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Time-Dependent Aerosol Models and Homogeneous Nucleation Rates

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Two types of numerical models for homogeneous nucleation and particle growth are compared: models in which the time rate of change in the stable aerosol population is given by an analytical expression for the nucleation rate, and discrete models, in which an expression for the nucleation rate is not required nor explicitly calculated. The classical expression for the homogeneous nucleation rate, coupled to a moment model, is found to produce poor agreement with a discrete-sectional model except for very low values of dimensionless surface tension. A new expression for the homogeneous nucleation rate is proposed, which when coupled to a moment model produces excellent agreement with a discrete-sectional model over a wide range of dimensionless surface tensions. The new expression is also consistent with experimental data on homogeneous nucleation of dibutylphthalate.

INTRODUCTION

Current numerical models for homogeneous nucleation and particle growth from an initially supersaturated vapor fall into two classes. In the first class, a nucleation rate is calculated based on an analytically derived expression from nucleation theory, and this rate is coupled to a model for the evolution of the stable aerosol. In the second class, a nucleation rate is never used nor explicitly calculated. Instead, particle formation is simulated by applying the aerosol general dynamic equation to a discrete representation of the particle size spectrum for monomers and small clusters. Larger sizes (the stable aerosol) are treated more approximately. We refer to these two classes of model respectively as "nucleation-coupled" and "discrete."

The most common examples of nucleation-coupled models are models which calculate the first few moments of the particle size distribution. These include Friedlander (1983), Warren and Seinfeld (1985), Brock et al. (1986), Nguyen et al. (1987), Okuyama et al. (1987), Pratsinis (1988), Turner et al. (1988), and Phanse and Pratsinis (1989). We also include in this category other methods in which the homogeneous nucleation rate is treated as a source term to the aerosol general dynamic equation, as in the analytical model of Pesthy et al. (1983) and the sectional model of Warren and Seinfeld (1984).

Discrete models have considered homogeneous nucleation in two physical regimes, according to whether backward reactions (evaporation) play a significant role: collision-controlled (e.g., McMurry, 1980) and condensation/evaporation-controlled. The collision-controlled (coagulation-limited) regime applies to cases with very high rates of monomer formation, or very low vapor pressures. In this regime the monomer itself is stable for growth, and evaporation can be neglected. However in this paper we are concerned with the condensation/evaporation-controlled regime (which has been the concern of classical nucleation theory), in which monomer formation rates are not so high, or vapor pressures are not so low, so...
that evaporation from small clusters plays a crucial role in the nucleation process. Rao and McMurry (1989) examined criteria for the two regimes and the transition between them. They used a discrete-sectional model, with evaporation terms included, to simulate nucleation and growth for an isothermal system. Girshick and Chiu (1989, 1990a) extended this approach to nonisothermal systems, with cooling rate as a parameter.

Discrete models presumably provide an "exact" treatment of the subcritical cluster dynamics, limited only by the accuracy of the physical modeling of coagulation and evaporation coefficients, and by the accuracy of the numerical solution method. Nucleation-coupled models, in contrast, inherently neglect cluster–cluster coagulation and cluster scavenging by stable particles. However nucleation-coupled models, especially moment models, have an important advantage in computational economy: they are easily executed on a microcomputer, whereas discrete models in the condensation/evaporation-controlled regime typically require a supercomputer.

In this paper we compare results obtained by a nucleation-coupled (moment) model and by a discrete model. If the moment model assumes the classical expression for the homogeneous nucleation rate, we find that agreement with the discrete model is quite poor except for a narrow range of physical conditions. We propose a new expression for the homogeneous nucleation rate, which when coupled to a moment model produces excellent agreement with a discrete model over a wide range of physical conditions. A preliminary examination of experimental data is consistent with this new expression.

The new nucleation rate is based on an extension of a derivation by Katz and Wiedersich (1977) and Katz and Donohue (1979). Katz and Donohue claimed that their result (for the case of a vapor which behaves as an ideal gas) was "identical to classical nucleation theory," but included in their final expression an unevaluated normalization constant. We suggest an evaluation of this normalization constant which results in a nucleation rate which is significantly different than the classical rate.

We consider the following simple situation. A vapor existing with a specified initial supersaturation \( S_0 \) is allowed to evolve in a non-reacting, isothermal system without any walls. The behavior of this system is calculated using three different methods:

1. The moment model presented by Friedlander (1983), coupled to the classical Becker-Döring expression for the homogeneous nucleation rate. We refer to this as the "moment/classical model."

