property that must be satisfied by a distribution. It is primarily a mathematical convenience to have a single formula that is “valid” for all values of g . One can, and should, legitimately redefine the distribution to equal the monomer density when the function used for other values of g fails to return the proper value at $g = 1$. The point is that distributions based on the capillarity approximation are not expected to accurately describe the concentrations of very small g -mers, much less the monomer density. Although the physical inapplicability of the capillarity approximation for small values of g is widely recognized, there is undeniable appeal in “one-size-fits-all” formulas, particularly when they are motivated by the idea of a size-dependent surface tension. It is, thus, not surprising that there have been a number of attempts to adapt this simple formalism to all cluster sizes.

Dufour and Defay³⁰ were apparently the first to act on this idea. Their approach was to implicitly regard the surface tension as size dependent such that, in effect, $\Theta(1)=0$. Goodrich³² made the first explicit implementation of limiting consistency by reducing the surface free energy of a g -mer by the formal surface free energy of a monomer. A similar modification was later made independently by Ziabicki and Jarecki.^{33,34} This approach was subsequently employed by Shizgal and Barrett⁸ in extending Goodrich’s work. Most recently, it was reinvented by Gershick and Chiu,⁹ who emphasized its significant quantitative effect on the nucleation rate. This modification corresponds to replacing $g^{2/3}$ with $g^{2/3} - 1$ in Eq. (3) to obtain

$$N_g^{\text{SCC}} = N_1^s \exp[-\Theta(g^{2/3} - 1) + g \ln S]. \quad (5)$$

Following Gershick,¹⁰ Eq. (5) will be referred to as the self-consistent classical distribution. In work that preceded the more recent developments, Draine and Salpeter³⁵ had already employed a variant of this approach, ultimately using as their working equation:

$$N_g^{\text{DS}} = N_1^s \exp[-\Theta(g - 1)^{2/3} + g \ln S]. \quad (6)$$

As Katz⁷ has already noted with respect to Eq. (5), each of these modifications can be regarded as making the surface tension (or Θ) in Eq. (3) an explicit function of size, $\Theta(g)$. Draine and Salpeter³⁵ actually noted that Θ should depend on g , but in their calculations they treated it as a constant whose value was intended to be characteristic of a critically sized cluster and not of a planar surface.

C. Effects of self-consistency on nucleation rate

The changes imposed on the Frenkel distribution to achieve limiting or mass action consistency affect the calculated nucleation rate. These effects were first noted by Courtney²⁹ for mass action consistency and by Gershick and Chiu^{9,10} for limiting consistency. An easy way to appreciate these effects is by considering the exact solution for the steady state nucleation rate J ,³⁶

$$J = \left(\sum_{g=1}^G \frac{1}{\alpha \beta s_g N_g} \right)^{-1}, \quad (7)$$

where β is the collision frequency of monomers with g -mers per unit area, α is the sticking probability, $s_g = s_1 g^{2/3}$ is the surface area of a g -mer, and G is much larger than the critical size but otherwise arbitrary. Since the $g=1$ term is almost always negligible, and since the ratio of any pair of distribution functions considered here (except the Draine–Salpeter distribution) is some constant independent of g , it follows that the ratio of the respective nucleation rates is the same constant. Thus, the ratio of the Courtney and Frenkel rate expressions is

$$\frac{J^C}{J^F} \approx \frac{N_g^C}{N_g^F} = \frac{1}{S}, \quad (8)$$

which is Courtney’s result. When the SCC distribution, Eq. (5), is used to evaluate the rate, the Gershick–Chiu result,

$$\frac{J^{\text{SCC}}}{J^F} \approx \frac{N_g^{\text{SCC}}}{N_g^F} = \frac{e^\Theta}{S}, \quad (9)$$

