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Kinetics of heterogeneous nucleation for low mean cluster populations

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The process of nucleation is normally described using rate equations for the mean populations of molecular clusters. This approach can be justified for cases where these mean populations are large. However, it may be unsuitable in the case of heterogeneous nucleation on small particles if the mean populations are of the order of unity or less. In such a case, considering the average populations might be erroneous since the statistical fluctuations in the molecular populations should be taken into account. Here a stochastic treatment of heterogeneous nucleation kinetics is presented that is described by a set of master equations, and a modified expression for the nucleation rate has been deduced. Furthermore, a numerical method for solving the stochastic system has been examined, and the results show that the rate of nucleation can differ greatly from that obtained with the traditional kinetics. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1538605]

I. INTRODUCTION

Transformations of the phase of substances are very common; dramatic examples can be found in the atmosphere, where the condensation of water vapor, driven below its dew point, gives rise to the formation of water and ice clouds of great variety and beauty.[1] Similar processes on a grander scale are believed to take place in the vicinity of stars, giving rise to equally beautiful dusty nebulae. Domestic examples are also familiar, and processes such as melting, freezing, boiling or condensation are common in industry. However, the rate at which these processes occur is not easy to predict.

Most of these phase transformations are first order, which is to say that a latent heat is transferred during the process, and a surface tension exists between the two phases at equilibrium. The transformation usually involves the emergence of assemblages, or clusters, of molecules with characteristics (density, symmetry, etc) of the new phase. However, these clusters are not necessarily all thermodynamically more stable than the original phase. Small clusters, with high proportions of "surface," tend to be unstable. For moderate degrees of metastability of the original phase, there exists a "bottleneck" in the process, corresponding to the need to form a so-called critical molecular cluster. Once one has been formed, further growth is thermodynamically favorable. This is the process of nucleation, driven fundamentally by thermal fluctuations. However, for greater degrees of metastability of the original phase, the phase transformation can become deterministic, with no thermodynamic bottleneck. The process then becomes spinodal decomposition.[2]

Most research into nucleation is concerned with the homogeneous process, where the metastability of the original phase is overcome without the presence of special nucleation sites in the system. The critical clusters form in the absence of foreign bodies and container surfaces. However this is not the process responsible for most of the familiar phase transformations described earlier. The atmosphere is not entirely free of suspended matter, and cloud formation, for example, takes place by a process of so-called heterogeneous nucleation. The water clusters, and ultimately the cloud droplets, form on the surfaces of suspended particles called cloud condensation nuclei (CCN), since it is far easier thermodynamically to do this than to form a critical cluster homogeneously.[3–6] Heterogeneous nucleation has been previously investigated via free energy calculation approach.[7,8]

Cloud condensation nuclei are solid or liquid aerosols, often only a fraction of a micrometer in diameter. Now, the metastability of a vapor is measured in terms of its supersaturation S, defined as the ratio of the vapor pressure to the saturated vapor pressure, and the critical supersaturation required to drive nucleation at a given rate is a measure of the ease with which critical clusters can be formed. While a value of S of order 10 might be necessary in some circumstances to drive homogeneous nucleation, only $S \sim 0.01$ is sufficient to drive the heterogeneous process if CCN surfaces are present.[9] In the atmosphere, supersaturations are usually limited to these values, so heterogeneous nucleation is the dominant process.

It is generally considered that the kinetics of nucleation were correctly described by Becker and Döring[10] almost 70 years ago. This solution applies to the formation of clusters of a single molecular species, by a process of single molecule attachment and loss. Usually, the slightly unrealistic steady state situation is assumed, where the supersaturation of the original phase is held constant in spite of the consumption of material in the formation of new phase. Nevertheless, this is a reasonable approximation when the rate of consumption is low, and so the processes of homogeneous and heterogeneous nucleation are considered to be well represented by the formula for the nucleation rate,

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$$J=\frac{\beta_1 n_1}{1+\sum_{i=2}^{i_{\max}}\prod_{j=2}^{i}(\gamma_j/\beta_j)}, \tag{1}$$

where β_i is the rate at which monomers attach to cluster of size i, γ_i is the rate at which they detach from the same cluster, and $i_{\max}$ is the maximum cluster size allowed in the system. The growth rates β_i are proportional to the monomer population n_1, since they represent monomeric attachment.

The Becker–Döring expression, Eq. (1), is obtained by solving a basic set of rate equations describing the difference between $\beta_i n_i$, the number of growth events from size i to $(i+1)$, and γ_{i+1}, the number of decays from size $(i+1)$ to i,

$$J=\beta_i n_i-\gamma_{i+1}n_{i+1}, \tag{2}$$

where n_i is the steady state population of clusters of size i. These equations are held to apply for i from unity up to $i_{\max}-1$. The Becker–Döring solution applies when the growth ladder is terminated by the assumption that clusters at size $i_{\max}+1$ do not decay, hence $J=\beta_{i_{\max}}n_{i_{\max}}$. For many realistic situations, the solution is insensitive to the choice of $i_{\max}$, as long as it is large enough.

However, the Becker–Döring approach makes an assumption about the kinetics which may not be valid. The rate equations are what we might call *classical* in that the number of growth transitions from size i to $(i+1)$, for example, is taken to be the population of i-clusters n_i multiplied by a rate coefficient β_i proportional to n_1. If n_1 were a precise constant, then this assumption would be valid, but in fact all cluster populations in the problem, including n_1, display fluctuations about a mean value, since the processes of growth and decay occur as stochastic events. As we shall show in the next section, the growth rate actually requires us to evaluate the mean of the product of the populations of monomers and i-clusters, rather than the product of the mean.

The error involved by the neglect of fluctuations is small when the populations of clusters are large, by the usual statistical arguments. This is almost always the case in practical cases of homogeneous nucleation: the system is a sample of vapor, say, in a macroscopic container, so that the number of monomers present in the system is huge. However, when the process under consideration is heterogeneous nucleation taking place on the surface of a microscopic particle, the possibility arises that populations could be small. An experiment involving vapor condensation could be conducted in a macroscopic container, but the actual "reaction vessel" would be the surface of one of the many particles suspended inside the container. In experiments involving heterogeneous nucleation, therefore, it is possible for the Becker–Döring kinetics to be inappropriate.

It is this possibility that we investigate in this study. There have been some attempts at considering the discrete nature of the nucleating molecules with the aid of stochastic arguments. In particular, Ebeling *et al*. have examined a master equation approach in dealing with the nucleation kinetics.[11] To a limited extent, it is similar to what we propose in the next section of this paper, but the theory of Ebeling *et al*. gives only a general picture of the kinetics, and is not intended for treating small systems with tiny mean populations of molecules. The possibility of low mean populations encountered in precipitation in small droplets has been considered by Manjunath *et al.*, through stochastic simulations involving a series of the so-called product density equations.[12] Dimer formation taking place on the surface of tiny dust particles in low density conditions of interstellar medium and thin atmospheres has also been previously studied.[13]

In this paper, we consider the complete solution to the heterogeneous nucleation kinetics of growth and decay of clusters of various sizes, where the possibility of fluctuations is properly taken into account. This requires us to set up and solve master equations for the probability distributions of cluster populations. We consider a simple set of rate coefficients which allow us to perform the computational tasks in an efficient manner, and contrast the resulting nucleation rate with the Becker–Döring solution. We expose the conditions necessary for large differences to exist between the "classical" Becker–Döring solution and the more appropriate "stochastic" solution to the master equations.