2. The same moment model, coupled to the proposed new nucleation rate. Following the terminology of Katz and co-workers we refer to this rate as the "kinetic nucleation rate" and to the model as the "moment/kinetic model."


We take the moment model of Friedlander as being representative of nucleation-coupled models, and the discrete-sectional code of Rao and McMurry as being representative of discrete models. However, we are confident that the results presented below would be substantially unchanged if we had instead chosen other available models, for example a nucleation-coupled sectional model and/or a discrete-continuous model. Nucleation-coupled models differ in their treatment of the stable aerosol, but all have in common the assumption of an a priori expression for the nucleation rate. Similarly discrete models differ over the treatment of the stable aerosol, but subcritical clusters are always represented discretely. For systems dominated by homogeneous nucleation the effects of differences in the treatment of the stable aerosol are relatively minor compared to the effects of differences in the treatment of subcritical clusters, which effectively determines the nucleation rate.

All three models share the following
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physical assumptions: (a) surface tension is size-independent (capillarity approximation); (b) mass accommodation coefficients equal unity; (c) particles are spherical and charge-neutral; (d) London-van der Waals forces are neglected; (e) the system is sufficiently dilute that evaporation coefficients depend only on cluster properties and on temperature.

HOMOGENEOUS NUCLEATION RATES

Homogeneous nucleation theory (for standard presentations, see Frenkel, 1946; or Seinfeld, 1986; for a review, see Springer, 1978) begins by considering the reaction:

\[ A_1 + A_{g-1} \rightleftharpoons A_g, \]  

(1)

where \( A_g \) represents a cluster containing \( g \) molecules (a \( g \)-mer). The net rate of \( g \)-mer formation \( J_g \) (\( m^{-3} \cdot s^{-1} \)) can be written:

\[ J_g = \frac{\beta_{1,g-1} n_1 n_{g-1}}{12} \left[ 1 - \frac{E_g}{n_g} \right], \]  

(2)

where \( \beta_{ij} \) (\( m^3 \cdot s^{-1} \)) is the collision-frequency function for collisions between \( i \)-mers and \( j \)-mers, \( n_g \) (\( m^{-3} \)) is the concentration of \( g \)-mers, and \( E_g \) (\( s^{-1} \)) is the evaporation coefficient.\(^1\) Typically \( \beta_{ij} \) is known (e.g., from gas kinetic theory), and \( E_g \) can be evaluated by referring to the reaction given by Eq. (1) for a system in a known equilibrium state:

\[ E_g = \beta_{1,g-1} n_1 \left( \frac{n_{g-1}^e}{n_g^e} \right) \]  

(3)

where the superscript \( e \) denotes equilibrium concentrations.

Where the classical nucleation theory and the kinetic theory differ is over the choice of equilibrium state. The classical theory considers equilibrium to mean the metastable equilibrium which would exist for a vapor having the same supersaturation \((S > 1)\) and temperature as the vapor in question, and constrained to be at steady state by the artifice that monomers are continually replenished by the dissociation of particles which grow beyond a certain size (Maxwell demons). The kinetic theory considers equilibrium to mean the stable equilibrium of a saturated vapor \((S = 1)\) at the same temperature as the vapor in question.

Both theories then proceed by the same sequence of arguments to derive a nucleation rate when can be written

\[ J = N \frac{\beta_{11} n_1}{12} \sqrt{\frac{\Theta}{2\pi}} \exp \left[ -\frac{4\Theta^3}{27(\ln S)^2} \right]. \]  

(4)

Here \( N(m^{-3}) \) is a normalization constant and \( \Theta \) is a dimensionless surface tension given by

\[ \Theta = \frac{\sigma s_s}{kT}, \]  

(5)

where \( \sigma \) is surface tension (\( N \cdot m^{-1} \)), \( s_s \) is the surface area of a monomer, and \( k \) is Boltzmann's constant.

Thus both nucleation rates are indeed identical except for a possible difference in the normalization constant \( N \). In both theories this constant is the same as appears in the Boltzmann distribution for the cluster population at equilibrium:

\[ n_g^e = N \exp \left[ -\frac{\Delta G(g)}{kT} \right], \]  

(6)

where \( \Delta G(g) \) is the Gibbs free energy of a \( g \)-mer.