is found. The effect of the Draine–Salpeter distribution is a bit harder to ascertain since the ratio N_g^{DS}/N_g^F depends on g . However, if consideration is restricted to large values of the critical size g^* , and the classical value of Θ is used in Eq. (6), contrary to the intent of Draine and Salpeter, we may obtain the approximate result

$$\frac{J^{\text{DS}}}{J^F} \approx \frac{N_{g^*}^{\text{DS}}}{N_{g^*}^F} \approx S^{1/(6g^*)}, \quad (10)$$

where the classical (Kelvin) expression, $\ln S = (2\Theta/3) \times g^{*-1/3}$, has also been used to simplify the result. I have verified numerically that this correction factor is accurate to within a few percent and is always close to unity, provided $g^* > 10$. Thus, it is rather remarkable that the Draine–Salpeter distribution, which fulfills both mass action and limiting consistency, should reproduce almost perfectly the rate predictions of the Frenkel distribution, which satisfies neither condition.

In contrast with the modest correction in Eq. (8) and the negligible correction in Eq. (10), the self-consistency correction in Eq. (9) can be large.⁹ In commenting on it, Gershick has drawn attention to an apparent paradox that “the self-consistency correction does not affect the forward or backward rates, yet it changes the nucleation rate!”¹⁰ He offers no resolution of this paradox, but appeals to the results³⁷ of numerical calculations with time-dependent population balance equations to support it. Actually, this paradox is the result of imprecision in terminology and of an oversight of a key property of the evaporation coefficients. To appreciate this, let us proceed by reviewing some key kinetic concepts.

The net rate ($\text{cm}^{-3} \text{s}^{-1}$) of formation of g -mers from $(g-1)$ -mers is usually written as

$$J_g = \alpha \beta s_{g-1} n_{g-1} - E_g n_g, \quad (11)$$

where n_g is the nonequilibrium number density of g -mers, and E_g is the frequency with which a g -mer loses a monomer, i.e., the evaporation rate of a g -mer. From Eq. (11), the detailed balance prescription for E_g is

$$E_g = \alpha \frac{\bar{c}}{4} s_{g-1} N_1 \frac{N_{g-1}}{N_g}, \quad (12)$$

where the mean molecular speed of monomers, \bar{c} , appears after substituting the usual kinetic theory expression for $\beta [= (\bar{c}/4)N_1]$. For an ideal mixture of vapor and clusters, E_g should be a function of temperature only. The dependence on the monomer concentration N_1 is only apparent, since it is canceled by compensating factors in N_{g-1} and N_g leaving only temperature dependent terms.

It is not true that the *forward rate* is unaffected by the self-consistency correction. What is unaffected is the *forward rate coefficient*, which equals $\alpha(\bar{c}/4)s_{g-1}$. The forward rate is the product of this rate coefficient, the monomer concentration, and n_g . Because n_g is directly affected by the self-consistency correction, the forward rate is similarly affected. The same reasoning applies to the *backward rate*, $E_g n_g$, regardless of whether or not E_g , the *backward rate coefficient*, is affected by the self-consistency correction. This terminology is consistent with usage in the field of chemical kinetics, yet it is commonly neglected in discussions of nucleation kinetics too numerous to cite here.

It is easy to show how n_g is affected by the self-consistency correction for steady state nucleation. In this case, n_g can be expressed exactly in terms of the N_g as³⁶

$$\frac{n_g}{N_g} = J \sum_{i=g}^G \frac{1}{\alpha \beta s_i N_i} = \sum_{i=g}^G \frac{1}{s_i N_i} \bigg/ \sum_{j=1}^G \frac{1}{s_j N_j}. \quad (13)$$

The right-hand side of Eq. (13) is nearly unaffected by self-consistency corrections, thus any change in N_g is immediately reflected in n_g and, therefore, in the separate forward and backward rates. Despite the transparency of this demonstration, it does not provide a satisfactory explanation for the effect in kinetic terms.