II. KINETICS OF HETEROGENEOUS NUCLEATION

A. Classical rate equations

Consider a host particle surrounded by gas phase molecules (monomers) that occasionally strike and stick to the particle. Once adsorbed, such a monomer may move around the particle. It may encounter another monomer and the two may form a dimer. The growth of the adsorbed molecular cluster may progress further due to attachments of more monomers. The cluster may also decay by loss of monomers, induced, perhaps, by energy input from the substrate. Clusters need to reach a critical size i^* before they will, on average, be able to grow further. In other words, for clusters consisting of i molecules, with $i<i^*$, the probability per unit time for a cluster to grow, divided by the probability for it to lose a molecule (decay) is less than unity. For sizes greater than the critical size, the ratio of growth to decay probabilities is greater than unity. Most clusters tend to languish in the subcritical size region, and only occasionally do they manage, by a lucky sequence of growth steps, to reach the critical size, and thereafter grow.

Traditionally, such a system is modeled using the rate equations,

$$\frac{dn_i}{dt}=\beta_{i-1}n_{i-1}-\gamma_i n_i-\beta_i n_i+\gamma_{i+1}n_{i+1} \tag{3}$$

for $i\geqslant 2$, where n_i is the mean population of clusters of size i in the system. β_i is the rate at which molecules attach themselves to clusters of size i, and γ_i is the rate at which molecules are lost from clusters of size i. The growth rates β_i are proportional to the number of monomers n_1 in the system, so that we can write

$$\beta_i=\beta_i' n_1. \tag{4}$$

For $i=1$ the dynamics are expressed by

$$\frac{dn_1}{dt}=j-\lambda n_1-2\beta_1 n_1+2\gamma_2 n_2-(\beta_2 n_2-\gamma_3 n_3)$$
$$-(\beta_3 n_3-\gamma_4 n_4)-\cdots-\beta_{i_{\max}} n_{i_{\max}}$$
$$=j-\lambda n_1-2(\beta_1 n_1-\gamma_2 n_2)$$
$$-\sum_{i=2}^{i_{\max}-1}(\beta_i n_i-\gamma_{i+1} n_{i+1})-\beta_{i_{\max}} n_{i_{\max}}, \qquad (5)$$

where j is the source rate of monomers attaching themselves to the surface from the surrounding medium and λ is the evaporation rate of monomers from the particle surface.

When fluctuations in populations about mean values are taken into account, it would seem reasonable that the rate equations (3) should be replaced by something like

$$\frac{d\langle N_i\rangle}{dt}=\beta'_{i-1}\langle N_1 N_{i-1}\rangle-\gamma_i\langle N_i\rangle-\beta'_i\langle N_1 N_i\rangle$$
$$+\gamma_{i+1}\langle N_{i+1}\rangle, \qquad (6)$$

where the angled brackets represent an averaging over the fluctuations and the cluster populations are written in upper case N_i to remind us that they are fluctuating stochastic variables. Equation (5) would similarly be replaced. We shall see in the next section how such equations can be derived from a stochastic treatment of the populations, and how the averages can be evaluated.

B. Stochastic approach

In the stochastic approach we consider a probability distribution that describes the state of the system in terms of the exact populations of all the allowed cluster sizes. Let the probability that the system contains N_1 monomers, N_2 dimers, and in general N_i i-clusters at time t be $W(N_1,N_2,\ldots,N_i,\ldots,N_{i_{\max}};t)\equiv W(\{N_i\};t)$. In order to limit the number of elements in this array, we introduce a maximum cluster size $i_{\max}$. We also limit each N_i to be less than or equal to $N_i^{\max}$. The rate of change of this probability is then given by

$$\frac{dW}{dt}=jW(N_1-1,\ldots)-jW(\cdots)+\lambda(N_1+1)W(N_1+1,\ldots)-\lambda N_1 W(\cdots)+\beta'_1(N_1+2)(N_1+1)W(N_1+2,N_2-1,\ldots)$$
$$-\beta'_1 N_1(N_1-1)W(\cdots)+\sum_{i=2}^{i_{\max}-1}\beta'_i(N_1+1)(N_i+1)W(N_1+1,\ldots,N_i+1,N_{i+1}-1,\ldots)$$
$$+\beta'_{i_{\max}}(N_1+1)(N_{i_{\max}}+1)W(N_1+1,\ldots,N_{i_{\max}}+1)-\sum_{i=2}^{i_{\max}}\beta'_i N_1 N_i W(\cdots)$$
$$+\gamma_2(N_2+1)W(N_1-2,N_2+1,\ldots)+\sum_{i=3}^{i_{\max}}\gamma_i(N_i+1)W(N_1-1,\ldots,N_{i-1}-1,N_i+1,\ldots)-\sum_{i=2}^{i_{\max}}\gamma_i N_i W(\cdots). \qquad (7)$$

On the right hand side of the above equation, t has been omitted for simplicity. The dots represent values of the N_j that are the same as on the left hand side.

The processes considered are the growth transitions $1+(i-1)\rightarrow i$ and $1+i\rightarrow(i+1)$ due to monomer attachment, as well as the decay processes $i\rightarrow(i-1)+1$ and $(i+1)\rightarrow i+1$ due to monomer detachment from the cluster. The attachment and detachment of dimers, trimers, and higher size clusters are neglected. The first two terms (the j terms) describe the addition of a monomer from the surroundings, leading to a monomer population change $N_1\rightarrow N_1+1$. The third and fourth terms represent loss of a monomer from the particle surface due to the population jump $N_1\rightarrow N_1-1$. The rest of the terms are constructed using similar arguments for monomeric attachment and detachment to and from dimers, trimers and in general i-clusters. There is a term for $\beta_{i_{\max}}$, but no term involving $\gamma_{i_{\max}+1}$ since clusters at size $i_{\max}$ may grow, but the population at this size receives no additions from the decay of the next larger cluster. This acts as the boundary condition of the problem.

The classical limit corresponds to the probability distribution W being unity for only one set of possible populations of the i-clusters, that is the mean populations. That is, $W(n_1,n_2,\ldots,n_i\ldots)=1$ and all other elements are zero. Formally, this is represented, using the Kronecker delta, as

$$W(N_1,N_2,\ldots)=\prod_{i=1}^{i_{\max}}\delta_{N_i n_i}. \qquad (8)$$

In the steady state and this classical limit, solving Eq. (7) would be equivalent to solving Eqs. (3), (5), and (1), as shown in the Appendix.