In the classical theory \( N \) is equated to the monomer concentration. That is, the normalization constant in the classical theory is given by

\[ N_{cl} = n_1 = n_1, \]  

(7)

where the last equality is intrinsic to the

\(^1\)We adopt a nomenclature which is somewhat different from the conventional nomenclature of nucleation theory but which is consistent with the usual nomenclature of discrete models. Thus, for example, \( \beta_{1,g-1} n_1 \) is equivalent to the conventional \( \beta s_{g-1} \), where \( \beta \) is the monomer flux to the surface and \( s_s \) is the surface area of a \( g \)-mer.
assumed equilibrium state of classical theory.2

In their kinetic derivation of Eq. (4), Katz and Donohue (1979) assume that for a saturated vapor in equilibrium the free energy of a cluster is given by

$$\Delta G(g) = \sigma \bar{s}^r(g) = \sigma s_{1/3} g^{2/3}, \quad (8)$$

so that Eq. (6) can be written

$$n^s_g = N \exp(-\Theta g^{2/3}). \quad (9)$$

We suggest that the kinetic normalization constant $N_{kin}$ be evaluated simply by requiring that Eq. (9) be satisfied for monomers. Then

$$N_{kin} = n_s \exp(0), \quad (10)$$

where $n_s$ is the equilibrium saturation monomer concentration at temperature $T$.3 Combining Eqs. (9) and (10) yields an expression for the equilibrium cluster distribution in the kinetic theory:

$$n^e_g = n_s \exp\left[-\Theta\left(g^{2/3} - 1\right)\right]. \quad (11)$$

An alternative and preferable interpretation of this result is as follows. Eq. (11) describes the cluster distribution for a saturated vapor, in a state of phase and thermal equilibrium. In this state the chemical potential of a molecule in the vapor equals that of a molecule in the condensed phase. Therefore under these conditions a monomer should be assigned a ground-state chemical potential. For an ideal vapor $\Delta G(g)$ then represents simply the difference in free energy between a g-mer and a monomer, both considered to be in the condensed phase. That is, the normalization constant in the Boltzmann distribution is given by $n_s$, and

$$\Delta G / kT = \Theta\left(g^{2/3} - 1\right). \quad (12)$$

Either interpretation leads to the same result. Inspecting Eqs. (4), (7) and (10), and noting that $\bar{S} = n_1/n_s$, we find that the nucleation rates from the two theories are related by

$$J_{kin} = \frac{\exp(\Theta) J_{cl}}{S}. \quad (13)$$

The difference between the classical and the kinetic expressions for the nucleation rate may be small or it may be large. Table 1 shows values of $\Theta$ for various substances. Large values of $\Theta$ (≈ 10–50) are found for substances with high values of surface tension or large molecular volumes. Additionally $\Theta$ increases as temperature decreases, not only because it is normalized by $kT$ but also because surface tension for most liquids increases with decreasing temperature.

**Table 1.** Typical Values of Dimensionless Surface Tension $\Theta$

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T$ (K)</th>
<th>$\Theta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibutylphthalate (DBP)</td>
<td>300</td>
<td>22</td>
</tr>
<tr>
<td>Iron</td>
<td>1900</td>
<td>17</td>
</tr>
<tr>
<td>Mercury</td>
<td>290</td>
<td>50</td>
</tr>
<tr>
<td>Methanol</td>
<td>350</td>
<td>3</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>200</td>
<td>23</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>300</td>
<td>12</td>
</tr>
<tr>
<td>Water</td>
<td>300</td>
<td>8</td>
</tr>
</tbody>
</table>

3While the correct evaluation of $\Delta G(g)$ has been controversial, a common feature of classical theories is that $\Delta G(1) \neq 0$, thus Eq. (6) is not satisfied for monomers with this choice of $N$. This has not been considered a problem, because in the derivation of the nucleation rate only the free energy around the critical cluster size is needed.

