Upper critical dimension for aggregation processes

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Aggregation kinetics are often described by the population balance (or Smoluchowski coagulation) equation. The population balance equation is a mean-field equation for an aggregation process. An upper critical dimension d_c calculated for a given aggregation frequency has been used by other investigators to characterize the validity of this mean-field equation. It is shown that the upper critical dimension is also related to the singularity of the self-similar spectrum. This paper demonstrates that the usefulness of the upper critical dimension for determining the validity of the population balance equation is lost when the aggregation frequency is unknown. The validity of the equation can be inferred from the similarity or scaling distribution and the evolution of the average particle size in such cases.

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I. INTRODUCTION

The kinetics of aggregation are described by an infinite hierarchy of product-density equations [1–4]. The first-order product density equation gives the evolution of the transient size distribution, $n(v,t)$, as

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v K(v-v',v')n_2(v-v',v',t)dv' - \int_0^\infty K(v,v')n_2(v,v',t)dv'$$

where $n(v,t)$ is the number density of clusters of mass m at time t normalized so that

$$\int_0^\infty vn(v,t)dv = 1.$$

$n_2(v,v',t)$ is the joint density of pairs of size v and v' at time t and $K(v,v')$ is the binary agglomeration frequency function. Notice that the above equation is unclosed because the evolution of $n(v,t)$ depends on $n_2(v,v',t)$. The second-order product density equation that gives the evolution of $n_2(v,v',t)$ will feature the third-order density and so on.

A convenient restatement of the above equation is

$$\frac{\partial n(v,t)}{\partial t} = \frac{1}{2}\int_0^v K^s(v-v',v',...)n(v-v',t)n(v',t)dv' - \int_0^\infty K^s(v,v',...)n(v,t)n(v',t)dv' \quad (1)$$

where $K^s(x,y,...) = K(x,y)n_2(x,y,t)/n(x,t)n(y,t)$. If $K^s = K$, we have

$$n_2(v,v',t) = n(v,t)n(v',t), \quad (2)$$

which is the mean-field or superposition closure hypothesis [4]. The first-order product density equation with the first-order closure hypothesis is referred to as the population balance equation (PBE) or the Smoluchowksi coagulation equation. The dots in the argument of the function K^s represent potential dependence of this effective agglomeration frequency on other particles in the distribution or on the state of the population. This dependence manifests itself as dependence on time.

Basically the above closure approximation is tantamount to neglecting any correlations in the pair density $n_2(v,v',t)$ which may arise either due to slowness of spatial mixing resulting in segregational or correlation effects [5, 6] or due to the smallness of particle populations [7, 8].

In this paper we investigate the statistical foundation of the population balance equation (or Smoluchowski coagulation equation) and address the issue of an upper critical dimension for an aggregation process raised by Kang and Redner [5]. A fundamental understanding of the basis of the population balance equation is essential to assess the conditions under which the first-order closure hypothesis is valid. The motivation for investigating the validity of the closure hypothesis of course lies in testing the ability of the resulting population balance equation to predict experimental observations.

In this paper, the validity of the idea of an upper critical dimension for agglomerating systems is investigated. We show that the upper critical dimension is not the best way to categorize the validity of the mean-field population balance equation for agglomeration particularly when the aggregation frequency is unknown. In fact, the expected number of particles in a cell volume is the important characterizing quantity. The cell volume is the maximum spatial volume in which a particle may interact with other particles within the time scale of observation. The results obtained by this approach are compared with previous literature results.

Some work has been done in the chemical engineering literature on the question of closure. Sampson [7–9] performed Monte Carlo simulations of Brownian coagulation of spherical particles and compared the predictions of the PBE with the simulation results. Under certain circumstances, deviations from the PBE were observed. In order to investigate the closure problem, the first-order

product-density equation (which is the PBE without the closure hypothesis) and the second-order product-density equation were used to describe the system. Various forms of closure hypotheses in the second-order product density equation were used and a "best" closure hypothesis was determined by comparison of Monte Carlo simulation and the product density predictions.