If Eq. (7) can be solved by some means, knowledge of W would allows us to generate probability distributions $P_i(N_i)$ for the population of i-clusters,

$$P_i(N_i)=\sum_{(j\neq i)}\sum_{N_j=0}^{N_j^{\max}}W(N_1,\ldots,N_j,\ldots,N_i,\ldots). \qquad (9)$$

The P_i are likely to look like Gaussian distributions for large n_i, or Poisson distributions for small n_i. Ideally, the values of all the $N_j^{\max}$ ought to be infinity for a "perfect" evaluation of $P_i(N_i)$. However in practice, as we shall see in Sec. III C, satisfactory results may be obtained when the $N_j^{\max}$ are limited to reasonably small values.

It is also possible to calculate joint probabilities, such as $P_{li}(N_l,N_i)$, which is the probability that we find N_l l-clusters and N_i i-clusters in the system. These distributions are given by

$$P_{li}(N_l,N_i) = \sum_{j\neq l,i} \sum_{N_j=0}^{N_j^{\max}} W(N_1,\ldots,N_j,\ldots,N_l,\ldots,N_i,\ldots). \tag{10}$$

If the steady state W are known, it is possible to calculate the nucleation rate. This is done by summing all the probabilities of growth from any size i to size $i+1$ and subtract those for decay in the opposite direction,

$$J=\sum_{\{N_j\}} (\beta_i' N_1 N_i W(\{N_j\}) - \gamma_{i+1} N_{i+1} W(\{N_j\})), \tag{11}$$

which by introducing the notation

$$\langle N_i\rangle = \sum_{N_i} N_i P_i(N_i) \tag{12}$$

and

$$\langle N_l N_i\rangle = \sum_{N_l,N_i} N_l N_i P_{li}(N_l,N_i), \tag{13}$$

allows us to write

$$J=\begin{cases} \beta_i'\langle N_1 N_i\rangle - \gamma_{i+1}\langle N_{i+1}\rangle & \text{if } i\geqslant 2 \\ \beta_i'\langle N_1(N_i-1)\rangle - \gamma_{i+1}\langle N_{i+1}\rangle & \text{if } i=1. \end{cases} \tag{14}$$

Any value of $i\geqslant 2$ in the first of the above expressions would give the same result in the steady state as the nucleation current should be independent of cluster size. If one uses $i=1$ to compute the nucleation rate, a slight modification is required as in the second expression in Eq. (14), since having just a single monomer in the system cannot give rise to a nucleation current towards the critical size. In contrast, the nucleation rate given in Eq. (2) according to the standard rate Eq. (3), in the same notation, reads

$$J^{\text{clas}} = \beta_i'\langle N_1\rangle\langle N_i\rangle - \gamma_{i+1}\langle N_{i+1}\rangle. \tag{15}$$

One would expect relative fluctuations in the populations to become negligible when the populations are large, so that a mean of a product becomes the product of the means. It is therefore evident from the comparison of Eqs. (14) and (15) that the standard rate equations are valid in the large population limit. It is also possible to visualize how the standard result for the nucleation rate must be modified for small systems. By writing

$$\beta_i'\langle N_1 N_i\rangle = (1+\epsilon_i)\beta_i'\langle N_1\rangle\langle N_i\rangle, \tag{16}$$

the expression for the rate given in Eq. (1) can be used to see that, to a good approximation,

$$J_{\text{small}} = J_{\text{large}} \prod_{i=1}^{i^*} (1+\epsilon_i), \tag{17}$$

where i^* is the critical size, where the rate coefficients for growth and decay are equal ($\beta_i=\gamma_i$). We are interested in calculating the modification factor.

III. CALCULATIONS

A. Parametrization

The master equations (7) are driven by the input parameters j, λ, β_i', and γ_i. In order to investigate the problem of heterogeneous nucleation in small systems, we must carefully choose the input parameters that are likely to lead to small cluster populations.

Let us introduce a size parameter ξ, which may be taken to be proportional to the surface area of the host particle. The coefficients λ and γ_i are the decay rates of monomers ($i=1$) and i-mers ($i\geqslant 2$), respectively, and hence may be taken as independent of the system size. The attachment rate j of monomers onto the particle surface, however, should increase linearly with ξ. It is useful to consider temporarily the dynamics in the absence of any dimer production, in which case the mean monomer population would be given by a balance between j and λ, namely, $\langle N_1\rangle \simeq j/\lambda$. If j_0 is the value of j at $\xi=1$ then we can write

$$j=\xi j_0, \tag{18}$$

so that

$$\langle N_1\rangle \simeq \frac{j_0}{\lambda}\xi. \tag{19}$$

For convenience, let us postulate that $\xi=1$ is the system with a nominal mean monomer population of unity. This imposes the condition $j_0=\lambda$.

For simplicity, we assume the growth rate β_i' to be independent of the cluster size i, i.e., $\beta_1'=\beta_2'=\cdots=\beta_{i_{\max}}'$. On the other hand, β_i' will be inversely proportional to ξ since it measures the likelihood that an adsorbed monomer will encounter an adsorbed i-mer. As the system gets bigger, this likelihood would diminish. Furthermore, we may fix β_i' such that at $\xi=1$ the mean growth rate of an i-mer is unity. Remembering from Eq. (4) that $\beta_i=\beta_i'\langle N_1\rangle$, this means that $\beta_i'=1$ at $\xi=1$, and in general

$$\beta_i' = \frac{1}{\xi}\ . \tag{20}$$

The choice of the parameters γ_i must satisfy the requirement that at the critical size i^*, a cluster is as likely to decay as it is likely to grow, i.e., $\gamma_{i*}=\beta_{i*}'\langle N_1\rangle$. With the above stated choice of β_i' and $\langle N_1\rangle$, this means that $\gamma_{i*}=1$ at $\xi=1$. Indeed, this should be true for any value of ξ as the decay rates are independent of the system size. The i-dependence of γ_i may be chosen on the grounds that small clusters are more likely to decay than large clusters. We therefore choose

$$\gamma_i = \left(\frac{i^*}{i}\right)^p, \tag{21}$$

where p is some constant to be decided. Entirely for computational convenience, and without suggesting that the model should represent a real system, we shall choose $p=2$ and $i^*=2$. This form of γ_i ensures that a cluster below the critical size ($i<i^*$) has a high probability of decay, whereas those above the critical size ($i>i^*$) will find it easier to grow.

The relative values of j_0 (and λ) and β_i' control the degree to which the mean monomer population is close to the estimate (19). We shall explore cases where $j_0 \gg 1$ and $j_0=1$ in Sec. III C.

B. Classical solution

The most convenient way of deducing the classical nucleation rate for a given set of parameters j_0, λ, ξ, β_i, and γ_i is through the expression (1). However the n_1 appearing in that equation still needs to be known. Although in the large j_0 limit expression (19) for $\langle N_1 \rangle$ may provide a reasonable estimate, this is not guaranteed to be true in general. A better method of finding n_1 is as follows.