III. KINETIC INTERPRETATION

The effect of the self-consistency correction can be understood better by considering the steady state solutions of Eq. (11) for n_g and J expressed solely in terms of the forward and backward rate coefficients. The original Becker-Döring¹⁵ solution for J , which was independently rediscovered by Katz and Spaepen²⁴ using a different argument, can be written as

$$J = \alpha \beta s_1 N_1 \bigg/ \left(1 + \sum_{j=2}^G \prod_{k=2}^j \frac{E_k}{\alpha \beta s_k} \right). \quad (14)$$

It is straightforward to extend the kinetic approach to express the steady state cluster concentrations solely in terms of kinetic quantities. The result is

$$n_g = \frac{J}{\alpha \beta s_g} \left(1 + \sum_{j=g+1}^G \prod_{k=g+1}^j \frac{E_k}{\alpha \beta s_k} \right), \quad (15)$$

which seems not to have been published previously.

From the ingredients of Eqs. (14) and (15), it is clear that only the behavior of the E_k can affect the steady state values of n_g and J for the various models under consideration. Gershick's conclusion¹⁰ that the evaporation coefficients are un-

affected by the choice of distribution function used to evaluate them is not completely valid. Let us first consider just the Frenkel (Refs. 2 and 3), Courtney (Ref. 29), and SCC (Refs. 8–10) distribution functions. These functions are given by Eqs. (1), (3), and (5), and all yield the same result for E_g when substituted into Eq. (12) except when $g=2$. When Eq. (12) is explicitly written out for this special case, one finds

$$E_2 = \alpha(\bar{c}/4)s_1 N_1^2 / N_2, \quad (16)$$

where N_1 should not be mistakenly evaluated using either Eq. (1) or (3). It is apparent that E_2 , in contrast with all other E_g , depends directly on the functional form chosen for N_2 . The first consequence of Eq. (16) is that the Frenkel form for E_2 is unphysical because it depends on N_1 . Next, any changes introduced in the formula for N_g to ensure mass action or limiting consistency will immediately be reflected in E_2 . These changes, in turn, directly affect the values of n_g and J as given by Eqs. (14) and (15) since each term in the denominator of J , save the initial, is multiplied by E_2 . Thus, in the kinetic approach, the changes contained in Eq. (3) or (5) affect the dimer break-up rate which alters the dimer concentration. Through Eq. (11), this then affects the trimer concentration and so on up the ladder of cluster sizes. The model of Draine and Salpeter,³⁵ which Gershick¹⁰ did not consider, is more equitable in its influence since the values of all E_g are affected to some extent with the biggest effect found for the smaller values of g . In this case, however, these changes must be mutually compensating since, as we have already seen, the steady state rates hardly differ from the Frenkel values.

Similar behavior is found when the rate and cluster concentrations are computed by solving the time-dependent population balance equations,

$$\frac{dn_g}{dt} = J_g - J_{g+1}. \quad (17)$$

The different values of E_2 , based on Eqs. (1), (3), and (5), directly affect the dimer concentration which, because of its presence in J_3 , then affects the trimer concentration and so on. In this way the influence of each E_2 is leveraged all the way up the sequence of cluster sizes through the birth and death equations. If this were not so, it would be impossible for the time-dependent cluster population equations to evolve numerically into the different steady state solutions appropriate for each version of nucleation theory. Thus, Courtney's³⁸ pioneering numerical solutions reflect the use of Eq. (3), while Abraham³⁹ used Eq. (1). Neither of these authors began the solution at $g=2$. Rather, the model specific information was inserted by holding the concentration of a larger, but subcritical, cluster size at an equilibrium value determined by the indicated distribution function. Despite this, the net effect is the same because the steady state concentrations of the smaller subcritical clusters are always very close to the equilibrium values. The recent results of Girshick *et al.*³⁷ agree with the steady state rates of SCC theory simply because Eq. (5), rather than Eq. (1) or (3), was used to evaluate E_2 . There is no paradox.