3Katz and Spaepen (1978) did evaluate the normalization constant in formulating a kinetic nucleation rate applicable to condensed systems (e.g., nucleation of crystals in a melt). In this case Eq. (6) is assumed to be valid only down to a size $g_0$, which represents the minimum number of atoms required to have an identifiable nucleus, and $N$ is evaluated by requiring that Eq. (6) be satisfied for size $g_0$. Katz and Spaepen noted that a classical theory of nucleation in condensed systems which evaluated $N$ in this way would produce an identical result. In any case, in general for a condensed system neither $g_0$ nor $n^{s}_{g_0}$ is known, whereas for a dilute system $n_s$ is known.
\[
\frac{dS}{dt} = - \frac{Jg^*}{n_s} - (S - 1) \frac{B_1 A}{2v_1 n_s} \tag{15}
\]

\[
\frac{dM_1}{dt} = Jd_{p}^* + (S - 1) B_1 N \tag{16}
\]

\[
\frac{dA}{dt} = Jg^{2/3} S_1 + 2\pi B_1 (S - 1) M_1 \tag{17}
\]

In these equations \(N (m^{-3})\) is the population density of stable particles \((g \geq g^*)\), \(d_p\) is particle diameter, \(A\) is the total surface area of the stable aerosol, \(v_1\) is the volume of a monomer, and an asterisk denotes properties of a critical cluster. \(B_1\) and \(M_1\) are defined by

\[
B_1 = 2n_v v_1 \sqrt{\frac{kT}{2\pi m_1}} \tag{18}
\]

where \(m_1\) is the mass of a monomer, and

\[
M_1 = \int_{d_p^*}^{\infty} n(d_p) d(d_p) \tag{19}
\]

where \(n(d_p, t)\) is the particle size distribution function. The critical cluster size \(g^*\) is given by

\[
g^* = \left(\frac{2}{3 \ln S}\right)^3 \tag{20}
\]

Eqs. (14) through (17) form a set of four coupled ordinary differential equations which describe the time evolution of the stable aerosol. The nucleation rate \(J\) is a source term. For the situation of interest the initial conditions are given by \(N = 0, M_1 = 0, A = 0,\) and \(S = S_0\).

**DISCRETE MODEL**

Under the stated assumptions the rate of change in the monomer concentration can be written

\[
\frac{dn_1}{dt} = - n_1 \sum_{j=1}^{\infty} \beta_{ij} n_j + \sum_{j=2}^{\infty} (1 + \delta_{2j}) E_j n_j, \tag{21}
\]

where \(\delta_{2j}\) is the Kronecker delta function, which accounts for the production of two monomers when a dimer dissociates. For dimers and larger particles

\[
\frac{dn_k}{dt} = \frac{1}{2} \sum_{i+j=k} \beta_{ij} n_i n_j - n_k \sum_{j=1}^{\infty} \beta_{jk} n_j + E_{k+1} n_{k+1} - E_k n_k, \quad k \geq 2. \tag{22}
\]

For our purposes it is sufficient to assume that all particles are much smaller than the mean free path for molecular collisions in the gas, so that the kinetic theory expression for the collision frequency function can be used (Friedlander, 1977):

\[
\beta_{ij} = \frac{3v_1}{4\pi} \sqrt{\frac{6kT}{\rho_p}} \left(\frac{1}{i} + \frac{1}{j}\right) \times \left(i^{1/3} + j^{1/3}\right)^2 \tag{23}
\]

where \(\rho_p\) is particle mass density.

The evaporation coefficient \(E_g\) is obtained from Eq. (3). In the context of a discrete model—which is inherently a kinetic model—the choice of equilibrium state for evaluating Eq. (3) seems rather obvious: a saturated vapor in equilibrium. It would make little sense here to invoke the constrained equilibrium of classical nucleation theory. Thus, assuming a Boltzmann distribution at equilibrium, with \(n_z^e\) given by Eq. (11), we obtain

\[
E_g = \beta_{1,g-1} n_s \exp\left\{\Theta\left[g^{2/3} - (g - 1)^{2/3}\right]\right\}. \tag{24}
\]

This is the form of \(E_g\) as it appears in the text by Seinfeld (1986) and in Girshick and Chiu (1990a). Some previous applications of discrete-sectional codes (Wu and Flagan, 1988; Girshick and Chiu, 1989; Rao and McMurry, 1989) have adopted this expression, except that \(\beta_{1,g-1}\) was erroneously replaced by \(\beta_{1,g}\).