The Monte Carlo simulations of Sampson which are of interest to us are the so-called constant number simulations of Brownian coagulation. In these simulations, the number of particles were kept fixed and the volume of mixing was allowed to increase with time. These simulations reflect Brownian coagulation because the number of particles within a mixing volume is constant throughout agglomeration. This fact was confirmed by large-scale spatial simulations of Brownian coagulation. The nature of these simulations and the physics of Brownian coagulation will allow us to draw some conclusions about Sampson's results upon completion of this analysis.

In recent years, the question of validity of the population balance equation has arisen within the physics literature. The population balance equation in the physics literature is often called the Smoluchowski equation and is also referred to as a mean-field equation since spatial fluctuations are averaged over. The question of validity of the mean-field approach has centered on the idea of an upper critical dimension, d_c. For agglomeration occurring in a Euclidean dimension above the upper critical dimension the mean-field population balance equation is valid and predicts transient agglomeration well from an uncorrelated initial condition. In other words, the commonly written first-order closure hypothesis is valid. For agglomeration occurring in a Euclidean dimension less than or equal to the upper critical dimension, the population balance equation does not necessarily predict the transient evolution of an agglomerating population. The first-order closure hypothesis is not valid.

Kang and Redner [5] were the first to investigate the question of an upper critical dimension for agglomeration. Via direct simulation, they determined the upper critical dimension for a constant agglomeration frequency, $K_{ij} = 1$, to be $d_c = 2$. Computational results suggested to Kang and Redner that the upper critical dimension for all agglomeration processes may be 2. van Dongen [10] determined an expression for the upper critical dimension for given homogeneous agglomeration frequencies. He found that the upper critical dimension may range from 2 to infinity depending on the agglomeration frequency.

II. CLASSIFICATION OF PROBLEM

Investigations into the validity of the closure hypothesis can be classified into three basic approaches. The first approach is that used by Kang and Redner [5] and also by van Dongen [10]. We shall refer to this as the mean-field approach. It assumes that a time-independent agglomeration frequency is known. With the use of this agglomeration frequency, an upper critical dimension is determined by computational means or by analysis of the the stochastics of agglomeration. One of the inherent problems with this approach is that it assumes that the agglomeration frequency remains the same for different Euclidean dimensions as the dimension in which the agglomeration is occurring changes. This is a highly suspect assumption, and in fact for the only agglomeration mechanism in which the dimensional dependence is known, the assumption is not valid. This approach also assumes that in the face of possible particle interdependence (as the closure hypothesis is violated) a time-independent agglomeration frequency can be determined that represents the agglomeration process for fixed Euclidean dimension.

The second approach, which is the one which we pursue, may be called the self-consistent mean-field approach. It assumes that agglomeration processes lead to the development of self-similar size distributions independent of the validity of the closure assumption. Effective agglomeration frequencies can be determined via our inverse problem [11–13] approach that describe the evolution of the transient size distribution. This extracted agglomeration frequency is tested for implicit dependence on time. If significant time dependence is found then the closure hypothesis is not valid. The basis of this approach is the observed self-similar size distribution and not an *a priori* assumed agglomeration frequency. The consequences for the validity of the closure hypothesis are examined further in this paper.

The third possible approach is what we will call the empirical approach. This approach consists of empirically observing the rate of agglomeration between particle pairs and determining their rates of agglomeration. This approach has the same drawbacks as the direct observation approach mentioned previously. The agglomeration frequency in this approach will be explicity dependent on time in general.

III. CLOSURE HYPOTHESIS VALIDITY

In this section, the self-consistent mean-field approach is used to determine the validity of the first-order closure hypothesis. The approach is to assume that an agglomerating system evolves to a self-similar size distribution. The evolution of the average particle size can be written as [12, 13]

$$\frac{dS}{dt} = \langle b \rangle S^{\lambda}. \tag{3}$$

The parameters $\langle b \rangle$ and λ are known for the process of interest. Also, the details of the similarity distribution, such as the order of singularity τ, are also known. This approach focuses on the cell representation of an agglomerating system.