Equation (5) in the steady state may be written, with the help of Eq. (2), as

$$0=j_0\xi-\lambda n_1-2J-(i_{\max}-2)J-J$$
$$=j_0\xi-\lambda n_1-(i_{\max}+1)J, \tag{22}$$

where J is given by Eq. (1). Let us assign a function

$$\mathcal{F}(n_1)=j_0\xi-\lambda n_1-(i_{\max}+1)J. \tag{23}$$

This function falls with increasing n_1. As an initial approximation, we provide $n_1=j_0\xi/\lambda$, which in all practical cases is at least a slight overestimation of the actual value of n_1. We then iteratively search for a zero of the function $\mathcal{F}(n_1)$ by subtracting a very small amount (typically $\sim 10^{-6}$) from the trial value of n_1 and evaluating a new value of $\mathcal{F}(n_1)$. This process is continued until a solution is found within a very small tolerance. The final value of n_1 that corresponds to $\mathcal{F}(n_1)=0$ can then be utilized in Eq. (1) to find the classical value of the nucleation rate.

C. Solving the master equation

Given all the necessary parameters given in Sec. III A, we are in a position to solve the master equations (7) which should ultimately render the stochastic solution to the system. Solving Eq. (7) analytically does not appear to be a feasible task. We therefore look for an appropriate numerical technique to act as a substitute.

Computationally, we discretize time t, and replace the dt by a very small but finite Δt in Eq. (7). The $dW(t)$ may then be replaced by $W(t+\Delta t)-W(t)$, thus allowing Eq. (7) to be solved iteratively. As an initial condition, we set $W(0,0,0,\ldots,0;t=0)=1$ with all the remaining elements of the array $W(\{N_i\})$ set to zero, specifying an empty system to start with. The system thereafter evolves in time until a steady state is reached.

Equations (7) represent a set of coupled differential equations. $i_{\max}$ is the largest size of cluster that can form on the particle, and needs to be specified explicitly at the beginning. In principle, it should be large enough so that the contribution due to terms with $i_{\max}+1$ in the series appearing in Eq. (1) is negligible.

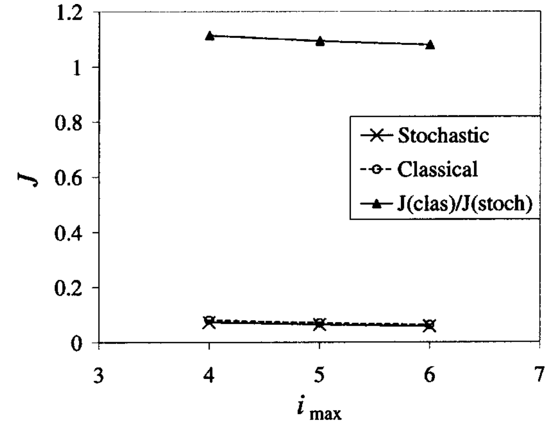

FIG. 1. Nucleation rate as a function of $i_{\max}$ with $i^*=2$, $j_0=\lambda=1$, and $\xi=1$. It is reasonably safe to choose $i_{\max}=4$, since the results obtained with a higher $i_{\max}=6$, for instance, are approximately the same.

Strictly speaking, the multidimensional array $W(\{N_i\})$ consists of an infinite number of elements, but for computational purpose we may set an upper limit on the maximum number of i-clusters the system can possess at any time. In other words the array $W(\{N_i\})$ takes the form $W(0{:}N_1^{\max},0{:}N_2^{\max},\ldots,0{:}N_{i_{\max}}^{\max})$. These values $N_1^{\max},N_2^{\max},\ldots,N_{i_{\max}}^{\max}$ should be decided by educated guess such that all of the $i_{\max}$ probability distributions in Eq. (9) die down to negligible levels at $N_i=N_i^{\max}$ at the end of the iterations.

Steady state is considered to have been reached when all the elements of $W(\{N_i\})$ have converged within a very small tolerance. The nucleation rates J with different values of i in Eq. (14) will normally evolve differently with time, but eventually they will all converge upon a common value. This convergence of J with different values of i in fact serves as a ''double check'' for ensuring that a steady state has indeed been achieved.

In Fig. 1 we plot the classical as well as the stochastic nucleation rates obtained under different values of $i_{\max}$, with fixed values of $i^*=2$, $j_0=\lambda=1$, and $\xi=1$. As can be seen, the nucleation rate J is not very sensitive to $i_{\max}$. The sto-

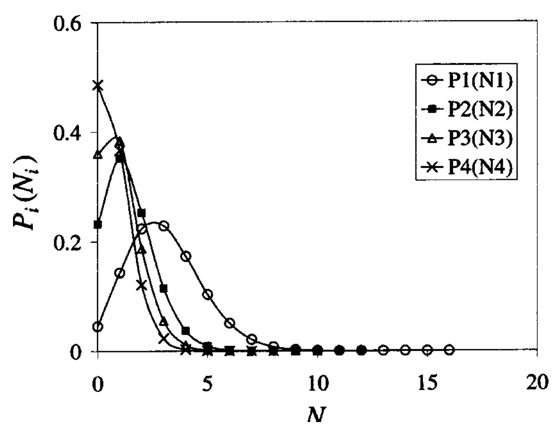

FIG. 2. A typical example of probability distributions $P_i(N_i)$. Only values plotted at integer N are physical; the curves have been fitted as a guide to the eye. In this example, $N_1^{\max}=16$, $N_2^{\max}=12$, etc. were sufficient to give satisfactorily smooth probability distributions for the mean populations.

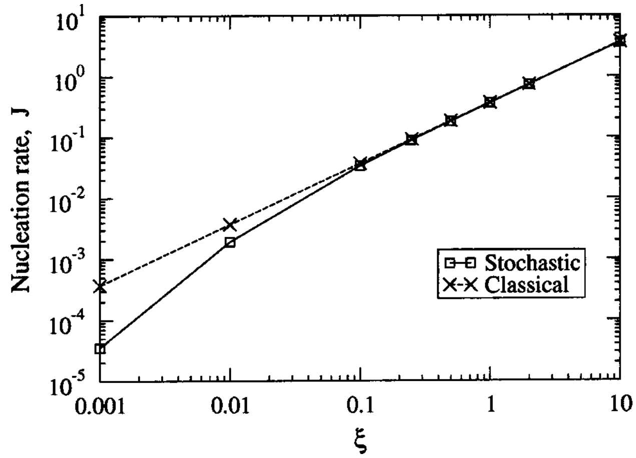

FIG. 3. Nucleation rate as a function of the size parameter ξ for the $j_0 = \lambda = 100$ model. The prediction of rate equation approach is shown with cross signs, and the squares are the results of the stochastic model presented here.

chastic J decreases slightly with increasing i_{max}, but the essential message is that a value of $i_{max}=4$ may be trusted in order to demonstrate at least the qualitative behavior of the system.

