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Two-Group Approach to the Kinetics of Particle Cluster Aggregation

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We present a numerical scheme for the treatment of particle agglomeration phenomena. The method is based on separating clusters into two groups according to size: small clusters containing up to x^* particles and larger clusters with more than x^* particles. In the first group, a set of equations describes the evolution of individual clusters; moment equations are derived for the second group. These two sets of coupled equations are solved numerically for, and giving good agreement with, a case where an exact solution is available. In a second step, the full distribution function is reconstructed from its moments. Here we use a nonlinear method based on the maximum entropy principle. The superiority of this method over a Gram–Charlier expansion is demonstrated for an example taken from the condensation of atomic clusters on a surface. © 1992 Academic Press, Inc.

1. INTRODUCTION

The general phenomenon of particle aggregation and clustering is encountered in many seemingly unrelated research fields. For example, this concept has been used to describe the particle size distribution in aerosol physics [1] and star cluster size in astrophysics [2]. Other examples are found in materials science (e.g., in thin film formation [3–5]), swelling of nuclear fuel materials [6], metal clusters in metal vapors [7], and in expanding nozzle flows [8]. The one feature these systems have in common is that they may be characterized by the size distribution of aggregates or clusters.

The shape of the size distribution of clusters and its evolution in time is governed by microscopic processes (e.g., aggregation, coalescence, dissociation, and evaporation). In order to learn about these processes and their relative importance from the size distribution in a given system, it is necessary to understand their influence on the aggregation kinetics. This can be achieved with a detailed model that incorporates all potentially relevant processes and allows the calculation of the distribution.

In this paper, we develop a model based on kinetic rate equations. In Section 3, we describe, in detail, the basic idea of separating the clusters into two groups according to size. In Section 3.1, a set of coupled equations is derived for the individual concentrations of clusters in the first group and for moments of the distribution in the second group. Section 3.2 is devoted to the problem of reconstruction of the distribution from its moments; an illustrative example is given in Section 4. The paper concludes with a discussion on the merits and drawbacks of the method.

2. BALANCE EQUATIONS

We consider here a system for clusters that are characterized by the number of their constituents (typically atoms). Other degrees of freedom, such as the shape of clusters, are disregarded. Allowance is made for coalescence reactions where two clusters combine to form a large one that contains the sume of atoms of the two coalescing clusters.

Let $C_i(t)$ be the concentration of clusters consisting of i atoms at a given time t. Depending on the system considered, the concentration may be given as either the number of clusters per unit *volume* or per unit *area*. Then the rate of coalescence per unit volume (or per unit area) of an i-cluster with a j-cluster is given by $K(i,j)\, C_i C_j$, where $K(i,j)$ is a rate constant that, in the general case, depends on the sizes of both coalescing clusters. A general conservation equation for the cluster concentrations may be written as [9, 10]

$$\frac{\partial}{\partial t} C_i = \frac{1}{2} \sum_{j=1}^{i-1} K(j, i-j)\, C_j C_{i-j} - \sum_{j=1}^{\infty} K(i,j)\, C_i C_j + Q_i, \qquad (1)$$

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where Q_i denotes an external source rate per unit volume (or per unit area) of clusters (mostly monomers).

In some systems, clusters may not be entirely stable but rather dissociate spontaneously into two fragments. In that case, a term of the form

$$-\tfrac{1}{2}\sum_{j=1}^{i-1} F(j, i-j)\, C_i + \sum_{j=1}^{\infty} F(i,j)\, C_{i+j} \qquad (2)$$

has to be added to the right-hand side of Eq. (1). Here $F(i,j)$ denotes the rate at which a cluster of $i+j$ atoms dissociates into two clusters of i and j atoms.

Finally there may be a possibility that clusters leave the system altogether (e.g., due to evaporation off a surface). This process may be accounted for by adding a term

$$-v_i C_i \qquad (3)$$

to the right-hand side of Eq. (1), where v_i is the loss rate of an i-size cluster.

Equation (1), and its extensions by terms (2) and/or (3), has been surveyed in some detail [11]. Exact solutions are known for a few cases where the coalescence rate is a bilinear function of the cluster sizes. For the more general case where the coalescence rate is some homogeneous function of the sizes, similarity solutions have been studied [6].

To go beyond the limitations of these attempts, recourse to numerical techniques is necessary. Straightforward numerical time integration of Eq. (1) is possible, but the number of equations to be taken into account may become very large, especially at large times. Another method of solution is a direct Monte Carlo simulation [12, 13].

3. TWO-GROUP APPROACH

In this section, we wish to establish a method of solution for the agglomeration equation (Eq. (1)). The method is based on separating the clusters into two groups according to size: the first containing clusters with up to x^* atoms, and the second containing clusters with more than x^* atoms. The quantity x^* is some small integer that may be suggested, in some cases, by physical properties of the clusters (e.g., their stability). For the first group, a set of discrete equations describes the concentrations of individual cluster sizes; the second group is characterized by a set of equations for the moments of the distribution. Although this strategy is somewhat similar to an existing approach [14, 15], it only considered single particle transitions. Here, we wish to relax this restriction in the general formulation. Consequently, we do not approximate the evolution equation for large clusters by a Fokker–Planck equation, but instead aim at deriving moment equations from the original equation (1).

