Fokker-Planck equation for particle growth by monomer attachment

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The population balance equation (PBE) for growth by attachment of a monomeric unit is described in the discrete domain by an infinite set of differential equations. Transforming the discrete problem into the continuous domain produces a series expansion which is usually truncated past the first term. We study the effect of this truncation and we show that by including the second-order term one obtains a Fokker-Planck approximation of the continuous PBE whose first and second moments are exact. We use this truncation to study the asymptotic behavior of the variance of the size distribution with growth rate that is a power-law function of the particle mass with exponent a. We obtain analytic expressions for the variance and show that its asymptotic behavior is different in the regimes $a<1/2$ and $a>1/2$. These conclusions are corroborated by Monte Carlo simulations.

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I. INTRODUCTION

In crystallization, polymerization, and particle synthesis in general, control of the size distribution is a consideration of great practical interest. Tightest control of polydispersity is achieved in seeded growth, namely, when nucleation and coagulation are suppressed and particles grow through the deposition of precipitating species ("monomer"). There are several factors that contribute to the widening of the size distribution even under conditions of seeded growth. Most significantly, the growth rate is generally a function of size, causing different modes of the size distribution to grow at different rates. Nevertheless, even among particles of the same size and in the same reaction environment, it is often observed that a distribution of growth rates exists [1,2]. This source of polydispersity has been called *growth dispersion*, a term used to collectively refer to various mechanisms that can give rise to such behavior, for example, presence of gradients in the reaction medium arising from inefficient mixing, fluctuations due to turbulence, or the existence of an intrinsic distribution of growth rates (e.g., variability of growth sites among particles) [2,3]. Growth dispersion is manifested most clearly when the precipitation medium is seeded with a monodisperse population of particles. In the presence of dispersion, the spread of the size distribution increases with time leading to a polydisperse system.

The classical approach to modeling the size distribution in growth (precipitation) by the monomer attachment is based on the population balance equation written in the form [2]

$$\frac{\partial f(x;t)}{\partial t} = -\frac{\partial K(x) f(x;t)}{\partial x}, \tag{1}$$

where f is the size distribution, x is the chosen size coordinate, and $K(x)$ is the growth rate for size x. Equation (1) is not capable of producing dispersion: if the distribution is initially monodisperse, it will continue to remain so indefinitely. This limitation has been addressed in the literature by adding a diffusive term whose strength is usually fitted to experiments [2]. In conjunction with fragmentation, diffusive growth has been used to model dynamic instabilities in microtubule polymerization [4], and explain size distributions observed in as diverse systems as crystals in ice sheets and length distributions of α helices in proteins [5]. More recently, Olesen *et al.* [6] incorporated size diffusion into the fragmentation/coagulation equation and obtained analytic solutions. In most of these studies, the diffusive term is introduced *ad hoc* and represents an artificial correction to the PBE with a diffusion coefficient that is treated as an adjustable parameter.

As it has been pointed out in previous works [7–9], a diffusive term emerges *naturally* when the discreteness of the growth process is taken into consideration. The attaching monomer, although often small compared to the particle to which it attaches, is nevertheless a discrete unit. From this viewpoint, Eq. (1) represents an approximation to the rigorous population balance equation (PBE) that is valid in the limit that such discreteness may be ignored. If this limit is not quite reached, Eq. (1) must be corrected with terms that include the second-order and higher derivatives of the size distribution with respect to size. The connection between dispersion and discreteness of the attaching unit can be understood by viewing the growth process in stochastic terms. In a population of particles competing for the same pool of monomers, growth occurs in discrete steps in size and time. At each step, the particle that captures a monomer, thereby increasing its mass by one unit, represents a fluctuation. Such fluctuations grow in time in a diffusive manner and are further amplified if growth favors larger sizes over the smaller ones, as is usually the case. The size distribution that emerges from this process is determined by the coupling between fluctuations and the growth law. The effect of dispersion and its relationship to the growth mechanism is a question that has to be addressed when measured size distributions are used to deduce the growth mechanism [1,7]. More generally, the accuracy and limitations of Eq. (1) arise in the broader context of designing crystallizers and developing their optimization and control schemes [10–13]. A small number of studies has focused directly on the broadening that arises by including higher-order terms in the PBE. McCoy [8] and Madras and McCoy [12] wrote the continu-

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ous PBE in a form that explicitly accounts for the discreteness of the depositing unit and applied this formulation to crystal precipitation in the presence of nucleation and dissolution but did not address directly the effects of dispersion. More recently, Haseltine *et al.* [9] in a numerical study of nucleation and growth in crystallizers showed that Eq. (1) with the diffusive term included leads to good agreement with the results from discrete stochastic simulation. Matsoukas and Gulari [7] used a combination of moment analysis and simulations to obtain a scaling between the variance and the mean size in the absence of nucleation. While that study provided a useful connection between the growth law and the observed polydispersity, the question of how size fluctuations propagate in time remains unresolved.