An example of the probability distributions $P_i(N_i)$, as defined in Eq. (9) and calculated once the steady state has been reached, is shown in Fig. 2. $P_1(N_1)$ is the probability distribution for the monomer population, $P_2(N_2)$ is the same for dimmers, and so on.

Figure 3 shows the stochastic and classical nucleation rates as a function of the particle size parameter ξ for $j_0 = \lambda = 100$. The calculation has been performed with $i^* = 2$ and $i_{max}=4$. Figure 4 shows the mean monomer population for the same system as predicted by the two models. There is a good agreement between the two models for the monomer population in this limit of $j_0 \gg 1$. The nucleation rates in Fig. 3 according to the two models, however, start diverging as ξ falls below 0.1. It is interesting to note that the monomer population between $\xi = 0.1$ and $\xi = 1$ is below unity and yet

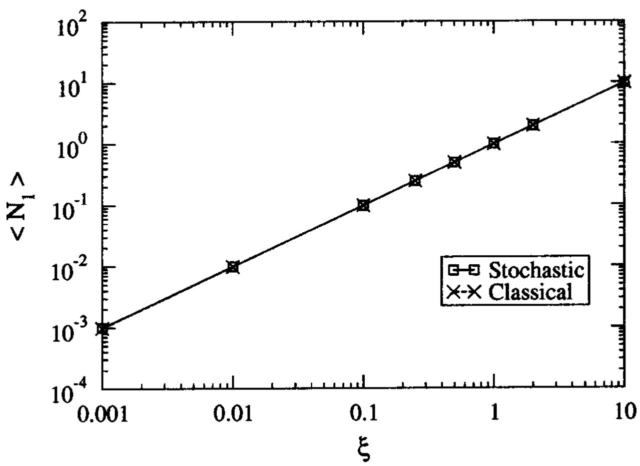

FIG. 4. Stochastic and classical mean monomer population, $\langle N_1 \rangle$, as a function of ξ for the $j_0 = \lambda = 100$ model. Both models predict essentially the same mean populations for this choice of parameters.

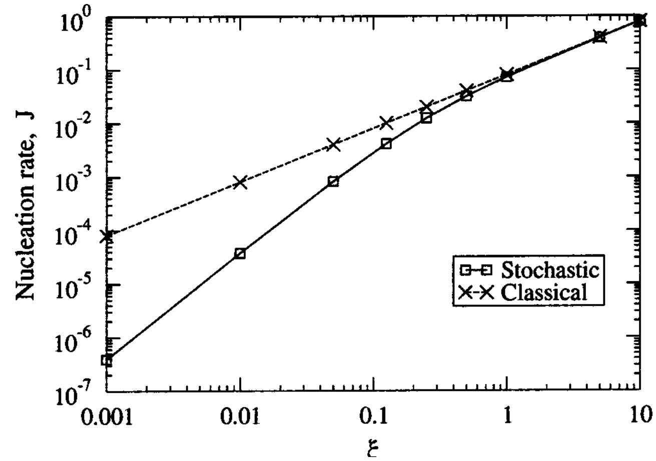

FIG. 5. Nucleation rate as a function of ξ for the $j_0 = \lambda = 1$ model. Difference between the stochastic and classical models emerges below $\xi = 1$.

the stochastic nucleation rate does not differ considerably from its classical counterpart in this range, and for these parameters.

In Fig. 5 the nucleation rate is plotted again as a function of ξ, but this time with $j_0 = \lambda = 1$, the rest of the parameters being the same as in Fig. 3. The mean monomer population for the same system is plotted in Fig. 6, and now we see that the stochastic $\langle N_1 \rangle$ does differ from classical $\langle N_1 \rangle$ once ξ goes below unity. Approximately below the size $\xi = 1$, where the mean monomer population is below unity, visible difference between the classical and stochastic nucleation rates is again evident in Fig. 5. The linear dependence of J with respect to ξ exhibited in the classical theory is lost when one deals with very small particle sizes. Note that the stochastic model gives a smaller nucleation rate, but a higher mean population of monomers than the classical prediction, since a higher nucleation rate would leave fewer monomers on the surface.

The ratios $J_{classical}/J_{stochastic}$ derived from both cases, $j_0 = \lambda = 100$ and $j_0 = \lambda = 1$, have been plotted in Fig. 7. This is

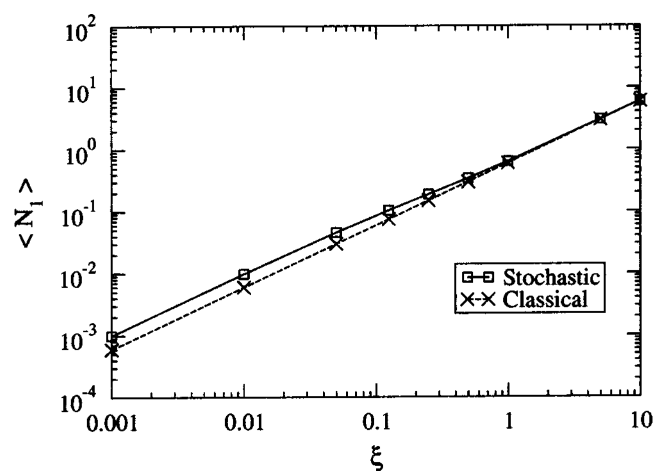

FIG. 6. Stochastic and classical mean monomer population, $\langle N_1 \rangle$, as a function of ξ for the $j_0 = \lambda = 1$ case. Unlike the $j_0 = \lambda = 100$ case, some difference can be seen here between the mean populations according to the two models.

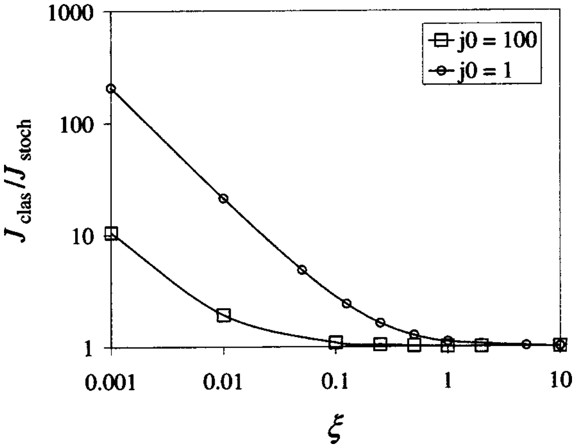

FIG. 7. The ratio of classical vs stochastic nucleation rate calculated as a function of ξ for the $j_0=\lambda=100$ and $j_0=\lambda=1$ models.

simply the factor by which the classical Becker–Döring kinetics overestimates the nucleation rate as compared with the stochastic model presented here. The overestimation grows as we look at ever smaller sizes (ξ) of the host particle. Also, the ratio is larger for the $j_0=\lambda=1$ calculations, compared with the $j_0=\lambda=100$ case. This is due partly to the fact that a large value of j_0 produces a mean monomer population closer to the classical prediction as discussed in Sec. III A.