3.1. *Moment Equations*

Introduce power moments N_k of the cluster size distribution according to

$$N_k(t) = \sum_{i=1}^{\infty} i^k C_i(t). \qquad (4)$$

The concentration of all clusters irrespective of their size is denoted by $N_0(t)$ and $N_1(t)$ is the concentration of atoms contained in these clusters. Multiplying Eq. (1) by i^k and summing over all i, one obtains [11]

$$\frac{\partial}{\partial t} N_k = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} C_i C_j K(i,j) \times [(i+j)^k - i^k - j^k] + \sum_{i=1}^{\infty} i^k Q_i. \qquad (5)$$

The intuitive meaning of this equation is clear by observing that, in a coalescence event between clusters of sizes i and j, the moment N_k changes by

$$(i+j)^k - i^k - j^k. \qquad (6)$$

In the following, we want to perform the classification of clusters into two groups of sizes, $i \leqslant x^*$ and $i > x^*$. For the large clusters, we wish to use a continuous description so we write $C(x)$, instead of C_i, for $x = i > x^*$. Sums over C_i are replaced by integrals over $C(x)\,dx$ in the obvious way. Equation (1) then becomes, approximately, for the small clusters,

$$\frac{\partial}{\partial t} C_i = \frac{1}{2} \sum_{j=1}^{i-1} K(j, i-j)\, C_j C_{i-j} - \sum_{j=1}^{x^*} K(i,j)\, C_i C_j - \int_{x^*}^{\infty} dx\, K(i,x)\, C_i C(x) + Q_i. \qquad (7)$$

Next we introduce moments M_k of the large cluster continuum,

$$M_k = \int_{x^*}^{\infty} dx\, x^k C(x). \qquad (8)$$

These are related, approximately, to the full moments N_k in Eq. (4) by

$$M_k = N_k - \sum_{i=1}^{x^*} i^k C_i. \qquad (9)$$

Substituting Eq. (9) into the moment equation (5) and performing the separation, we obtain

$$\begin{aligned}\frac{\partial}{\partial t}M_k = &-\sum_{i=1}^{x^*} i^k \frac{\partial}{\partial t}C_i + \frac{1}{2}\sum_{i=1}^{x^*}\sum_{j=1}^{x^*} C_i C_j\\ &\times K(i,j)[(i+j)^k - i^k - j^k]\\ &+\sum_{i=1}^{x^*} C_i \int_{x^*}^{\infty} dx\, C(x)\, K(i,x)\\ &\times[(i+x)^k - i^k - x^k]\\ &+\frac{1}{2}\int_{x^*}^{\infty}\int_{x^*}^{\infty} dx\, dy\, C(x)\, C(y)\\ &\times K(x,y)[(x+y)^k - x^k - y^k]\\ &+\sum_{i=1}^{\infty} i^k Q_i. \end{aligned} \tag{10}$$

Our final goal is to obtain from Eqs. (7) and (10) a closed set of equations for the small cluster concentrations C_i, $i = 1, 2, ..., x^*$, and the first few continuum moments M_k, $k = 0, 1, ..., n$, where n is some small integer. To achieve this, we need to express the integrals in Eqs. (7) and (10) over the continuum distribution in terms of the moments M_k.

Consider the quantity

$$G = \int_{x^*}^{\infty} dx\, C(x)\, g(x), \tag{11}$$

where $g(x)$ is some arbitrary function. Our task is to obtain an approximate expression for G in terms of the moments M_k of Eq. (8). This problem is, of course, of a general nature, but its solution is not unique. An ingenious method to obtain bounds for G based on a representation of $C(x)$ by an array of delta functions is given in [16]. Here, however, we wish to use a somewhat simpler scheme that gives accurate results if the distribution $C(x)$ is fairly localized and if $g(x)$ varies only slowly.

Expand the function $g(x)$ in a Taylor series around some point x_0,

$$\begin{aligned} g(x) &= \sum_{n=0}^{\infty}\frac{1}{n!}(x - x_0)^n g^{(n)}(x_0)\\ &= \sum_{n=0}^{\infty}\frac{1}{n!} g^{(n)}(x_0)\sum_{v=0}^{n}\binom{n}{v} x^v (-x_0)^{n-v}. \end{aligned}\tag{12}$$

Inserting this expression into Eq. (11) gives the desired result,

$$G = \sum_{n=0}^{\infty}\frac{1}{n!} g^{(n)}(x_0)\sum_{v=0}^{n}\binom{n}{v}(-x_0)^{n-v} M_v. \tag{13}$$

Although Eq. (13) is valid for any expansion point, the preferable choice for x_0 is the average cluster size,

$$x_0 - x^* = \bar{x} = M_1/M_0, \tag{14}$$

particularly so if the distribution $C(x)$ is uni-modal.