In the discrete-sectional approach Eq. (21) is written for monomers, Eq. (22) is written for dimers, trimers, etc., up to some specified size, and larger particles are treated by writing population balance equations of the
form of Eq. (22) for size sections, logarithmically spaced by particle volume. Within each section the particle size distribution is assumed to be uniform. The initial conditions in the present calculations are given by

\[ n_s(0) = \begin{cases} n_0, & g = 1 \\ 0, & g \geq 2 \end{cases} \tag{25} \]

where \( n_0 = S_0 n_s \).

In the present calculations 200 simultaneous equations were solved: 180 for the discrete spectrum, while particles larger than \( g = 180 \) were divided into 20 sections. This unusually large choice of the discrete spectrum was made to ensure that in all cases the critical cluster size lay within the discrete regime. The full set of equations was solved at each time step using the stiff equation code EPISODE (Hindmarsh and Byrne, 1977). A complete calculation typically required 200–300 CPU seconds on a Cray-2 supercomputer.

RESULTS

The calculations were conducted by casting the equations to be solved in nondimensional form. The results are presented in terms of dimensionless time and dimensionless concentration of stable particles, defined respectively by

\[ \tau = n_0 \beta_{11} t, \tag{26} \]

and

\[ N^* = \frac{N}{n_0}, \tag{27} \]

where \( N \) is the number of stable particles. \( N \) is directly calculated by the moment model, whereas in the discrete model it is evaluated as the total number of particles for which \( g \geq g^* \).

In the calculations \( \Theta \) and \( S_0 \) were treated as parameters. Figures 1 and 2 show results for the case \( \Theta = 19 \), \( S_0 = 200 \). This case is representative of materials with high values of surface tension or high molecular volumes, for which peak supersaturations may climb to high values before the onset of homogeneous nucleation. From Eq. (13) the kinetic nucleation rate in this case exceeds the classical nucleation rate by a factor \( e^{19/200} = 9 \times 10^5 \). Thus, as seen in Figure 1, for early times the number of particles nucleated at the kinetic rate exceeds the number nucleated at the classical rate by a factor \( \sim 10^6 \). At \( \tau \approx 3000 \) the curve calculated with the kinetic nucleation rate levels off, a consequence of the quenching of nucleation by condensation: the saturation ratio has relaxed to unity. However the curve calculated with the classical rate continues to increase. In this case the surface area for condensation increases at a much slower pace, so that it takes much longer for nucleation to be quenched.

For the earliest times, up to \( \tau \approx 4 \), the number of particles calculated by the discrete model is less than the result of the moment/kinetic model. The reason for this is that the initial conditions for the two calculations are not identical. Whereas the moment model immediately begins to nucleate particles—a distribution of subcritical clusters at time zero is implicitly assumed—the discrete model at time zero begins with all monomers, and must create critical-size clusters before nucleation can begin. This process is fast. For example, for iron at 1600 K and \( S_0 = 200 \), \( \tau = 4 \) corresponds to \( \sim 5 \mu s \). Thereafter the agreement between the moment/kinetic and discrete models is excellent. This result indicates that the cluster population rapidly achieves a distribution which corresponds to the steady-state kinetic nucleation rate.

The corresponding results for the volume-mean diameter of stable particles are plotted in Figure 2. The growth curves for the moment/kinetic and discrete calculations are quite close, whereas in the moment/classical model particles continue to grow to larger sizes, because the number of monomers available for condensation per stable particle is greater. In the moment/classical calculation the particles
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FIGURE 1. Time evolution of the number of stable particles calculated by the three models, for the case $\Theta = 19$, $S_0 = 200$.

FIGURE 2. Time evolution of the volume-mean diameter calculated by the three models, for the case $\Theta = 19$, $S_0 = 200$. The curve for the moment/classical calculation continues climbing until reaching a dimensionless mean diameter of $\sim 8000$ at $\tau \approx 3 \times 10^5$. 
I continue growing until $\tau \approx 3 \times 10^5$, reaching a final dimensionless mean diameter of about 8000, compared to about 250 in the other two calculations.

Figures 3 and 4 show the results for the case $\Theta = 8$, $S_0 = 6$. This value of $\Theta$ corresponds to a substance such as water. In this case $e^\Theta/S_0 = 500$, and the difference in the number of particles nucleated in the moment/kinetic and moment/classical cases is more modest than in the previous case. However, the difference in particle size is still large: the growth curve in the moment/kinetic case levels off at a dimensionless mean diameter of 78, whereas in the moment/classical calculation the mean diameter climbs to 360. Again the agreement between the moment/kinetic and discrete calculations is quite good regarding both number of particles (for times $\tau > 50$) and mean particle size.