The classical treatment requires there to be a large population of the nucleating species so as to be able to use a mean value of the populations in treating the kinetics. However, when the mean monomer population is below unity, there are instances when there are no monomers present on the surface and only by a lucky chance are there more than one monomers present. Since the classical kinetics ignores this discrete nature of the molecular species, it assumes a higher reaction rate between the molecules, hence yielding an overestimated nucleation rate.

IV. CONCLUSIONS

We have studied the problem of heterogeneous nucleation under conditions where the mean populations of the nucleating clusters may be of the order of unity. The traditional rate equation approach, which treats the kinetics in terms of the mean cluster populations, is likely to fail in such a limit. To investigate this, we have proposed a new master equation approach that takes into account the stochastic fluctuations in cluster populations, and replaces the classical rate equations.

A method for solving the master equation numerically has been explored. The results of the model calculations performed here indicate a large difference in the nucleation rates as predicted by the stochastic and classical treatments as the nucleation site becomes very small. However, if the system is large, the stochastic treatment reproduces the classical Becker–Döring kinetics.

For simplicity, only monomer attachment and detachment to the nucleating cluster has been allowed in the stochastic model here. The master equation can nevertheless be extended easily to include the loss and gain of dimers, trimers, etc., solving which would clearly require a much greater deal of computational power.

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APPENDIX: REDUCTION OF MASTER EQUATIONS TO RATE EQUATIONS

It is possible to show that the master equations (7) do indeed reduce to the rate equations (3) and (5) in the classical limit of relatively large populations. To do this, let us define an operator $\hat{O}$ such that

$$\hat{O}\cdot f=\sum_{\{N_i\}=0}^{\infty} N_l\cdot f, \tag{A1}$$

i.e., we multiply the given term f by N_l (where $l=1,\ldots,i_{\rm max}$) and sum the result over all the $\{N_i\}$. Let us perform this operation on both sides of Eq. (7). This makes the left-hand side read as

$$\sum_{\{N_i\}=0}^{\infty} N_l\frac{dW(\{N_i\})}{dt}=\frac{d\langle N_l\rangle}{dt}, \tag{A2}$$

which is equivalent to the left-hand side of Eqs. (3) and (5). Now consider the consequence of this operation on the right-hand side of Eq. (7). On the right-hand side, one needs to treat separately the cases of $l=1$ and $l>1$ since there are different rate equations for the two cases of N_1 and N_l ($l>1$) in the classical picture. Let us consider terms proportional to the parameters j, λ, β_i', and γ_i one by one and try to compare them with those found in the rate equations (3) and (5).

1. *The j terms*

a. l=1

Operating the first term in Eq. (7) by $\hat{O}$ along with $l=1$ will render

$$\sum_{\{N_i\}=0}^{\infty} jN_1\ W(N_1-1,\ldots).$$

In order to bring the probability W in the same form as on the left-hand side, that is, $W(N_1,N_2,\ldots,N_{i_{\rm max}})$, we can make the substitution $N_1\rightarrow N_1+1$, which is what happens to the monomer population due to the j term. The above notation will then turn into

$$\sum_{\{N_i\}=0}^{\infty} j(N_1+1)W(N_1,\ldots)=j\langle N_1+1\rangle. \tag{A3}$$

The sum over this new N_1 label should run from -1 to ∞, but clearly the unphysical first term in the series vanishes, so that the lower limit is indeed zero.

Operating upon the second term in Eq. (7) with $\hat{O}$ will give

$$-\sum_{\{N_i\}=0}^{\infty} jN_1\ W(\cdots)\ =\ -j\langle N_1\rangle. \tag{A4}$$

In the classical limit, the upper case N_1 together with angled brackets is replaced by n_1, so from Eqs. (A3) and (A4), the net result of applying $\hat{O}$ on both the j terms in Eq. (7) is

$$jn_1+j-jn_1=j. \tag{A5}$$

This is precisely what we have as the "j term" in the rate equation (5), which was written down explicitly for the monomeric $(l=1)$ population.

b. $l>1$

If l is not equal to 1, then the operation due to $\hat{O}$ will make the first term in Eq. (7) read

$$\sum_{\{N_i\}=0}^{\infty} jN_l\ W(N_1-1,\ldots),$$

where $l\neq 1$. This time the substitution $N_1\rightarrow N_1+1$ will lead to

$$\sum_{\{N_i\}=0}^{\infty} jN_l\ W(N_1,\ldots)=j\langle N_l\rangle. \tag{A6}$$

The second term of the master equation under the operation of $\hat{O}$ will be similar to expression (A4),

$$-\sum_{\{N_i\}=0}^{\infty} jN_l\ W(\ \ldots)\ =\ -j\langle N_l\rangle. \tag{A7}$$

Hence the sum of Eqs. (A6) and (A7) will be zero, and indeed, there is no j term in the rate equations (3).

2. The λ terms

a. $l=1$

If we apply the operator $\hat{O}$ to the third term of the master equation (7), we have

$$\sum_{\{N_i\}=0}^{\infty} \lambda N_1(N_1+1)\ W(N_1+1,\ldots).$$

This time we make the substitution $N_1\rightarrow N_1-1$ so that the above expression is converted into

$$\sum_{\{N_i\}=0}^{\infty} \lambda(N_1-1)N_1\ W(N_1,\ldots)=\lambda\langle(N_1-1)N_1\rangle. \tag{A8}$$

The lower limit for the sum over the shifted variable N_1 should be $+1$, but we can extend this to zero without changing the result of the summation.

Performing the operation $\hat{O}$ on the fourth term of the master equation will give us

$$-\sum_{\{N_i\}=0}^{\infty} \lambda N_1N_1\ W(\cdots)=-\lambda\langle N_1^2\rangle. \tag{A9}$$

Once again, to see the correspondence with the classical model, we replace the angled brackets and the upper case N_1 with the lower case n_1, so we are left with the net result

$$\lambda(n_1^2-n_1)-\lambda n_1^2=-\lambda n_1. \tag{A10}$$

This is the λ term found in the monomeric rate equation (5).

b. $l>1$

The third term of Eq. (7) under the influence of $\hat{O}$ will this time become

$$\sum_{\{N_i\}=0}^{\infty} \lambda N_l(N_1+1)\ W(N_1+1,\ldots),$$

and the substitution $N_1\rightarrow N_1-1$ will make it

$$\sum_{\{N_i\}=0}^{\infty} \lambda N_lN_1\ W(N_1,\ldots)=\lambda\langle N_lN_1\rangle. \tag{A11}$$

The operation due to $\hat{O}$ on the fourth term of Eq. (7) will give us $-\lambda\langle N_lN_1\rangle$. Hence the lambda term will vanish for the $l>1$ case, and is absent in the rate equation (3) also.