Applying this scheme to Eq. (7), we obtain

$$\begin{aligned}\frac{\partial}{\partial t}C_i = &\frac{1}{2}\sum_{j=1}^{i-1} K(j, i-j)\, C_j C_{i-j}\\ &-\sum_{j=1}^{x^*} K(i,j)\, C_i C_j\\ &-\sum_{n=0}^{\infty}\frac{1}{n!} K^{(0,n)}(i, \bar{x})\, C_i\\ &\times\sum_{v=0}^{n}\binom{n}{v}(-\bar{x})^{n-v} M_v + Q_i, \end{aligned}\tag{15}$$

where the symbol $K^{(m,n)}$ denotes the partial derivative,

$$K^{(m,n)}(x,y) = \frac{\partial^{m+n}}{\partial x^m\, \partial y^n} K(x,y). \tag{16}$$

Equation (10) may be treated similarly. The equations for M_0 and M_1 will be considered first. For $k = 0$, the square brackets in Eq. (10) are all equal to -1, and we obtain, by a procedure similar to the previous one,

$$\begin{aligned}\frac{\partial}{\partial t}M_0 = &-\sum_{i=1}^{x^*}\frac{\partial}{\partial t}C_i - \frac{1}{2}\sum_{i=1}^{x^*}\sum_{j=1}^{x^*} C_i C_j K(i,j)\\ &-\sum_{i=1}^{x^*} C_i \sum_{n=0}^{\infty}\frac{1}{n!}K^{(0,n)}(i,\bar{x})\\ &\times\sum_{v=0}^{n}\binom{n}{v}(-\bar{x})^{n-v} M_v\\ &-\frac{1}{2}\sum_{m=0}^{\infty}\sum_{n=0}^{\infty}\frac{1}{m!\, n!}K^{(m,n)}(\bar{x},\bar{x})\\ &\times\sum_{\mu=0}^{m}\sum_{v=0}^{n}\binom{m}{\mu}\binom{n}{v}\\ &\times(-\bar{x})^{m+n-\mu-v} M_v M_\mu + \sum_{i=1}^{\infty} Q_i. \end{aligned}\tag{17a}$$

The equation for M_1, which becomes particularly simple because the square bracket terms in Eq. (10) vanish, is

$$\frac{\partial}{\partial t}M_1 = -\sum_{i=1}^{x^*} i\frac{\partial}{\partial t}C_i + \sum_{i=1}^{\infty} iQ_i. \tag{17b}$$

Equation (17b) is in fact a conservation equation for the number of atoms in the system.

Performing all the pertinent Taylor expansions in Eq. (10) for $k \geqslant 2$, we finally obtain

$$\begin{aligned}\frac{\partial}{\partial t} M_k = &- \sum_{i=1}^{x^*} i^k \frac{\partial}{\partial t} C_i + \frac{1}{2} \sum_{i=1}^{x^*} \sum_{j=1}^{x^*} C_i C_j \\ &\times K(i,j)[(i+j)^k - i^k - j^k] \\ &+ \sum_{i=1}^{x^*} C_i \sum_{l=1}^{k-1} \binom{k}{l} i^{k-l} \sum_{n=0}^{\infty} \frac{1}{n!} \\ &\times K^{(0,n)}(i,\bar{x}) \sum_{v=0}^{n} \binom{n}{v} (-\bar{x})^{n-v} M_{l+v} \\ &+ \frac{1}{2} \sum_{l=1}^{k-1} \binom{k}{l} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} \frac{1}{m!\,n!} \\ &\times K^{(m,n)}(\bar{x},\bar{x}) \sum_{\mu=0}^{m} \sum_{v=0}^{n} \binom{m}{\mu} \binom{n}{v} \\ &\times (-\bar{x})^{m+n-\mu-v} M_{l+v} M_{k-l+\mu} + \sum_{i=1}^{\infty} i^k Q_i, \qquad (17c)\end{aligned}$$

where the term in the square brackets of Eq. (10) is

$$(x+y)^k - x^k - y^k = \sum_{l=1}^{k-1} \binom{k}{l} x^l y^{k-l}; \qquad k \geqslant 2. \qquad (18)$$

Equations (15) and (17) are two coupled sets of nonlinear ordinary differential equations for the small-size cluster concentrations and the continuum moments. If we take only the first two terms in the Taylor series for $K(x, y)$ into account (i.e., we truncate all terms with $m, n \geqslant 2$), then the system is self-contained for any number of moments M_k, $k = 0, 1, \ldots, N$, with $N \geqslant 1$. Since the coalescence rate $K(x, y)$ is supposed to be a smooth function of size for large clusters, as will be given in Eq. (19) below and Eq. (25), this truncation is not considered to be severe.

Although Eqs. (15) and (17), as they have been derived here, do not contain processes like fragmentation or loss of species, such phenomena may be readily included by adding the appropriate terms (2) and (3) to Eq. (1) and performing similar steps which led to Eqs. (15) and (17). We thus have a versatile tool to study numerically the kinetics of aggregation phenomena for a wide variety of physical systems.

To test the method developed here, we numerically integrated Eq. (15) for $x^* = 5$ and Eq. (17) for $N = 4$, using the coalescence rate

$$K(i,j) = ij. \qquad (19)$$

The initial condition was that only monomers are present, $C_i(t=0) = \delta_{i,1}$, and the source term was set equal to zero. For this case, the full solution is given analytically [17] for both the individual concentrations and the moments. We show the first five concentrations as a function of time in Fig. 1a. It is seen that the numerical values lie precisely on top of the analytical curves. In Fig. 1b are shown the first moments N_k up to $k = 4$. As the time approaches unity, the second and all higher moments diverge. This phenomenon is a well-known consequence of the product kernel in Eq. (19) and is interpreted as the sol/gel transition. Again, the numerical results agree quite well with the exact solution although, at the divergence, the numerical calculation seems to underestimate the moments.