IV. THE KELVIN MODEL

A. Relationship to SCC theory

Another variant of classical theory, termed the Kelvin solution by Katz,⁷ merits discussion because of its close relationship to the SCC theory. The Kelvin solution is found by using the Kelvin equation for the vapor pressure of a spherical drop to evaluate the E_g . This approach has considerable physical appeal despite the obvious inadequacy of the Kelvin equation for the smallest cluster sizes. Katz⁷ has found that nucleation rates calculated with the Kelvin solution are very close to the values found using SCC theory.

The relationship between these two approaches can be appreciated better by considering the equilibrium distribution for the Kelvin (K) solution. This is found by solving Eq. (11) with

$$E_g^K = \alpha(\bar{c}/4)s_{g-1}N_1^s \exp(\kappa/g^{1/3}), \quad (18)$$

where $\kappa=2\Theta/3$. The two rightmost factors in this equation are just the monomer density in equilibrium with a spherical drop containing g monomers as given by the Kelvin equation. Starting at $g=2$, one simply iterates Eq. (11) with $J_g=0$ and $n_g=N_g$ to obtain the following exact result:

$$N_g^K = N_1^s(N_1/N_1^s)^g \exp\left[-\kappa\left(\sum_{j=1}^g j^{-1/3} - 1\right)\right]. \quad (19)$$

Note that this distribution function automatically satisfies both mass action and limiting consistency, although the latter property merely results from the mathematical trick of adding and subtracting unity to and from the original sum that began at $j=2$. The steady state rate and cluster size distribution for the Kelvin model are easily found by combining Eq. (19) with Eqs. (7) and (13) or Eq. (18) with Eqs. (14) and (15). The result for the rate is

$$J^K = \alpha\beta s_1 N_1 \left/ \left[1 + \sum_{g=2}^G g^{-2/3} S^{1-g} \exp\left(\kappa \sum_{j=2}^g j^{-1/3}\right) \right] \right. \quad (20)$$

This expression differs slightly from the result reported by Katz⁷ due to a typographical error in his formula and to his different choice of surface area in evaluating the backward rate coefficient.⁴⁰

The sum in Eq. (19) is very well approximated by no fewer than the first three terms of the Euler–Maclaurin summation formula,

$$\sum_{j=2}^g j^{-1/3} = \frac{3}{2}(g^{2/3} - 1) - \frac{1}{2}(1 - g^{-1/3}) + \frac{1}{36}(1 - g^{-4/3}). \quad (21)$$

With this simplification, the equilibrium Kelvin distribution function is seen to equal the SCC form, Eq. (5), multiplied by an additional g -dependent factor. Thus, the ratio of steady state rates for the SCC and Kelvin theory should be well approximated by the following equation:

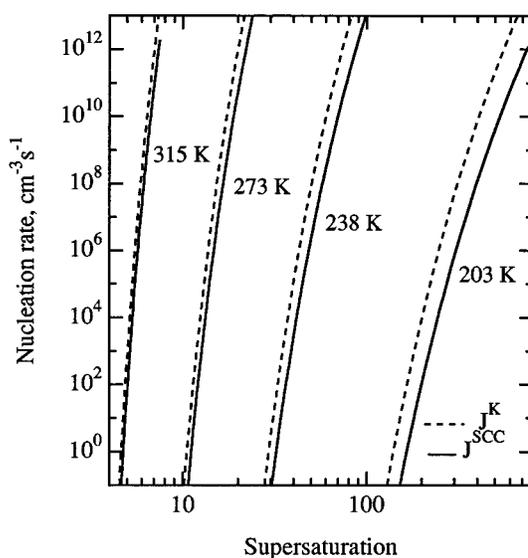


FIG. 1. Comparison of exact nucleation rates for the Kelvin (K) and self-consistent classical (SCC) models as a function of supersaturation for nonane at four different temperatures.