3. The β_i' terms

a. $l=1$

If we operate on the fifth term in the master equation (7) with $\hat{O}$, using $l=1$, we get

$$\sum_{\{N_i\}=0}^{\infty} \beta_1'N_1(N_1+2)(N_1+1)\ W(N_1+2,N_2-1,\ldots),$$

which with substitutions $N_1\rightarrow N_1-2$ and $N_2\rightarrow N_2+1$ becomes

$$\sum_{\{N_i\}=0}^{\infty} \beta_1'(N_1-2)(N_1-1)N_1\ W(N_1,\ldots)$$

$$=\beta_1\langle(N_1-2)(N_1-1)\rangle, \tag{A12}$$

where we have used the fact that $\beta_i=\beta_i'N_1$. The sixth term can be operated on without having to do any relabeling of N,

$$-\sum_{\{N_i\}=0}^{\infty} \beta_1'N_1N_1(N_1-1)\ W(\cdots)=-\beta_1\langle N_1(N_1-1)\rangle. \tag{A13}$$

The seventh term will however require relabeling in order to bring the W in the desired form. We first operate on it with $\hat{O}$ to get

$$\sum_{\{N_i\}=0}^{\infty}\sum_{i=2}^{i_{\max}-1} \beta_i'N_1(N_1+1)(N_i+1)$$
$$\times W(N_1+1,\ldots,N_i+1,N_{i+1}-1,\ldots),$$

and then use the substitutions $N_1\rightarrow N_1-1$, $N_i\rightarrow N_i-1$ and $N_{i+1}\rightarrow N_{i+1}+1$ in order to obtain

$$\sum_{\{N_i\}=0}^{\infty}\sum_{i=2}^{i_{\max}-1} \beta_i'(N_1-1)N_1N_i$$
$$\times W(N_1,\ldots,N_i,N_{i+1},\ldots)=\sum_{i=2}^{i_{\max}-1}\beta_i\langle(N_1-1)N_i\rangle. \tag{A14}$$

With some thought, it is possible to realize that result (A14) will hold true for any value of i in the $\Sigma_{i=2}{}^{i_{\max}-1}$ series. A similar procedure on the eighth term of Eq. (7) will give us

$$\beta_{i_{\max}}\langle(N_1-1)N_{i_{\max}}\rangle, \tag{A15}$$

which essentially completes the series in Eq. (A14) from $i=2$ to $i_{\max}$. Finally, we operate on the ninth term with $\hat{O}$ and obtain

$$-\sum_{\{N_i\}=0}^{\infty}\sum_{i=2}^{i_{\max}}\beta_i' N_1 N_1 N_i\ W(\cdots)=-\sum_{i=2}^{i_{\max}}\beta_i\langle N_1 N_i\rangle, \tag{A16}$$

which again holds no matter what value of i is chosen in the $\Sigma_{i=2}{}^{i_{\max}}$ series.

Hence the sum of all the β_i' terms in Eqs. (A12), (A13), (A14), (A15), and (A16) will be

$$\sum_{i=2}^{i_{\max}}\beta_i\langle(N_1-1)N_i\rangle-\sum_{i=2}^{i_{\max}}\beta_i\langle N_1 N_i\rangle$$
$$+\beta_1[\langle(N_1-2)(N_1-1)\rangle-\langle(N_1-1)N_1\rangle]. \tag{A17}$$

If we now replace the upper case N with its lower case counterpart, discarding the angled brackets to reflect the classical limit, expression (A17) is easily reduced to

$$-\sum_{i=2}^{i_{\max}}\beta_i n_i-2\beta_1(n_1-1). \tag{A18}$$

It can be seen that these are the β terms in the rate equation (5) provided that $n_1-1\approx n_1$ in the above expression. This is a fair approximation in the classical limit where the monomeric population is high.

b. $l>1$

Additional care is required when one deals with the case of $l\neq1$ in the β_i' terms. This is due to the series $\Sigma_{i=2}{}^{i_{\max}}$ involved and unlike the $l=1$ case, contributions due to different values of i need to be examined explicitly.

Consider the fifth term in Eq. (7) first. With the operator $\hat{O}$ applied, it will read

$$\sum_{\{N_i\}=0}^{\infty}\beta_1' N_l(N_1+2)(N_1+1)\ W(N_1+2,N_2-1,\ldots),$$

and the substitutions $N_1\rightarrow N_1-2$ and $N_2\rightarrow N_2+1$ will make it

$$\sum_{\{N_i\}=0}^{\infty}\beta_1' N_l N_1(N_1-1)\ W(\ldots)$$
$$=\beta_1\langle(N_1-1)N_l\rangle\quad\text{if}\quad l\geqslant3 \tag{A19}$$

and

$$\sum_{\{N_i\}=0}^{\infty}\beta_1' N_1(N_1-1)(N_2+1)\ W(\cdots)$$
$$=\beta_1\langle(N_1-1)(N_2+1)\rangle\quad\text{if}\quad l=2. \tag{A20}$$

The sixth term in Eq. (7) will not require any relabeling of N after being operated on by $\hat{O}$ and regardless of the value of l it will become

$$-\sum_{\{N_i\}=0}^{\infty}\beta_1' N_l N_1(N_1-1)\ W(\cdots)=-\beta_1\langle(N_1-1)N_l\rangle. \tag{A21}$$

Hence for $l\geqslant3$ the sum of the positive and negative β_1 terms, given in expressions (A19) and (A21), is zero. The rate equation (3) written down for $i\geqslant3$ will surely have no β_1 terms. For the special case of $l=2$, the sum of expressions (A20) and (A21) will leave $\beta_1(n_1-1)$ in the classical language. Considering the rate equation (3) for $i=2$ case, one would find the term $\beta_1 n_1$, which is approximately equal to the stochastic result $\beta_1(n_1-1)$, provided that $n_1\gg1$. This is a valid assumption in the classical limit, and so the β_1' terms in the stochastic master equation are reducible to those in the classical rate equations when the mean populations are large.

Let us now consider the seventh term in Eq. (7). With operator $\hat{O}$ acting on it, it would read

$$\sum_{\{N_i\}=0}^{\infty}\sum_{i=2}^{i_{\max}-1}\beta_i' N_l(N_1+1)(N_i+1)$$
$$\times W(N_1+1,\ldots,N_i+1,N_{i+1}-1,\ldots).$$

Consider the expansion of the second summation here,

$$\sum_{\{N_i\}=0}^{\infty}\beta_2' N_l(N_1+1)(N_2+1)\ W(N_1+1,N_2+1,N_3-1,\ldots)$$
$$+\sum_{\{N_i\}=0}^{\infty}\beta_3' N_l(N_1+1)(N_3+1)\ W(N_1+1,\ldots,N_3+1,N_4-1,\ldots)$$
$$+\sum_{\{N_i\}=0}^{\infty}\beta_4' N_l(N_1+1)(N_4+1)\ W(N_1+1,\ldots,N_4+1,N_5-1,\ldots)+\cdots.$$