3.2. *Reconstruction of the Continuum Size Distribution*

The general problem of reconstructing a distribution function from its moments is well established and arises in various areas of research such as ion implantation [18]. It is clear that the information from a finite set of moments cannot be sufficient to uniquely determine the unknown function. The problem, therefore, is to find, among the class of functions having all the same prescribed first few moments, the most reasonable one in some sense.

A number of reconstruction schemes are available which technically might be classified as linear and nonlinear. In linear reconstruction, the function is expanded in a set of orthogonal functions where the expansion coefficients are determined by the moment constraints. Making use of the orthogonality relations, the result is obtained in closed form. One such well-known technique is the Gram–Charlier series expansion [19]. For functions close to Gaussian, this method gives quite satisfactory results [18]. However, the method is not satisfactory for highly skewed functions, as will be shown here. One severe drawback inherent to all linear schemes is that the reconstructed curve may assume negative values, which is physically impossible for the true distribution function.

Nonlinear reconstruction schemes assume a certain form for the unknown function with adjustable free parameters to give the correct moments. This method is especially powerful if, for instance, theoretical considerations suggest some specific functional form. Certainly the reconstructed function can be *constrained* to be non-negative. However, since these methods are essentially nonlinear, existence and uniqueness of a solution might in some cases constitute a serious problem.

The most general nonlinear reconstruction method may be obtained from the maximum entropy principle. The foundation of this principle has been given by Jaynes [20]. It provides the means to select an unbiased estimate in the sense of Bayes of the distribution, given only the incomplete information of a finite set of expectation values (moments). Some of the countless applications may be found in [21, 22]. In brief, the idea is to assign a function $C(x)$ that maximizes the entropy S, where S is defined as

$$S = -\int_{x^*}^{\infty} dx\, C(x) \ln \frac{C(x)}{p(x)}, \qquad (20)$$

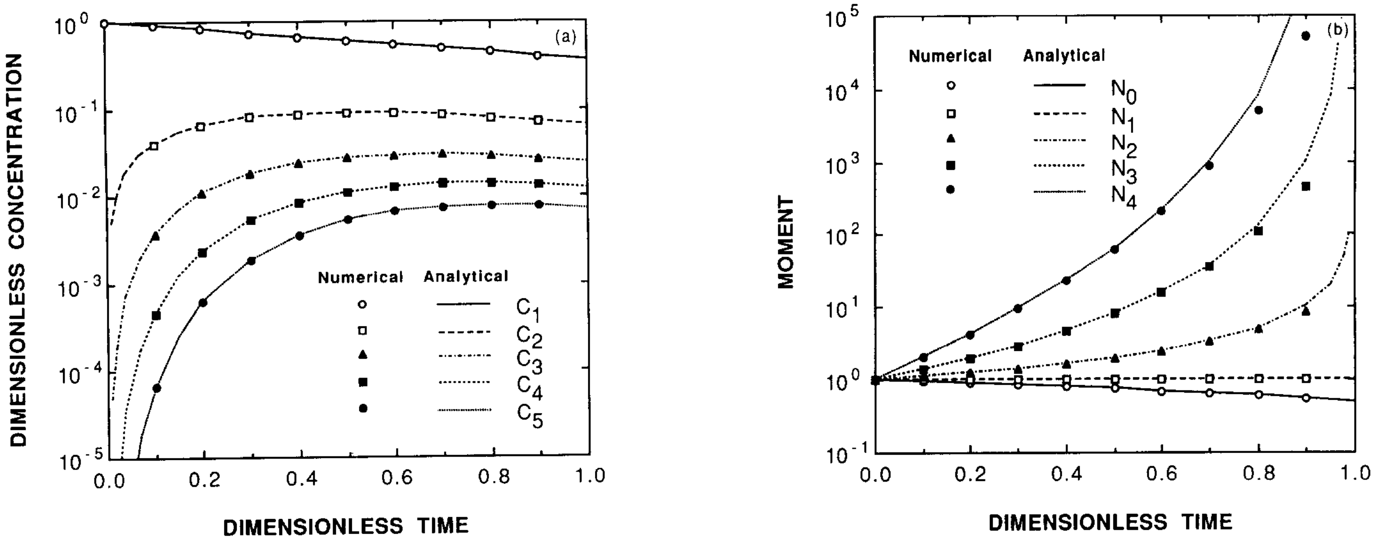

FIG. 1. (a) Discrete concentrations ($C_1 - C_5$) and (b) full moments ($N_0 - N_4$) of the size distribution as functions of time for the product kernel of Eq. (19).

and $C(x)$ satisfies the moment constraints. In Eq. (20), $p(x)$ denotes a prior probability or measure [23]. Roughly speaking, $p(x)\,dx$ is proportional to the number of states within the interval $(x, x+dx)$. In our case, the continuous variable x represents the number of atoms in a cluster, originally an integer, and thus we set $p(x)=1$. We note, however, that there is some ambiguity here (i.e., the number of ways a cluster of x atoms may be realized might depend on x). Fortunately, the influence of $p(x)$ on the results is only weak, and it decreases with an increase in the number of moment constraints.