The excellent agreement between the results of the moment/kinetic model and the discrete model is not fortuitous. The only processes occurring in our system are coagulation—which condensation is a special case—and evaporation. Condensation in both models is treated with the same expression. The models differ in that all other coagulation events are neglected in the nucleation-coupled model but included in the discrete model. Evidently the cases presented are sufficiently dilute so that neglecting coagulation (other than condensation) is reasonable. The evaporation coefficient in both models is the same insofar as it affects nucleation, because both choose the same equilibrium state for evaluating Eq. (3). In contrast the effective evaporation coefficient in the clas-

FIGURE 3. Time evolution of the number of stable particles calculated by the three models, for the case $\Theta = 8$, $S_0 = 6$.

4Evaporation from stable particles is treated slightly differently in the moment model, because the term $B_i$ defined by Eq. (18) neglects the Kelvin effect whereas Eq. (24) for the discrete model accounts for it. However this has a minor effect compared to evaporation from subcritical clusters.
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FIGURE 4. Time evolution of the volume-mean diameter calculated by the three models, for the case $\Theta = 8, S_0 = 6$.

Physical nucleation theory is quite different, because it is derived with reference to a different equilibrium state.

For systems which are densely loaded cluster-cluster coagulation and cluster scavenging may become significant effects, and the agreement between the moment/kinetic and the discrete model may deteriorate. To investigate this we compared calculations with the same value of $\Theta$ but with various values of $S_0$. We found that for any given value of $\Theta$ the agreement between the two models was quite good provided that the value of $S_0$ was not too large—the larger the value of $\Theta$, the larger the value of $S_0$ required to produce the discrepancy. Typical results, for the case $\Theta = 15$, are shown in Figures 5 and 6. For $S_0 = 50$ the agreement (after the initial transient) between the two models is excellent, both for the number of particles and the growth curves. For increasing values of $S_0$, the results are seen to diverge. In the case $S_0 = 200$ the results of the discrete model indicate that after nucleation is quenched the number of particles begins to decrease, and the particles grow at a faster rate than predicted by the moment/kinetic model. This discrepancy is due to the increased coagulation rates experienced in dense systems. But even at $S_0 = 200$ the differences between the two models are not large. In this case the particles produced are extremely small in both models, with a dimensionless volume-mean diameter $< 10$ at the end of the calculations.

5In nucleation theory the evaporation coefficient is never explicitly evaluated, but instead is replaced at an early step by the right-hand side of Eq. (3).

COMPARISON WITH EXPERIMENTAL DATA

The agreement between the moment/kinetic model and the discrete model does not necessarily mean that they are accurate. They
FIGURE 5. Comparison of the number of stable particles calculated by the moment/kinetic model and by the discrete model, for three different values of $S_0$, with $\Theta = 15$.

FIGURE 6. Comparison of the evolution of volume-mean diameter calculated by the moment/kinetic model and by the discrete model, for three different values of $S_0$, with $\Theta = 15$. 
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share a number of physical assumptions, such as the capillarity approximation, which may lead in some cases to significant errors.

For one test of the validity of the kinetic nucleation rate we consider experimental studies concerning homogeneous nucleation of dibutylphthalate. DBP is a large molecule for which the validity of the capillarity approximation may be particularly good. Although it has a low value of surface tension its large monomer surface area causes $\Theta$ to be large: $\Theta$ equals 22 at 30°C and 16 at 90°C.

In several earlier experimental studies of DBP nucleation, reviewed by Okuyama et al. (1987), the observed homogeneous nucleation rate was found to exceed the classical rate by a factor of $\sim 10^6$. Okuyama et al. (1987) initiated DBP nucleation by mixing high temperature DBP vapor with room temperature gas. They assumed that mixing was sufficiently rapid that nucleation did not occur until the measured mixing temperature was reached. They were thus able to control the initial supersaturation $S_0$, and by varying the ratios of hot and cold streams they could control the mixing temperature. Okuyama et al. (1987) compared their data on measured number concentrations to predictions based on a simple moment model coupled to either the classical nucleation rate expression or to the expression of Lothe and Pound (1962). They found that in all cases the classical nucleation rate significantly underpredicted the number of particles while the Lothe-Pound expression greatly overpredicted the number of particles. They reported two sets of data, according to the mixing ratio of hot gas to cold. These data were compared to the results of their moment model when they multiplied the classical nucleation rate by various factors. The factor which gave the best fit to the data was $\sim 10^8$ for one data set and $\sim 10^7$ for the other.