The cell representation of an agglomerating process views the total system as composed of cells of volume v. Particles may move between cells via diffusion. The diffusion coefficient of a particle of mass k is $D_k = Dk^{-\alpha}$. Agglomeration occurs within the cells. The vector $\mathbf{m} = \{..., m_{i\lambda}, ...\}$ describes the agglomerating system at any

instant where $m_{i\lambda}$ is the number of particles of mass i in cell λ at time t. In this representation, only discrete values of the particle mass are allowed.

We assume that the vector $\mathbf{m}$ defines the state of a Markov process. Markov processes are useful because if the state of the stochastic process is known at time t then the state at time $t' > t$ is known probabilistically. The mathematical statement of this property is the Chapman-Kolmogorov equation [14, 15]. The differential restatement of the Chapman-Kolmogorov equation is called the master equation [15] or the forward equation [14].

Let $P(\mathbf{m}, t)$ be the probability that the agglomerating system is in state $\mathbf{m}$ at time t from a given initial condition. A master equation is written for the evolution of P,

$$\frac{\partial P(\mathbf{m},t)}{\partial t} = \dot{P}_A(\mathbf{m},t) + \dot{P}_T(\mathbf{m},t), \tag{4}$$

where $\dot{P}_A$ is the rate of change of P due to agglomeration within the cells and $\dot{P}_T$ is the rate of change of P due to the crossing of cell boundaries (i.e., transport).

Let $W_A(\mathbf{m}'|\mathbf{m})$ be the transition probability per unit time (or the transition frequency) for a transition from state $\mathbf{m}$ to state $\mathbf{m}'$ due to agglomeration within the various cells. Let us investigate W_A in more detail. Only certain states are accessible from $\mathbf{m}$. Also, only certain states can lead to state $\mathbf{m}$. Let us assume that within the time scale of observation only binary agglomeration events are allowed to occur. This assumption can always be maintained by sufficiently reducing the time scale of observation. The accessible states to and from $\mathbf{m}$ are

$$\{..., m_{i\lambda}+1, m_{j\lambda}+1, m_{i+j,\lambda}-1, ...\} \Longrightarrow \mathbf{m} \Longrightarrow \{..., m_{i\lambda}-1, m_{j\lambda}-1, m_{i+j,\lambda}+1, ...\}.$$

To determine an expression for W_A, we look at the internal operations of agglomeration in a cell. Inside this cell labeled λ, there are a certain number of particles. Let us at this time instant label every particle in the cell as A,B,C, ... The position, velocity, and mass of each particle are known. For the moment, we assume that the probability that within the next observation time interval particles I and J agglomerate given that I and J are in the same cell is determinable as $K^{\dagger}_{IJ}$. Then the transition frequency is

$$W_A(\{..., m_{i\lambda}-1, m_{j\lambda}-1, m_{i+j,\lambda}+1\}|\mathbf{m}) = \sum_{I\in i,\ J\in j} K^{\dagger}_{IJ}. \tag{5}$$

If we assume that the agglomeration probability is only a function of the particle size and does not depend on the cell and that all other variables can be averaged over, then $K^{\dagger}_{IJ} = K^{\dagger}_{ij}$ and the transition frequency for agglomeration becomes

$$W_A(\{..., m_{i\lambda}-1, m_{j\lambda}-1, m_{i+j,\lambda}+1\}|\mathbf{m}) = K^{\dagger}_{ij} m_{i\lambda}(m_{j\lambda} - \delta_{ij}), \tag{6}$$

where δ_{ij} is the Kronecker delta.