The entropy in Eq. (20) is maximized, subject to the moment constraints given in Eq. (8) for $k=0, 1, \ldots, N$, by introducing Lagrange multipliers λ_k in the usual way, giving the result

$$C(x)=p(x)\exp\left(-\sum_{k=0}^{N}\lambda_k x^k\right). \qquad (21)$$

Indeed, if no constraints were given at all, $N=0$, Eq. (21) would result in $C(x)=p(x)$ which is consistent, since $p(x)$ is the prior probability.

Equation (21) is a formal solution in the sense that the Lagrange multipliers λ_k have yet to be determined from the moment constraints,

$$\int_{x^*}^{\infty} dx\, x^k \exp\left(-\sum_{l=0}^{N}\lambda_l x^l\right)=M_k, \qquad k=0, 1, \ldots, N. \qquad (22)$$

Equation (22) comprises a nonlinear system of equations for the λ_l that was solved numerically using the subroutine C05PBF (based on the Powell hybrid method [24]) of the NAG library [25]. The integrals were calculated using the subroutine D01BAF of the same library [25] using a 64-point Gauss–Legendre formula.

In order to check the method, we use an example of the condensation of atoms deposited on a substrate surface as it occurs in the early stages of thin film formation. For this system, an analytical solution is available (cf. the Appendix).

In Fig. 2a, we plot the distribution function together with the reconstruction from its moments by the maximum entropy principle. Good convergence is found even though the original distribution has a sharp peak and is highly skewed. The reconstructed curves oscillate somewhat around the true distribution, but the oscillations decay rapidly with the increasing number of moments used.

For comparison, we show a Gram–Charlier reconstruction of the same distribution in Fig. 2b. None of the curves approximates the true distribution satisfactorily. Convergence is slow and, in fact, if the solution was not known, the behavior could be quite misleading. For instance, by looking only at the curves for two and four moments, one might be tempted to conclude that the four moments reconstruction must already be close to the true solution, since it deviates from the Gaussian (two moments) by only a small amount. Clearly, this is by no means so. Even worse, going to higher moments does not improve matters very much but rather causes quite pronounced oscillations, suggesting a bimodal distribution. Note that for 10 moments, the oscillations are more severe than for eitht moments.

Although the maximum entropy reconstruction gives a quite satisfying overall approximation of the distribution, it systematically underestimates the distribution for small clusters. This phenomenon is similar to Fourier series