With appropriate relabeling as done before, and remembering that $\beta_i=\beta_i' N_1$, it is possible to show that the this term reduces to

$$\beta_{l-1}\langle N_{l-1}(N_l+1)\rangle+\beta_l\langle N_l(N_l-1)\rangle+\sum_{\substack{i=2\\ i\neq l-1,l}}^{i_{\max}}\beta_i\langle N_i N_l\rangle. \tag{A22}$$

The operator $\hat{O}$ will reduce the eighth term of Eq. (7) into

$$\sum_{\{N_i\}=0}^{\infty}\beta_{i_{\max}}' N_l(N_1+1)(N_{i_{\max}}+1)\ W(N_1+1,\ldots,N_{i_{\max}}+1),$$

and with the relabeling $N_1\rightarrow N_1-1$ and $N_{i_{\max}}\rightarrow N_{i_{\max}}-1$ will give us

$$\sum_{\{N_i\}=0}^{\infty} \beta'_{i_{\max}} N_l N_1 N_{i_{\max}} W(\cdots)$$
$$= \beta_{i_{\max}} \langle N_{i_{\max}} N_l \rangle \quad \text{if} \quad l=2,\ldots,i_{\max}-1,$$
$$\sum_{\{N_i\}=0}^{\infty} \beta'_{i_{\max}} (N_{i_{\max}}-1) N_1 N_{i_{\max}} W(\cdots)$$
$$= \beta_{i_{\max}} \langle N_{i_{\max}} (N_{i_{\max}}-1) \rangle \quad \text{if} \quad l=i_{\max}. \tag{A23}$$

A similar argument applies to the ninth term of Eq. (7). The operator $\hat{O}$ will reduce this term to

$$-\sum_{\{N_i\}=0}^{\infty} \sum_{i=2}^{i_{\max}} \beta'_i N_l N_1 N_i\ W(\cdots) = -\sum_{i=2}^{i_{\max}} \beta_i \langle N_i N_l \rangle \tag{A24}$$

regardless of the value of l. Hence summing the seventh, eighth and ninth terms of the master equation, given here as expressions (A22), (A23), and (A24), and replacing the upper case N with the lower case n in the classical picture will give us $\beta_{l-1} n_{l-1} - \beta_l n_l$, where $l=2,\ldots,i_{\max}$. These are the β_i terms in the classical rate equation (3).

4. The γ_i terms

a. l=1

The effect of the operator $\hat{O}$, with $l=1$, on the tenth term in the master equation (7) will be

$$\sum_{\{N_i\}=0}^{\infty} \gamma_2 N_1 (N_2+1) W(N_1-2, N_2+1,\ldots),$$

and the relabeling $N_1 \to N_1+2$ and $N_2 \to N_2-1$ will give us

$$\sum_{\{N_i\}=0}^{\infty} \gamma_2 (N_1+2) N_2\ W(\cdots) = \gamma_2 \langle (N_1+2) N_2 \rangle. \tag{A25}$$

The eleventh term of Eq. (7), under the operation due to $\hat{O}$ will become

$$\sum_{\{N_i\}=0}^{\infty} \sum_{i=3}^{i_{\max}} \gamma_i N_1 (N_i+1)$$
$$\times W(N_1-1,\ldots,N_{i-1}-1, N_i+1,\ldots),$$

which with the relabeling $N_1 \to N_1+1$, $N_{i-1} \to N_{i-1}+1$, $N_i \to N_i-1$ becomes

$$\sum_{\{N_i\}=0}^{\infty} \sum_{i=3}^{i_{\max}} \gamma_i (N_1+1) N_i\ W(\cdots) = \sum_{i=3}^{i_{\max}} \gamma_i \langle (N_1+1) N_i \rangle. \tag{A26}$$

The last term in Equation (7) is more straight forward and does not require any relabeling, so the operator $\hat{O}$ will make it

$$-\sum_{\{N_i\}=0}^{\infty} \sum_{i=2}^{i_{\max}} \gamma_i N_1 N_i\ W(\ldots) = -\sum_{i=2}^{i_{\max}} \gamma_i \langle N_1 N_i \rangle. \tag{A27}$$

Replacing the angled brackets and the upper case N with the lower case n in the classical limit, the sum of all the γ_i terms expressed in (A25), (A26), and (A27) will be

$$2\gamma_2 n_2 + \sum_{i=3}^{i_{\max}} \gamma_i n_i = 2\gamma_2 n_2 + \sum_{i=2}^{i_{\max}-1} \gamma_{i+1} n_{i+1}. \tag{A28}$$

These are precisely the γ_i terms appearing in the monomeric rate equation (5).

b. l>1

If we operate on the tenth term of Eq. (7) with $\hat{O}$, we get

$$\sum_{\{N_i\}=0}^{\infty} \gamma_2 N_l (N_2+1) W(N_1-2, N_2+1,\ldots),$$

and with the relabeling $N_1 \to N_1+2$ and $N_2 \to N_2-1$ it becomes

$$\sum_{\{N_i\}=0}^{\infty} \gamma_2 N_l N_2\ W(\cdots) = \gamma_2 \langle N_l N_2 \rangle. \tag{A29}$$

If operated upon by $\hat{O}$, the eleventh term of Eq. (7) will read

$$\sum_{\{N_i\}=0}^{\infty} \sum_{i=3}^{i_{\max}} \gamma_i N_l (N_i+1)$$
$$\times W(N_1-1,\ldots,N_{i-1}-1, N_i+1,\ldots).$$

With suitable substitutions, it can be shown that this expression is equivalent to

$$\gamma_l \langle N_l (N_l-1) \rangle + \gamma_{l+1} \langle N_{l+1} (N_l+1) \rangle + \sum_{\substack{i=3 \\ i \neq l, l+1}}^{i_{\max}} \gamma_i \langle N_l N_i \rangle. \tag{A30}$$

Finally, the last term in Equation (7) under the operation due to $\hat{O}$ will appear as

$$-\sum_{\{N_i\}=0}^{\infty} \sum_{i=2}^{i_{\max}} \gamma_i N_l N_i\ W(\cdots) = -\sum_{i=2}^{i_{\max}} \gamma_i \langle N_l N_i \rangle, \tag{A31}$$

where $l=2,\ldots,i_{\max}$. Hence the sum of the all the γ_i terms given in (A29), (A30), and (A31) will be

$$\gamma_l \langle N_l (N_l-1) \rangle + \gamma_{l+1} \langle N_{l+1} (N_l+1) \rangle - \gamma_l \langle N_l N_l \rangle$$
$$- \gamma_{l+1} \langle N_{l+1} N_l \rangle,$$

which under the classical limit can be simplified as $\gamma_{l+1} n_{l+1} - \gamma_l n_l$. These are the γ_i terms found in the classical rate equation (3), except that here the subscript l is used for labeling purpose.

We therefore conclude that the set of stochastic master equations (7) are reducible to the set of classical rate equations given in Eqs. (3) and (5) when the mean populations are large. Furthermore, it is possible to justify the stochastic expression for the nucleation rate, given in Eq. (14).

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