The purpose of this paper is to quantify size fluctuations in growth by monomer attachment and to assess the corrections to Eq. (1) that are necessary to capture this broadening. The paper is organized as follows: We begin in Sec. II by writing the exact population balance in discrete form and obtain analytical solutions in two special cases, size independent growth, and growth that is proportional to the particle mass. In Sec. III we derive the continuous population balance in the form of an infinite series, study the effect of truncation to a finite number of terms, and obtain analytic solutions with truncation that retains the diffusive term in the presence of power-law growth rates. In Sec. IV we present a systematic study by numerical simulation of the effect of the growth law on the size distribution and discuss the implications of our results.

II. DISCRETE POPULATION BALANCE

We consider particle growth by addition of a monomeric unit according to the reaction

$$A_i + A_1 \xrightarrow{K_i} A_{i+1}, \tag{2}$$

where A_1 represents the precipitating species ("monomer"), A_i is a particle of size i in units of the monomeric mass, and K_i is the rate constant of the reaction. To isolate the effect of dispersion we consider growth of an initial population of seed particles in the absence of further nucleation. Such seeds may be assumed to either form by a brief homogeneous nucleation burst, or could be introduced externally in the form of nucleation seeds.

The discrete population balance equation corresponding to Eq. (2) is

$$\frac{dc_i}{dt'} = K_{i-1}c_1c_{i-1} - K_ic_1c_i, \tag{3}$$

where c_1 is the concentration $(1/\mathrm{m}^{-3})$ of monomeric units, c_i is the concentration $(1/\mathrm{m}^{-3})$ of particles of mass i (in units of the monomer), and K_i is the rate constant $(\mathrm{m}^3/\mathrm{s})$ for the reaction between monomer and particle of size i, assumed to be a function of the particle size. The rate constant can be expressed in the form

$$K_i = K_0k_i, \tag{4}$$

where K_0 is the dimensional part $(\mathrm{m}^3/\mathrm{s})$ and k_i is the dimensionless growth rate normalized such that $k_1=1$. We are interested in growth rates of the power-law form

$$k_i = i^a. \tag{5}$$

In addition to mathematical convenience, this form encompasses a number of cases of practical interest. In diffusion-limited attachment of a solute onto a particle, the particle growth rate is $K_i=4\pi R_iD_1$, where R_i is the particle radius, D_1 is the diffusion coefficient of the solute, and n_1 is its concentration [14]. For spherical particles, $R_i \sim m_i^{1/3}$, i.e., $a=1/3$. For reaction-limited growth and for ballistic growth in the kinetic regime, the growth rate is proportional to the surface area, thus the growth law is again of the power-law type with $a=2/3$ [14]. With $a=0$ we obtain size-independent growth while with $a=1$ the growth rate is proportional to the particle mass. Values of a outside the interval [0, 1] do not represent physical systems and are not considered here.

We define the dimensionless concentration, n_i, and time, t, as

$$n_i = \frac{c_i}{C_0}, \quad t = K_0C_0\int_0^{t'} c_1dt', \tag{6}$$

where C_0 is the total particle concentration initially. With these definitions, the population balance becomes

$$\frac{dn_i}{dt} = k_{i-1}n_{i-1} - k_in_i. \tag{7}$$

In the transformed time t, the population balance is independent of the concentration of the monomer. If the amount of monomer is finite, then t approaches a finite value. If the initial supply of monomer is large, or if the monomer is continuously added to the reactor, the transformed time can be made arbitrarily large. The moment of order k is defined as

$$x_k = \sum_i i^kn_i, \tag{8}$$

and its evolution is obtained in the usual manner by multiplying the PBE by i^k and performing the summation over i. The result for integer k is

$$\frac{dx_k}{dt} = \sum_{m=0}^{k-1}\binom{k}{m}x_{a+m}. \tag{9}$$

In the two special cases $a=0$ and $a=1$, Eq. (9) is a closed set and permits an explicit solution for the moments. These two cases are discussed in more detail below.