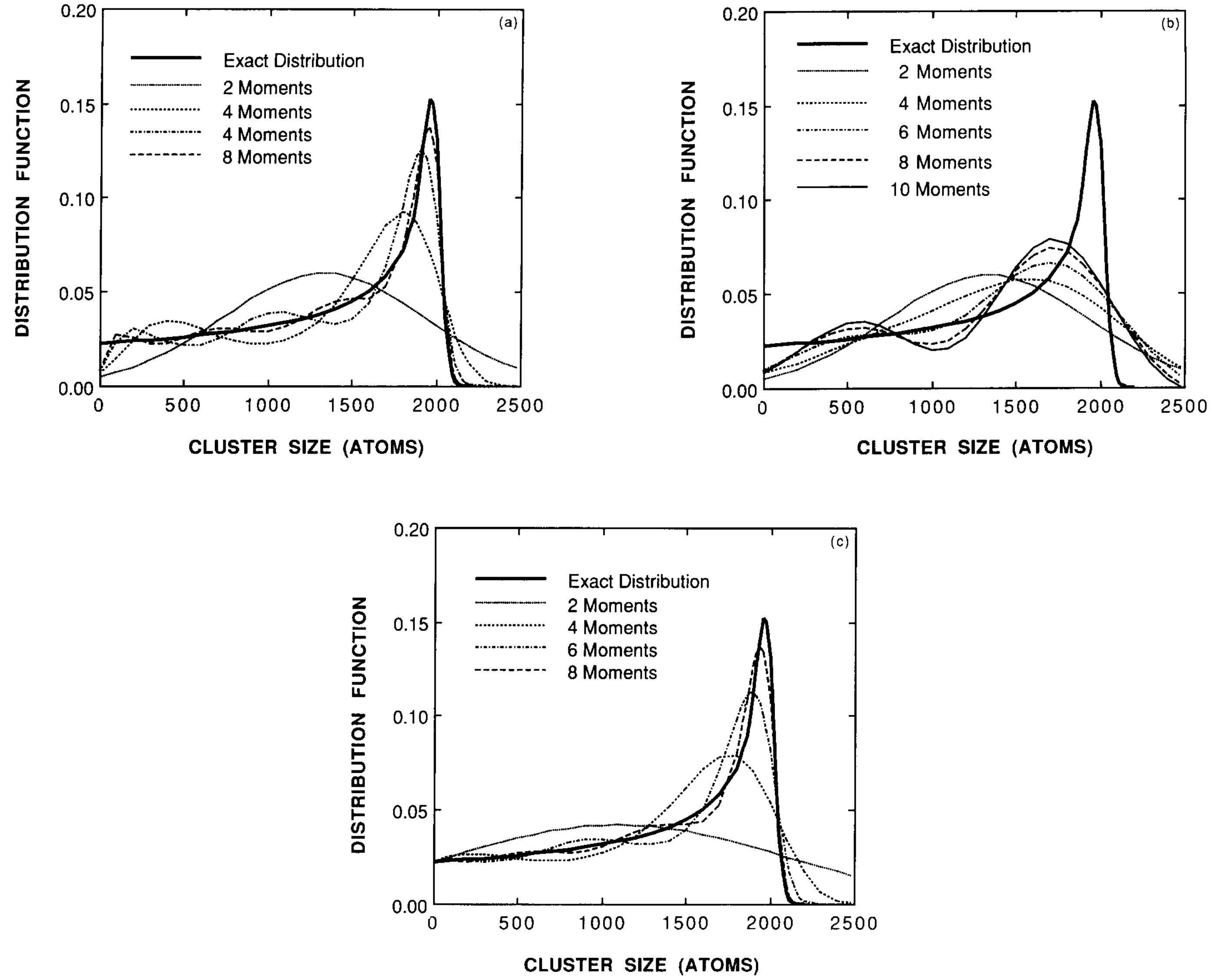

FIG. 2. Reconstruction of the size distribution for constant monomer aggregation coefficient using exact moments of Eq. (46) thick solid line: Eq. (37) for $\tau = 2000$; thin lines: reconstruction of (a) maximum entropy, (b) Gram–Charlier, and (c) reconstruction of the size distribution for constant monomer aggregation coefficient using exact moments of Eq. (46) (thick solid line: Eq. (37) for $\tau = 2000$; thin lines: reconstruction of (c) constrained maximum entropy).

expansion of discontinuous functions, where the series converges to the mean of the left and right limit at the discontinuity. It appears that one could improve the approximation by *constraining* the reconstructed function to the correct value at the left side. After all, we know the value of $C(x^*)$ from the discrete Eq. (15).

Doing this within the strict framework of the maximum entropy principle is straightforward but the result is not very helpful. The reconstructed function would be exactly the same as in Fig. 1 except for the point $x = x^*$ that would be shifted towards the prescribed value. This occurs because a single point has zero measure, thus leaving the moments unchanged.

In view of this situation, one is almost naturally led to a more pragmatic approach rather than remaining faithfully committed to the unconstrained maximum entropy principle. The most obvious method is to keep the functional form of Eq. (21) for the reconstruction, as suggested by the maximum entropy principle, but replace the Nth moment constraint (Eq. (22)) by the boundary constraint

$$\exp\left(-\sum_{l=0}^{N} \lambda_l (x^*)^l\right) = C(x^*). \tag{23}$$

The resulting function will *not* be the one with maximum entropy, but will give a better approximation for small clusters.

Figure 2c shows results for constrained maximum

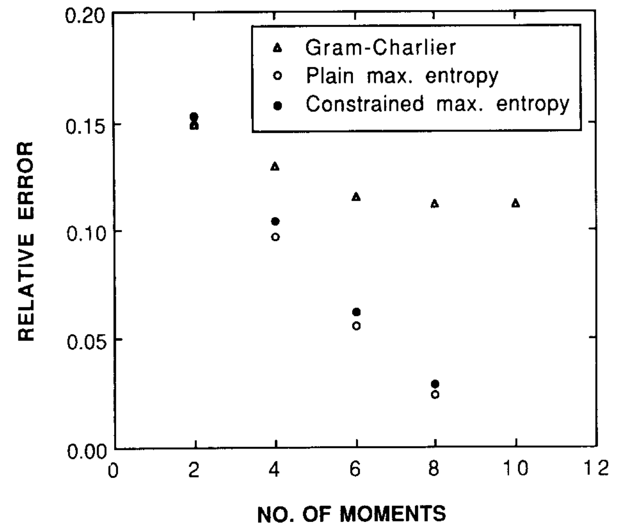

FIG. 3. Convergence of various reconstruction schemes according to Eq. (24).

entropy principle reconstruction of the test function. Compared to the curves in Fig. 3, the approximation is better for the small clusters where there are less oscillations in the reconstruction. The reproduction of the sharp peak at large cluster sizes is no worse than for the pure maximum entropy principle (Fig. 3). In conclusion, the constrained maximum entropy principle gives a satisfactory reconstruction even of the sharp-peaked test function presented here.

Figure 3 gives a quantitive measure of convergence according to the L_2-norm,

$$\text{relative error} = \left\{ \frac{\int_{x^*}^{\infty} [f(x) - \bar{f}(x)]^2 \, dx}{\int_{x^*}^{\infty} f(x)^2 \, dx} \right\}^{1/2}, \tag{24}$$

where $f(x)$ denotes the exact distribution and $\bar{f}(x)$ is its approximation. It is observed that the Gram–Charlier series converges only very weakly. Both the unconstrained and the constrained maximum entropy principle converge comparatively quickly. Note that the global error according to Eq. (24) is less for the plain maximum entropy principle than for the constrained maximum entropy principle, although the latter displays much better behavior for small clusters.

AN EXAMPLE: THE EFFECT OF COALESCENCE ON GROWTH PROPERTIES

In this section, we present an application of our method to the early stages of thin film formation. According to [26], the mobility of small islands of the desposit on the substrate may lead to coalescence events which should affect the size distribution. Calculations [27] where mobility coalescence was included as a perturbation support this conjecture. The present scheme allows us to take full account of mobility coalescence and to study its effects on the cluster size distribution.