$$\frac{J^K}{J^{\text{SCC}}} = \frac{N_{g^*}^K}{N_{g^*}^{\text{SCC}}} = \exp\left\{\frac{1}{3}\Theta[(1 - g^{*-1/3}) - \frac{1}{18}(1 - g^{*-4/3})]\right\}. \quad (22)$$

The same result can be found by evaluating Eq. (20) in the usual manner.⁹

The form of the correction factor indicates that the Kelvin rate always exceeds the SCC value, but unless Θ and g^* are very large, this factor should be of modest size. For example, with $g^*=10$ and 100 , J^K/J^{SCC} ranges from 25 to 130 when $\Theta=20$ but only from 5 to 11 when $\Theta=10$. To explore this point further I performed exact numerical calculations of nonane nucleation rates based on Eq. (7) or (14) using the simple, efficient algorithm described in the Appendix. The physical properties of nonane were treated in the manner described by Kalikmanov and van Dongen.²⁷ The results, shown in Fig. 1 support the behavior indicated by Eq. (22) in contrast to the results of Katz⁷ which showed that $J^{\text{SCC}} > J^K$ at high temperature. My results also establish that Eq. (22) overpredicts the exact Kelvin rate by no more than 4% with the worst agreement found at low temperatures (large Θ) and high nucleation rates, 10^{16} – 10^{22} $\text{cm}^{-3} \text{s}^{-1}$ (small g^*). Thus, an accurate prediction for the Kelvin theory can be readily obtained from Eq. (22) and the easily computed value of J^{SCC} .⁹

Now we may ask why the SCC theory, rather than the Frenkel³ or Courtney²⁹ versions of classical theory, gives results that are closest to the Kelvin solution. The answer is simply that the SCC expression for E_2 is a better approximation to the Kelvin result for $g=2$ than are either of the earlier two classical versions. In simplest terms, $2^{2/3}-1$ is a much better approximation to $(2/3)2^{-1/3}$ than is $2^{2/3}$. (Recall that the Frenkel version of E_2 also depends on the monomer partial pressure, which is unphysical.) Since the Frenkel, Courtney, and SCC distributions give identical values for all other

E_g , it is only the differences in E_2 that matter. This close correspondence between the Kelvin and SCC approaches should not be misconstrued as fundamental support for the SCC distribution. Because the Kelvin equation is fundamentally inadequate for very small clusters, the agreement between the Kelvin and SCC formulations merely indicates that both are equally unsatisfactory.

B. Assessment of some earlier results

As already mentioned, Becker and Döring¹⁵ derived a general expression for the steady state nucleation rate based solely on kinetic considerations. In evaluating their expression for the vapor-to-liquid transition, they actually employed the Kelvin equation to evaluate the evaporation coefficients. Why then is the familiar rate expression often attributed to Becker and Döring not, in fact, the expression for J^K given here? The answer is that Becker and Döring made a seemingly harmless simplification of their result by arguing that $(3g^{*-2/3} - 2g^{*-1})$ was small compared with one. As a result, they approximated as unity a factor that, expressed in conventional notation, equals $\exp(\Theta)/S!$ Thus, Becker and Döring should have obtained an expression close to the self-consistent classical rate, J^{SCC} . Due to the other mathematical approximations they used, they would not have found the remaining correction factors shown in Eq. (22), but this is a matter of lesser importance. When Volmer rederived the Becker–Döring theory in his famous book,¹⁶ it was still cast solely in kinetic terms with no use of equilibrium distributions. Volmer used a different method to evaluate the rate expression, but his results were nearly identical⁴¹ to those of Becker and Döring. Thus, he too found a multiplicative factor,⁴² equivalent to $\exp(\Theta)/S$, which he then approximated as $\exp(\lambda)$, where λ is the molecular heat of evaporation. In contrast to Becker and Döring, Volmer recognized that this factor was large, but he argued that it would be nearly compensated by a very small factor, missing from the theory, that accounted for the low probability of “triple collisions” needed to form stable dimers. Rather than modify the theory to assess the effect of the latter process, he simply removed the large factor from the final rate equation. He thereby obtained the expression that is usually regarded as the classical result for the nucleation rate. This result is also often attributed to Frenkel, who derived it later using the constrained equilibrium formalism without the need to argue away any large factors since none occurred in his approach. Somewhat later, Barnard¹⁹ carefully reviewed the theories of Frenkel and Becker and Döring, noted the importance of the terms that equal $\exp(\Theta)/S$ in the latter approach, and showed that they reduced the predicted critical supersaturations for water by about 10%. Reductions in the theoretical critical supersaturations for water and other substances would have worsened the agreement then found⁴³ with the experimental data of Volmer and Flood,⁴⁴ and Barnard’s observations apparently were not considered further.