An expression can now be determined for the rate of change of $\dot{P}_A$,

$$\dot{P}_A(\mathbf{m},t) = \frac{1}{2}\sum_{i,j,\lambda} K^{\dagger}_{ij}(E_{i\lambda}E_{j\lambda}E^{-1}_{i+j,\lambda} - 1) \times m_{i\lambda}(m_{j\lambda} - \delta_{ij})P(\mathbf{m},t) \tag{7}$$

where $E_{i\lambda}$ is called a step operator [15] and it acts upon a function of $\mathbf{m}$ as follows

$$E_{i\lambda} f(\{..., m_{i\lambda}, ...\}) = f(\{..., m_{i\lambda}+1, ...\}).$$

Similar arguments as those for W_A lead to an expression for the transition frequency for transport,

$$W_T(\{..., m_{k\kappa}+1, m_{k\lambda}-1, ...\}|\mathbf{m}) = \omega^k_{\kappa\lambda} m_{k\lambda}, \tag{8}$$

where $w^k_{\kappa\lambda}$ is the probability that within the next observation interval a particle of mass k will move from cell λ to cell κ. $\dot{P}_T$ is now determined,

$$\dot{P}_T(\mathbf{m},t) = \sum_{k,\kappa,\lambda} w^k_{\kappa\lambda}(E_{k\lambda}E^{-1}_{k\kappa} - 1)m_{k\kappa}P(\mathbf{m},t). \tag{9}$$

Combination of Eqs. (9), (7), and (4) give the evolution in time of $P(\mathbf{m}, t)$ for an agglomerating system. Although this master equation is a single closed equation for the evolution of an agglomerating system, its solution is difficult. The general approach to the solution of a master equation is to solve for various moments of the probability distribution.

We demonstrate the equivalence of the above master equation approach and the product-density framework for the evolution of agglomerating systems. By so doing, the basic assumptions that are present in the product-density approach become clear and also the assumptions necessary for the application of the first-order closure hypothesis are revealed.

The product-density approach is equivalent to writing moment-evolution equations from the probability distribution given by the master equation. For example, let $\langle m_k \rangle$ be the expected number of particles of mass k in a cell. Notice that all of the various cells have been averaged over. Also let $\langle m_i(m_j - \delta_{ij})\rangle$ be the expected number of particle pairs of masses i and j. By definition of an expectation $\langle m_k \rangle$ is

$$\langle m_k \rangle = \sum_{\lambda} m_{k\lambda} P(\mathbf{m},t). \tag{10}$$

By placing Eq. (10) into Eq. (4) and solving for the evolution of $\langle m_k \rangle$,

$$\frac{d\langle m_k\rangle}{dt} = \frac{\langle m_k\rangle}{v}\frac{dv}{dt} - \frac{1}{2}\sum_{i,j} K^{\dagger}_{ij}(\delta_{i+j,k} - \delta_{ik} - \delta_{jk}) \times \langle m_i(m_j - \delta_{ij})\rangle. \tag{11}$$

The first term on the right-hand side of Eq. (11) cor-

responds to the rate of increase of $\langle m_k \rangle$ due to a possible increase in the cell volume. The second term represents the rate of change of $\langle m_k \rangle$ due to agglomeration within the cells. Note that Eq. (11) is now an unclosed equation for the evolution of $\langle m_k \rangle$ Also notice that the evolution of $\langle m_k \rangle$ does not depend on the details of the motion between cells. This effect is a consequence of averaging over all the cells. Let $n(k)$ be the concentration of particles of mass k; $n(k) = \langle m_k \rangle / v$ and $n_2(i,j) = \langle m_i(m_j - \delta_{ij}) \rangle / v^2$. Notice that $K_{ij} = K^{\dagger}_{ij} v$. In this way, $K^{\dagger}$ is converted from a conditional probability based upon the cell volume to a conditional probability on a unit volume (which is the agglomeration frequency). Equation (11) becomes

$$\frac{dn(k)}{dt} = \frac{1}{2} \sum_{i,j} K_{ij} (\delta_{i+j,k} - \delta_{ik} - \delta_{jk}) n_2(i,j). \quad (12)$$