We adopt as a model for the coalescence rate constant the expression

$$K(i, j) = r^{i-1} + r^{j-1}, \tag{25}$$

where r is a parameter. This expression may be thought of as a sum of cluster diffusion coefficients, $D_i = r^{i-1}$, with the exponential size dependence being characteristic for rigid cluster diffusion [28]. Equation (25) provides a convenient expression where cluster mobility may be "turned on" continuously by increasing the value of r. For $r \to 0$, Eq. (25) yields $K = 0$ unless $i = 1$ or $j = 1$ (only single particle transitions are allowed). For $r > 0$, multiple transitions become possible.

Figure 4 shows size distributions for different values of r. Here we have assumed a unity monomer source rate, $Q_i = \delta_{i,1}$, where $\delta_{i,1}$ is the Kronecker delta function, and no evaporation or dissociation was included. Equations (15) and (17) were integrated numerically, and the reconstruction was performed using five moments. It is observed that mobility coalescence reduces the number of small clusters and increases the growth rate. Also, the steep cutoff past the maximum of the distribution seems to be smeared out to some extent by mobility coalescence. It is remarkable that even for very small cluster mobility, $r = 1/100$, there is a distinct effect on the distribution: the population of small clusters is reduced by almost a factor of two. The reason is that dimers are lost by aggregation to large clusters and, therefore, cannot serve as nucleation centers [28].

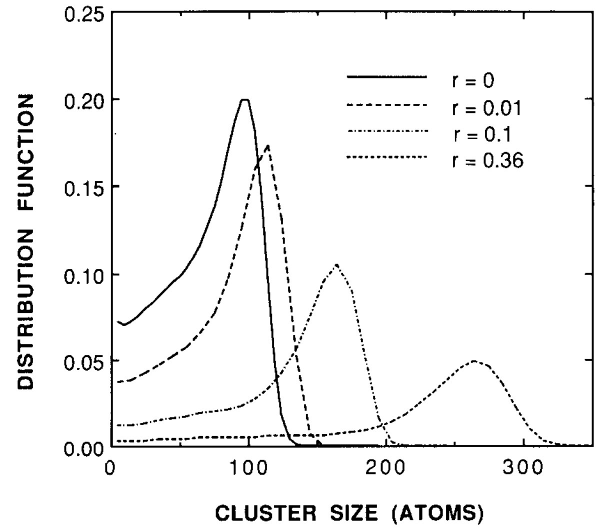

FIG. 4. Cluster size distributions for various degrees of mobility coalescence r of Eq. (25) ($t = 1000$).

5. CONCLUSION

We have presented a new method for the calculation of size distributions in aggregation and clustering problems. Its validity has been demonstrated for cases where an analytical solution exists to serve as a reference. In these cases, our method has been found to give good agreement with the exact solutions.

The major advantage of the basic concept used here is the vast reduction of equations describing the system. This is achieved by using the moment method instead of directly integrating thousands of equations. We believe that in most cases, the distribution function is sufficiently well characterized by less than 10 of its lowest moments.

On the other hand, we retain a number of discrete equations for small clusters of atoms up to a size x^*. Although one may well set $x^* = 1$ in our formalism, it is advantageous to have the option of $x > 1$. In this way, certain features of small clusters that are not continuous functions of size maybe included. In some surface clustering systems for instance, dimers have been observed to have *higher* mobilities than monomers [29], whereas for larger clusters, mobilities certainly decrease with size. The stability of small clusters may not be a continuous function of size either, a phenomenon expressed by the term "magic numbers" [30].

The reconstruction of the continuum distribution from its moments is carried out using a nonlinear method based on the maximum entropy principle. This method is superior over linear schemes like the Gram–Charlier series because it is essentially free from ambiguities as, for example, the choice of suitable base functions. Perhaps the major practical advantage of the method is that the reconstructed function is non-negative.

However, it is fair to note some of the drawbacks as well. One uncertainty lies in the truncation that is necessary to close the system of moment equations (17). There are two possibilities for improvement: First, retain more than two terms in the Taylor expansion of the coalescence rate $K(x, y)$. Second, dismiss Taylor expansion altogether and use an approach as suggested by [16] instead.

With regard to the reconstruction, the proposed method requires some computational effort to determine the Lagrange multipliers from the nonlinear Eq. (22). The subroutine C05PBF [25] requires an initial guess to start the iteration process. If the number of moments used is high, it may be very difficult to find an appropriate starting vector for the λ_k. Experience shows that, in general, the use of more than 10 moments is not practicable.

In some cases, we were not able to find a solution for even five moments. This may indicate that there is in fact no solution at all. Similar difficulties have been reported by others [31] who proposed necessary conditions for the existence of a maximum entropy solution. In cases where these conditions were violated, they were still able to obtain a solution in the form of a histogram.

The method developed here has been applied to a comprehensive investigation of the effects of mobility coalescence on the early stages of thin film growth. The results of this study will be reported separately [28].