Nguyen et al. (1987) initiated nucleation by flowing hot DBP vapor through a water-cooled tube. In this case the partial pressure of DBP was determined by the temperature of the saturator upstream of the hot zone. In this system nucleation presumably occurred as the hot vapor cooled, when the supersaturation reached its critical value. The data were compared to the predictions of the analytical model of Pesthy et al. (1983), again assuming either the classical or the Lothe-Pound expression for the nucleation rate. The trends were quite similar to those reported by Okuyama et al. (1987). It was concluded that the best fit to the data was obtained if the classical nucleation rate was enhanced by a factor $10^5$–$10^7$. The experiments of Nguyen et al. (1987) were also modeled by Phanse and Pratsinis (1989), who used a moment model. They found good agreement of their predictions with the data if the classical nucleation rate was multiplied by $10^6$.

These results can be compared to the kinetic nucleation rate, which exceeds the classical rate by a factor $e^{\Theta}/S$. In the experiments of Okuyama et al. (1987) the temperature of the nucleating vapor ranged from 26°C to 43°C, and saturation ratios ranged from about 90 to 340. For the experiments of Nguyen et al. we calculate critical nucleation temperatures which ranged from 28°C to 65°C, and critical supersaturations which ranged from about 40 to 130. Based on these conditions, we find that $e^{\Theta}/S$ could have ranged from $4 \times 10^6$ to $5 \times 10^7$ in the experiments of Okuyama et al. (1987), and from $2 \times 10^6$ to $4 \times 10^7$ in the experiments of Nguyen et al. (1987).

Thus the empirical nucleation enhancement factors suggested by Okuyama et al. (1987), Nguyen et al. (1987), and Phanse and Pratsinis (1989) can be reasonably accounted for if the kinetic expression for the nucleation rate is adopted. Because $\Theta$ for
DBP decreases with increasing temperature, the discrepancy between the kinetic nucleation rate and the classical rate at a given supersaturation also decreases with increasing temperature. Although neither Okuyama et al. (1987) nor Nguyen et al. (1987) provide enough information for an unambiguous assessment, the trends in the data appear to be consistent with this effect.

CONCLUSIONS

We have shown that close agreement can be obtained between a moment model and a discrete model provided that the moment model adopts the proposed new expression for the nucleation rate. The new expression, which is derived as an extension of kinetic nucleation theory, is given by

$$J_{\text{kin}} = \frac{\beta_{11} n_S^2 S}{12} \sqrt{\frac{\Theta}{2\pi}} \exp \left[ \frac{4\Theta^3}{27(\ln S)^2} \right].$$

(28)

We believe that the fact that the discrete model agrees quite poorly with the moment/classical model, but quite well with the moment/kinetic model, highlights a flaw in the derivation of classical nucleation theory which was first pointed out by Katz and Wiedersich (1977). Namely, evaporation coefficients should be obtained by referring to a saturated vapor in stable equilibrium, and not to a supersaturated vapor in constrained equilibrium.

The fast approach of the results of the discrete model to the results of the moment/kinetic model suggests that the latter model may be accurate even for systems with rapid changes in thermodynamic conditions, such as high cooling rates. However, our results do indicate that the moment/kinetic model suffers a small loss in accuracy in very dense systems, because of the neglect of coagulation.

A preliminary comparison of the new expression for the homogeneous nucleation rate with experimental data indicates an encouraging improvement on classical theory. A more detailed comparison with experimental data on several substances, reported in a subsequent paper (Girshick and Chiu, 1990b), is encouraging although in some cases the new expression appears still (in common with the classical expression) to require a temperature-dependent correction. However, even fair agreement between the theory and experiment is remarkable, in view of the physical approximations in the theory. Further gains in nucleation theory are likely to come from a more microscopic view of the properties of clusters. As long as certain other assumptions are not invalidated—particularly, that monomer addition is the dominant mode of cluster growth—new information on the physical properties of clusters could readily be incorporated into the kinetic theory.

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