This equation is the discrete form of the first-order product-density equation [Eq. (1)]. The assumptions of the product density equations become clear. They are (i) the particle mass (or particle volume) is the important physical variable, (ii) the other variables such as position in the cell or velocity of the particles in the cell can be averaged over or are correlated with particle mass (i.e., $\mathbf{m}$ defines the state of a Markov process) and (iii) the rate constant K_{ij} is independent of position.

Upon accepting the above basic assumptions, our attention can be turned to the closure hypothesis. The first-order closure hypothesis can be written as

$$n_2(i,j) = n(i) n(j) \quad (13)$$

in discrete form. This closure approximation is the same as

$$\langle m_i (m_j - \delta_{ij}) \rangle \rightarrow \langle m_i \rangle \langle m_j \rangle. \quad (14)$$

As $\langle m_i \rangle$ and $\langle m_j \rangle$ increase the expected number of pairs $\langle m_i(m_j - \delta_{ij}) \rangle$ approaches $\langle m_i \rangle \langle m_j \rangle$. Our approach assumes that similarity is observed; similarity imposes a constraint on the evolution of the size distribution such that the number of particles of one size relative to the entire population of particles must stay fixed in order for similarity to be maintained, then

$$\frac{\langle m_i \rangle}{\langle m_j \rangle} = \frac{n(i)}{n(j)} = \text{const.} \quad (15)$$

Thus as the total expected number of particles, $\langle N \rangle = \sum_k \langle m_k \rangle$, in a cell increases, the closure approximation becomes better. If the expected number of particles in a cell $\langle N \rangle$ becomes small the closure approximation worsens. Thus we use $\langle N \rangle$ as an indicator of the quality of the closure approximation.

An equation can be determined for the evolution of the expected number of particles in a cell from the master equation,

$$\frac{d\langle N \rangle}{dt} = M_0 \frac{dv}{dt} - \frac{1}{2} \sum_{i,j} K^{\dagger}_{ij} \langle m_i (m_j - \delta_{ij}) \rangle \quad (16)$$

where M_0 is the total number density $M_0 = \sum_k n(k)$. The second term on the right-hand side can be identified as the reciprocal mean first passage time $\langle \tau_m \rangle$ [14] between agglomeration events within a cell; i.e., between states $\{..., m_{i\lambda}, ...\}$ and $\{..., m_{i\lambda} - 1, m_{j\lambda} - 1, m_{i+j,\lambda} + 1, ...\}$.

The key physical input arises at this point. The mean first passage time $\langle \tau_m \rangle$ must be interpreted in terms of known quantities. The process envisaged here cannot be viewed strictly as a continuous time process, but actually as a discrete time process on a fine time scale τ_{obs}. If τ_{obs} is too small, the process cannot be viewed as a Markov process with respect to the variable $\mathbf{m}$. If τ_{obs} is too large then between observations one particle may have undergone multiple agglomeration events (a possibility we have already assumed to be negligible). A relationship between the cell size v and τ_{obs} can be obtained,

$$v^{1/d} = V_{\min} \tau_{\text{obs}}, \quad (17)$$

where $V_{\min}$ is the root-mean-square-minimum velocity of a particle in a cell. At this stage the analysis is restricted to diffusive processes so $V_{\min} = D^{1/2}_{\min} \tau^{-1/2}_{\text{obs}}$ where $D_{\min}$ is the minimum diffusion coefficient. We guarantee that the observation time τ_{obs} is small for all times by relating it to the mean first passage time (which may change in the course of agglomeration). Let

$$\tau_{\text{obs}} = K_1 \langle \tau_m \rangle, \quad (18)$$

where $K_1 \leq 0.01$.