APPENDIX: ANALYTICAL SOLUTION FOR MONOMER AGGREGATION

In the case where only monomers are mobile, clusters can grow only by single particle transitions and Eq. (1) may be simplified to

$$\begin{aligned} \frac{\partial}{\partial t} C_1 &= -2w_1 C_1^2 - \sum_{j=2}^{\infty} w_j C_1 C_j + Q, \\ \frac{\partial}{\partial t} C_i &= w_{i-1} C_1 C_{i-1} - w_i C_1 C_i, \qquad i \geqslant 2, \end{aligned} \tag{26}$$

where $w_1 = K(1, 1)/2$ and $w_i = K(1, i)$, $i \geqslant 2$. It has been assumed that there is a source providing monomers at a constant rate Q. The particularly simple case that all w_i are equal, $w_i \equiv w$, has been treated in some detail [32]. The problem may be simplified by introducing a synthetic time τ,

$$\tau = \int_0^t dt'\, w C_1(t'), \tag{27}$$

which transforms the second part of Eq. (26) to

$$\frac{\partial}{\partial \tau} C_i = C_{i-1} - C_i. \tag{28}$$

The differential difference equation (28) may be conveniently solved by the Laplace transform [33], defined by

$$\tilde{C}_i(s) = \int_0^{\infty} d\tau\, e^{-s\tau} C_i(\tau). \tag{29}$$

Equation (28) then becomes

$$s\tilde{C}_i = \tilde{C}_{i-1} - \tilde{C}_i, \tag{30}$$

with the solution

$$\tilde{C}_i(s) = \frac{1}{(s+1)^{i-1}} \tilde{C}_1(s). \tag{31}$$

Zinsmeister [32] showed that after a short transient, the monomer concentration is given by

$$C_1(t)=\left(\frac{2Q}{3w^2t}\right)^{1/3}. \tag{32}$$

Inserting Eq. (32) into Eq. (27) gives

$$\tau=(\tfrac{9}{4}wQt^2)^{1/3}, \tag{33}$$

and thus

$$C_1(\tau)=A\tau^{-1/2}, \qquad A=(\tfrac{4}{9})^{1/3}\,(Q/w)^{1/2}. \tag{34}$$

Taking the Laplace transform of Eq. (34) and inserting into Eq. (31) yields [34]

$$\tilde{C}_i(s)=A\,\frac{\sqrt{\pi}}{\sqrt{s}(s+1)^{i-1}}. \tag{35}$$

Although this expression cannot be inverted to direct space in a closed form, an asymptotic series expansion

$$\tilde{C}_i(s)=A\sum_{\nu=0}^{\infty}\frac{\Gamma(\nu+1/2)}{\Gamma(\nu+1)}\,(s+1)^{-\nu-i+1/2} \tag{36}$$

may be inverted term-by-term [33] to give

$$C_i(t)=A\tau^{i-3/2}e^{-\tau}\sum_{\nu=0}^{\infty}a_\nu\tau^\nu, \tag{37}$$

with the coefficients

$$a_\nu=\frac{\Gamma(\nu+1/2)}{\Gamma(\nu+1)\,\Gamma(\nu+i-1/2)}. \tag{38}$$

The series expansion in Eq. (37) converges for all τ, but the number of terms to be taken into account increases with increasing τ. If relative accuracy ε is desired, then the upper limit ∞ may be replaced by $N=[\tau/\varepsilon]-n$. Summation of Eq. (37) on a computer may be carried out up to $\tau=10^4$ without particular problems.

It is interesting to note that although the distribution can only be given as an infinite series, its moments may be written down in a closed form. A convenient way to show this is to first calculate the moments in Laplace space using Eq. (35),

$$\tilde{N}_k(s)=\left(\frac{\pi}{s}\right)^{1/2}A\sum_{i=1}^{\infty}i^k\left(\frac{1}{s+1}\right)^{i-1}. \tag{39}$$

Consider the sum in Eq. (39),

$$m_k=\sum_{i=1}^{\infty}i^kq^{i-1}, \qquad q=\frac{1}{s+1}. \tag{40}$$

For $k=0$, it is

$$m_0=\frac{1}{1-q}=\frac{s+1}{s}, \tag{41}$$

whereas for higher k, the m_k satisfy the recurrence relation

$$\begin{aligned} m_{k+1}&=\frac{d}{dq}(qm_k)\\ &=-(s+1)^2\frac{d}{ds}[(s+1)^{-1}m_k]. \end{aligned} \tag{42}$$

From Eq. (42), it may be shown that the m_k are of the form

$$m_k=(s+1)\sum_{l=0}^{k}a_{k,l}s^{-(l+1)}, \tag{43}$$

where the coefficients $a_{k,l}$ may be computed from the recurrence relation

$$\begin{aligned} &a_{0,0}=1,\\ &a_{k+1,l}=(l+1)\,a_{k,l}+la_{k,l-1}. \end{aligned} \tag{44}$$

Inserting Eq. (43) into Eq. (39), it follows that

$$\tilde{N}_k(s)=\sqrt{\pi}\,A\sum_{l=0}^{k+1}(a_{k,l}+a_{k,l-1})\,s^{-(l+1/2)}, \tag{45}$$

which may be inverted to direct space [34],

$$N_k(t)=A\sum_{l=0}^{k+1}b_{k,l}\tau^{l-1/2}, \tag{46}$$

with

$$b_{k,l}=\frac{2^l}{1\cdot3\cdot5\cdot\cdots\cdot(2l-1)}(a_{k,l}+a_{k,l-1}). \tag{47}$$

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