A. Size independent growth $(a=0)$

With $a=0$, the solution can be obtained by solving sequentially Eq. (7) of the discrete population balance. With arbitrary initial conditions $[n_i(0)=n_{i,0}]$ this solution is

$$n_i = e^{-t}\sum_{k=0}^{i-1}\frac{n_{i-k,0}}{k!}t^k. \tag{10}$$

The mean size, x_1, and variance, $\sigma_x^2=x^2-x_1^2$, are obtained from Eq. (9) with $a=0$. Integrating with initial conditions $x_{1,0}$, $\sigma_{x,0}^2$ we find

$$x_1 = t + x_{1,0} \sim t, \tag{11}$$

$$\sigma_x^2 = t + \sigma_{x,0}^2 \sim t. \tag{12}$$

At long times the distribution in Eq. (10) becomes a Gaussian function whose mean and variance, according to Eqs. (11) and (12) both increase as $\sim t$. Accordingly, the normalized variance σ_x^2/x_1^2 scales as $\sim 1/x_1$. While the absolute width of the distribution increases, the ratio σ_x^2/x_1^2 decreases. Such behavior has been called self-sharpening to emphasize the narrowing of polydispersity during growth.

B. Proportional growth law ($a=1$)

The proportional growth law, $a=1$, also leads to a closed system of equations for the moments. With arbitrary initial conditions the first few moments of the size distribution are

$$x_1(t) = e^t x_{1,0}, \tag{13}$$

$$x_2(t) = -e^t x_{1,0} + e^{2t}(x_{1,0} + x_{2,0}), \tag{14}$$

$$x_3(t) = e^t x_{1,0} - 3e^{2t}(x_{1,0} + x_{2,0}) + e^{3t}(2x_{1,0} + 3x_{2,0} + x_{3,0}). \tag{15}$$

For the normalized variance, σ_x^2/x_1^2, we then obtain

$$\frac{\sigma_x^2}{x_1^2} = \frac{\sigma_{x,0}^2}{x_{1,0}^2} + \frac{1}{x_{1,0}} - \frac{1}{x_1}, \tag{16}$$

where $\sigma_{x,0}^2$, $x_{1,0}$, are the variance and mean size at $t=0$. The size distribution at long times depends on the initial conditions. For monodisperse initial conditions with $x_{k,0}=1$ (i.e., all seeds have the same size as the depositing unit), the moment of order k is dominated by the leading term, i.e., $x_k \sim k! x_1^k$, which we recognize as the k-order moment of the exponential distribution:

$$n_i \sim \frac{\exp(-i/x_1)}{x_1}, \tag{17}$$

with $x_1 = e^t$. Dispersion in this case transforms a monodisperse distribution at $t=0$ into an exponential distribution with $\sigma_x^2/x_1^2 \approx 1$. This represents a substantial broadening of the distribution and shows that growth by monomer attachment can lead to distributions as wide as those produced by coagulation (coagulation with size-independent rate also results in the exponential distribution of Eq. (17) [14]).

III. THE CONTINUOUS POPULATION BALANCE

In practice it is far more convenient to work with a continuous representation of the distribution. In the continuous size domain x, the distribution is $f(x)$ such that $f(x)dx$ is the concentration of particles in the mass range $(x, x+dx)$, and x is the particle mass normalized by the size of the attaching unit. The governing equation of f is obtained from the discrete population balance equation using Taylor series to express the finite difference in Eq. (7). Noting that the particle mass x is normalized by the size of the monomer, the resulting equation is a power series in $\delta x = -1$:

$$\frac{\partial f}{\partial t} = (x-1)^a f(x-1) - x^a f(x) = \sum_{m=1}^{\infty} \frac{(-1)^m}{m!} \frac{\partial^m x^a f}{\partial x^m}. \tag{18}$$

The moments of the continuous distribution are defined by

$$x_k = \int x^k f(x) dx, \tag{19}$$

and their evolution is obtained by propagating this definition through Eq. (18). The derivation is given in the Appendix and the final result for integer k is

$$\frac{dx_k}{dt} = \sum_{m=1}^{k} \binom{k}{m} x_{k+a-m}. \tag{20}$$

It can be verified that Eqs. (20) and (9) produce identical results. Therefore the continuous population balance expressed by the infinite series in Eq. (18) is equivalent to the discrete equation in Eq. (7).