Another interesting aspect of the use of the Kelvin equation in nucleation theory involves the work of Goodrich.³² Although Goodrich made the first explicit effort to address the problem of limiting consistency, he did not fully define the SCC distribution, Eq. (5), as did Ziabicki,³⁴ Shizgal and

Barrett,⁸ and Gershick and Chiu⁹ much later. Obviously, he could not then have used it to evaluate J . Instead, he also used the Kelvin expression, Eq. (18), for the evaporation rate to derive the steady state rate from a higher order approximation of the continuous birth and death equations. The form of his expression does not lend itself to direct comparison with the exact result, but his calculated rates were significantly higher than those of standard classical nucleation theory, i.e., J based on Eq. (1), the Frenkel distribution. He attributed this behavior to his improved approximation scheme, although it is clear from Katz’ results⁷ and mine that most, if not all, of the increase in J that he found must be due to the use of the Kelvin equation.

V. SUMMARY AND CONCLUSIONS

In unary homogeneous nucleation theory, equilibrium cluster size distributions based on the capillarity approximation vary in their degree of self-consistency. The Frenkel distribution does not obey the law of mass action, nor does it satisfy limiting consistency, i.e., return the monomer concentration when evaluated for a single monomer. The Courtney distribution also fails to satisfy limiting consistency, but it does follow the law of mass action. The Draine–Salpeter, SCC, and Kelvin distributions satisfy both types of self-consistency. The self-consistency factors that convert one distribution into another affect the individual forward and reverse rates of cluster formation, as well as the overall rate of nucleation. Since the forward rate *coefficients* are unaffected by the self-consistency corrections, all such effects arise directly from differences in the reverse or evaporation rate *coefficients*. From a kinetic perspective, the Frenkel, Courtney, and SCC versions of classical theory differ only in their dimer evaporation coefficients, since all other evaporation coefficients are identical in these theories. This remark is also true for any alternative version of classical theory one might care to “derive” using the arguments of Weakliem and Reiss.²⁸ The behavior of the Draine–Salpeter and Kelvin models is more complicated because their evaporation coefficients differ from each other and from the other classical values for all cluster sizes. Of course, the evaporation coefficients based on each of the distributions asymptotically approach the Kelvin value, Eq. (18), for large cluster sizes,²⁸ and they remain moderately close to the Kelvin value down to relatively small cluster sizes. This behavior is preordained because the Kelvin equation originates from the same thermodynamic considerations as those used to derive the classical free energy of cluster formation. Despite this common foundation for the evaporation rate coefficients in these various versions of classical theory, only the SCC (Refs. 8–10) model gives results that are quantitatively similar to those of the Kelvin model, and these results differ substantially from those of the Frenkel and Courtney models.