IV. EXPECTED NUMBER OF PARTICLES IN CELL

With the physical connection between the mean first passage time and the observation time scale, it is possible to determine expressions for $\langle N \rangle$.

The solution to Eq. (16) is

$$\langle N \rangle = (K_1 D_{\min})^{d/d+2} M_0 \left(-\frac{dM_0}{dt} \right)^{-d/d+2}. \quad (19)$$

The number of particles in a cell will increase, decrease, or remain constant depending on the Euclidean dimension. If similarity is observed then Eq. (19) can be cast in a more compact form since the evolution of M_0 is determined by the evolution of $S(t)$. The evolution of M_0 depends on the degree of singularity τ of the similarity distribution $\Phi(z)$. See [12] for an explanation. The evolution of M_0 and thus Eq. (19) can be broken into two cases. Case (i) occurs when $\tau < 1$ and case (ii) occurs when $\tau \geq 1$. If the similarity distribution is not singular at the origin then $\tau = 0$, and case (i) holds.

In this case, $M_0 = p_0 S^{-1}$ and $D_{\min} = K_2 D S^{-\alpha}$. Equation (19) becomes

$$\langle N \rangle = \left(\frac{K_1 K_2 D}{p_0 \langle b \rangle} \right)^{d/d+2} p_0 S^{\chi(d)}, \quad (20)$$

where

$$\chi(d) = \frac{d}{d+2} (1 - \alpha - \lambda - 2/d).$$

This is where the identification of an upper critical dimension d_c could be made. If α and λ were a fixed

function of the Euclidean dimension, then we could let d_c be the dimension such that $\chi(d) = 0$,

$$d_c = \frac{2}{1-\alpha-\lambda}. \tag{21}$$

From the point of view of our self-consistent mean-field approach, the upper critical dimension is not necessary or useful because the parameters λ and α are only known in Euclidean dimensions in which the agglomeration process has been observed. The expression given above is for comparison purposes only. Equation (21) can be compared with previous expressions determined by other investigators. It is identical to an expression for the upper critical dimension determined by van Dongen [10] by different arguments. He did not, however, address case (ii) which must also be considered.

For this case $M_0 = \overline{p_0} S^{\tau-2}$. Equation (19) becomes

$$\langle N \rangle = \left(\frac{K_1 K_2 D}{\overline{p_0}(2-\tau)\langle b \rangle} \right)^{d/d+2} \overline{p_0} S^{\chi(d)}, \tag{22}$$

where

$$\chi(d) = \frac{d}{d+2}\left(1-\alpha-\lambda-\frac{2(2-\tau)}{d}\right).$$

Again an upper critical dimension could be identified as

$$d_c = \frac{2(2-\tau)}{1-\alpha-\lambda}. \tag{23}$$

The upper critical dimensions, determined in the past for specific agglomeration frequencies when the relative motion is diffusion, are in agreement with those obtained from (21) or (22) as the case may be. For the reaction constant $K_{ij} = (ij)^{\lambda/2}$ with $\alpha = 0$ and $\lambda > 0$, there is some disagreement in the literature over the upper critical dimension. Kang *et al.* [16] determined $d_c = 2$, while van Dongen applied equation (21) and calculated $d_c = 2/1 - \lambda$. Our approach to the upper critical dimension for this reaction constant is as follows. First, the self-similar size distribution gives $\tau = 1 + \lambda$ from the asymptotic behavior. Thus case (ii) and Eq. (23) are used to determine that $d_c = 2$ in agreement with Kang *et al.*