A. Fokker-Planck truncation and its moments

The usual form of the PBE is a truncation of the full PBE in which only the convective term is retained. If the second-order term is retained, we obtain a diffusive contribution that introduces dispersive character in the PBE. In general, we can produce a truncation with J terms. To determine the degree of approximation that is introduced when the infinite series is truncated to a finite number of terms, we retain the first J terms in the right-hand side of Eq. (18) and recalculate the moments based on the truncated PBE. This is done easily once we notice that each term of order m of the series in Eq. (18) gives rise to a term that contains x_{k+a-m}, as in Eq. (20). Then, if the PBE is truncated past the Jth term, the corresponding integer moments are governed by the truncated series

$$\frac{dx_k}{dt} = \sum_{m=1}^{J} \binom{k}{m} x_{k+a-m} = \sum_{m=1}^{\max\{k,J\}} \binom{k}{m} x_{k+a-m}. \tag{21}$$

The replacement of J by $\max\{k,J\}$ in the upper limit of the summation is made possible by the fact that the binomial coefficient is zero when $J > k$. Through direct comparison we recognize Eq. (21) for the moments of the truncated PBE as a truncation of Eq. (20) to J terms. For the moment of order k, the rigorous Eq. (20) produces a summation with k terms; the truncated Eq. (21) produces a summation that has *at most* J terms. Therefore all integer moments of order $0 \leqslant k \leqslant J$ of the truncated PBE are in exact agreement with those of the complete PBE while moments of higher order are only approximate. It follows that the truncation that retains only the convective term reproduces the correct evolution of the mean size but not that of the variance. This explains the inability of Eq. (1) to account for dispersion.

To track the variance, it is sufficient to include the second-order term. This produces an equation of the Fokker-Planck type with a convective and a diffusive term:

$$\frac{\partial f}{\partial t} = -\frac{\partial x^a f}{\partial x} + \frac{1}{2}\frac{\partial^2 x^a f}{\partial x^2}. \tag{22}$$

The convective term represents the mean growth rate and the diffusive term introduces size fluctuations with diffusion coefficient $D = x^a/2$. The moments corresponding to this truncation are obtained from Eq. (21) with $J=2$:

$$\frac{dx_k}{dt} = kx_{k+a-1} + \frac{k(k-1)}{2}x_{k+a-2}. \tag{23}$$

It is easy to verify that the moments of order 0, 1, and 2, and these only, are identical to those of the full PBE. From here on we will adopt the two-term truncation and we will investigate the effect of dispersion for growth exponents in the "natural" range $0 \leqslant a \leqslant 1$.

B. The PBE in other coordinates

In Eq. (22), both the convective and the diffusive term are functions of size. A simpler equation can be written by removing the size dependence of the convective term. To do this we write the population balance in a new size coordinate, z, defined as (see also Appendix Sec. 3)

$$z = \frac{x^{1-a}}{1-a} \quad (a \neq 1). \tag{24}$$

[In the special case $a=1$ the corresponding transformation is $z=\ln(x)$ but since the solution to $a=1$ is known, this case is of no further interest. Hence we assume $a \neq 1$ and use Eq. (24) throughout of the rest of the paper.] The size distribution, $g(z)$, in the transformed coordinate z, is governed by the following differential equation (see Appendix Sec. 3):

$$\frac{\partial g}{\partial t} = -\frac{\partial g}{\partial z} + \frac{1}{2}\frac{\partial}{\partial z}\left(\frac{1}{k}\frac{\partial g}{\partial z}\right). \tag{25}$$

Here, $k=k(z)$ is the growth law expressed in terms of the size coordinate z, namely

$$k(z) = \left(\frac{z}{1+\beta}\right)^{\beta} \tag{26}$$

with

$$\beta = \frac{a}{1-a}. \tag{27}$$

We note that the growth law remains a power-law function in the transformed size z and that the corresponding growth exponent is β, with $0 \leqslant \beta < \infty$. The PBE in the size variable z consists of a convective term, whose coefficient is independent of size, and of a diffusion term with diffusivity $1/k$. As explained in the Appendix, the condition that removes the size dependence of the convective term is $k(dz/dx)=1$, from which Eq. (24) follows.