As noted by Weakliem and Reiss,²⁸ however, each of these classical models fails to properly account for the translational free energy of the clusters. From this perspective, none of these models is fundamentally superior to another. Weakliem and Reiss have also shown that there are an unlimited number of possible self-consistency correction factors for the nucleation rate besides the most familiar $1/S$ and

$\exp(\Theta)/S$. Without a correct molecular theory as a guide, there is no fundamental justification to prefer one particular distribution and, thus, correction factor over another. One can compare theory with experimental results as a pragmatic basis for a preference, but inevitably no single distribution is adequate for all substances or even for a single substance over a wide temperature range.

Nevertheless, it is clearly a fundamental requirement that any distribution should, at a minimum, obey the law of mass action. The same cannot be said for limiting consistency. There is no fundamental reason why a cluster size distribution must be a simple functional form applicable to every size. Cluster beam experiments and accurate Monte Carlo calculations show that certain special sizes exist for which cluster stability is enhanced compared to neighboring sizes.⁴⁵ This suggests that an exact theory would not be characterized by the type of smoothly varying size distributions and free energy functions used in our current simple theories. Thus, although imposing limiting consistency on a distribution may favorably improve the predicted nucleation rates, this should not be interpreted as evidence for a fundamental improvement in the theory.

Because limiting consistency emerges quasi naturally in the Kelvin model, it is tempting to think that the quantitative similarity of the Kelvin and SCC models provides some fundamental support for the concept. To dispel this view, we need only to recall that all of the "improvement" in this case stems from the relatively close agreement of the SCC and Kelvin dimer evaporation rates. Given the questionable applicability of the Kelvin equation to dimers and other small clusters, we see that it is erroneous to regard the SCC theory as fundamentally improved. Despite this last objection, the SCC and Kelvin approaches do appear to provide the best predicted temperature dependence of the nucleation rate for the simpler capillarity-based nucleation theories.⁷ Nevertheless, the predicted temperature dependence is still far from satisfactory, and quantitative improvement in the magnitudes of the predicted rates is not always found.⁹

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APPENDIX: EXACT NUMERICAL COMPUTATION OF THE STEADY STATE RATE

This algorithm for calculating J is simple, efficient and accurate. Since it seems not to have been discussed previously, it may be worthwhile to describe it. It relies on rewriting the sum in Eq. (7) as a nested product of terms,

$$s_1 N_1 \sum_{g=1}^G \frac{1}{s_g N_g} = 1 + R_2[1 + R_3(1 + \dots + R_{G-1}(1 + R_G) \dots)], \quad (\text{A1})$$

where

$$R_g = s_{g-1} N_{g-1} / (s_g N_g). \quad (\text{A2})$$

Then, using the recursion relation

$$F_{g-1} = 1 + R_g F_g \quad (\text{A3})$$

and beginning with

$$F_G = 1, \quad (\text{A4})$$

the F_g are successively computed in descending order. The steady state rate J is then related to F_1 by the expression

$$J = \frac{\alpha \beta s_1 N_1}{F_1}. \quad (\text{A5})$$

An added benefit of this approach is that the steady state cluster distribution n_g is also easily found from F_g without any additional computational work:

$$n_g = \frac{N_1 s_1 F_g}{s_g F_1}. \quad (\text{A6})$$

The kinetic version of R_g is obtained by replacing the ratio, N_{g-1}/N_g , with the value found by applying the detailed balance condition, Eq. (12),

$$R_g = \frac{E_g}{\alpha \beta s_g}. \quad (\text{A7})$$

With this expression for R_g we see that Eq. (A1) is just an expanded version of the (inverted) kinetic expression of Becker and Döring¹⁵ and Katz and Spaepen,²⁴ Eq. (14). To obtain the Kelvin solution, just use Eq. (18) for E_g . This gives

$$R_g = \frac{s_{g-1}}{s_g} \frac{1}{S} \exp\left(\frac{\kappa}{g^{1/3}}\right). \quad (\text{A8})$$

This recursive procedure for evaluating the rate thus avoids both the need to directly compute the sums appearing in Eq. (7), (14), or (20) and the possible loss of precision accompanying that procedure.

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