V. BROWNIAN COAGULATION OF COMPACT CLUSTERS

An example illustrates our contention that validity of the mean-field equation is not determined strictly by adherence to an upper critical dimension. Let us examine the Brownian coagulation of compact clusters in greater detail. In this case there is dimensional dependence of α and λ. For Brownian coagulation of compact clusters in a Euclidean dimension $d > 2$, $\alpha = 1/d$ and $\lambda = (d-3)/d$. The self-similar size distribution $\Phi(z)$ falls to the origin as $z \to 0$. With the aid of Eq. (20), $\chi(d) = 0$ for every dimension. This indicates that there is no way of independently varying the dimension d to vary the value of $\chi(d)$. In this case, if we examined the upper critical dimension for Brownian coagulation of compact clusters, we find that every dimension is a critical dimension, i.e., gives a value of $\chi(d) = 0$. This example illustrates that although the mechanism of relative motion of particles can be kept fixed for various Euclidean dimensions, the agglomeration frequency cannot be held fixed, and thus λ cannot be held fixed and thus the upper critical dimension cannot be determined.

The fact that $\chi(d) = 0$ means that the expected number of particles in a cell, $\langle N \rangle$, is constant througout the course of agglomeration since $\langle N \rangle$ does not depend on $S(t)$. The implication of this is that if the ratio of diffusion to agglomeration represented by $D/\langle b \rangle$ in Eq. (20) is large initially then the expected number of particles in a cell will be large and the first-order closure hypothesis is valid. If, however, the ratio of diffusion to agglomeration $D/\langle b \rangle$ is initially small, then the first-order closure hypothesis is not useful initially or at any later time.

The observations of Sampson [9] can be explained with respect to the above statements. He observed via large-scale spatial simulations of Brownian coagulation that the number of particles N_{mix} within a mixing volume V_{mix} stayed approximately constant. The volume of mixing increased with time and engulfed more particles that offset the loss of particles due to agglomeration. He could therefore view Brownian coagulation of compact clusters as made up of a series of independent mixing volumes which contained a constant number of particles. This view is identical with our view with the realization that $\langle N \rangle = N_{\text{mix}}$ and $v = V_{\text{mix}}$. Sampson's view led him to approximate the full scale spatial simulations with a series of smaller simulations in which the number of particles within a mixing volume were held constant. These simulations are Sampson's constant-number simulations. From these constant number simulations he tested the validity of various closure hypotheses. He found that for a large number of particles in the cell, the first-order closure hypothesis was valid. He also found that if the number of particles in the cell became smaller, $\langle N \rangle \sim 50$, the significant deviations from the first-order closure hypothesis could occur. He also found that the validity of the closure hypothesis did not change in the course of agglomeration. All of these features can be explained by the approach outlined above. Since the expected number of particles $\langle N \rangle$ does not change with time, the only deviations from the first-order closure hypothesis should arise from the initial condition, i.e., the initial number of particles in a cell.

VI. SUMMARY AND CONCLUSIONS

The cell representation of an agglomerating population gives rise to a master equation for the probability that the system is in state $\mathbf{m}$ at time t, $P(\mathbf{m}, t)$. This equation cannot in general be solved. Equations for the evolution of the various moments of the probability density can be written from the master equation. This series of equations is identical to the product-density hierarchy. The product-density hierarchy is an infinite set of equations for the moments of the probability density and is unclosed since the solution of the lower-order product-

density equations require the solution of the higher-order equations. In order to solve this set of equations a closure hypothesis must be made. The first-order closure hypothesis replaces this infinite set of equations with a single equation. This single equation is commonly called the population balance equation.

In this paper, we have addressed the assumptions of the population balance equation for an aggregating system. We also developed criteria for the applicability of the first-order closure hypothesis. Our criteria assumed that the agglomerating population evolved to a self-similar size distribution. Our approach, which we call the self-consistent mean-field approach, is contrasted with mean-field approach of van Dongen and Kang and Redner. Their mean-field approach assumed that the agglomeration frequency is known *a priori*. This assumption allows the calculation of an upper critical dimension, d_c. We show that while our approach enables a determination of an upper critical dimension for agglomeration it does not adequately describe the validity of the first-order closure hypothesis. The actual quantity of interest is the expected number of particles in a cell $\langle N \rangle$, expressions for which are determined.

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