The moments z_k of order k in z are obtained in the usual manner and, as shown in the Appendix, the general result is

$$\frac{dz_k}{dt} = kz_{k-1} + \frac{k(k-1)}{2}(1+\beta)^{\beta} z_{k-\beta-2}. \tag{28}$$

With $k=1$ we confirm that the first moment is linear in time, as expected from the fact that the convective term in Eq. (25) is independent of z. The evolution of the variance, $\sigma_z^2 = z_2 - z_1^2$, follows by application of Eq. (28) and by straightforward manipulation we find

$$\frac{d\sigma_z^2}{dz_1} = (1+\beta)^{\beta} z_{-\beta}. \tag{29}$$

This equation is coupled to the moment of order $-\beta$ but the closure problem can be resolved if the distribution is narrow. In this case, an approximate expression for $z_{-\beta}$ is (see Appendix Sec. 5)

$$z_{-\beta} \approx z_1^{-\beta}\left[1 + \frac{\beta(1+\beta)}{2}\frac{\sigma_z^2}{z_1^2}\right], \tag{30}$$

and Eq. (29) becomes

$$\frac{d\sigma_z^2}{dz_1} = \left(\frac{1+\beta}{z_1}\right)^{\beta}\left[1 + \frac{\beta(1+\beta)}{2}\frac{\sigma_z^2}{z_1^2}\right], \tag{31}$$

which is now in closed form.

C. Behavior at long times

The solution to Eq. (31) can be expressed analytically in terms of the exponential integral function, as shown in Appendix Sec. 5. However, the behavior of the variance can be analyzed more easily if a further simplification is made. If σ_z^2/z_1^2 decreases in time, the variance may be dropped from the right-hand side of Eq. (31) to obtain a simpler equation:

$$\frac{d\sigma_z^2}{dz_1} \approx \left(\frac{1+\beta}{z_1}\right)^{\beta}. \tag{32}$$

This is readily integrated from $z_{1,0}$, $\sigma_{z,0}^2$, to obtain

$$\sigma_z^2 = \sigma_{z,0}^2 + \frac{(1+\beta)^{\beta}}{1-\beta}(z^{1-\beta} - z_{1,0}^{1-\beta}). \tag{33}$$

Depending on the value of the growth exponent we distinguish two cases: For $\beta < 1$ (or $a < 1/2$), the variance at long times is

$$\sigma_z^2 \sim \frac{(1+\beta)^{\beta}}{1-\beta} z^{1-\beta}, \tag{34}$$

i.e., it grows as a power-law function of z_1 with exponent $1-\beta$. For $\beta > 1$ (or $a > 1/2$), on the other hand, the variance at long times reaches a constant value, given by

$$\sigma_{z,\infty}^2 = \sigma_{z,0}^2 + \frac{(\beta+1)^{\beta}}{\beta-1} z_{1,0}^{-(\beta-1)}. \tag{35}$$

In the borderline case $\beta=1$ (or $a=1/2$), Eq. (32) integrates to

$$\sigma_z^2 = \sigma_{z,0}^2 + 2\ln\frac{z}{z_{1,0}}, \tag{36}$$

i.e., in this case the variance increases logarithmically in z_1. The results can be summarized as follows:

$$\sigma_z^2 \sim \begin{cases} z_1^{1-\beta} = z_1^{(1-2a)/(1-a)} & (0 \leqslant a < 1/2), \\ z_1^0 & (1/2 < a \leqslant 1). \end{cases} \tag{37}$$

For growth exponents larger than 1/2, the variance at long times becomes constant, implying that the distribution is translated along the z axis without any changes in its shape. This behavior can also be inferred from Eq. (25) by noting that the diffusive term is proportional to the inverse of the growth rate; accordingly, for large growth exponents, k is a rapidly increasing function of z, rendering the diffusion term negligible. Under such conditions, the PBE is dominated by the convective term thus leading to the condition σ_z^2=const. For growth exponents with weak dependence on size ($a < 1/2$) the variance increases as a power-law function of z whose exponent is a function of a. In all cases, the ratio σ_z^2/z_1^2 decreases, thus the assumption that the distribution is narrow holds true and the approximation that led to Eq. (31) is appropriate.

The scaling behavior of z obtained above can be expressed in terms of the original size variable x (particle mass). First we note that according to Eq. (37), the normalized variance σ_z^2/z_1^2 is a decreasing function of time, i.e., the distribution in z is self-sharpening and becomes a delta function in the limit $z_1 \to \infty$. For narrow distributions we can write the following relationships between the moments in x and in z (see also Appendix Sec. 1):

$$x_1 \approx [z_1(1-a)]^{1/(1-a)}, \tag{38}$$

$$\frac{\sigma_x^2}{x_1^2} \approx \frac{1}{(1-a)^2}\frac{\sigma_z^2}{z_1^2}. \tag{39}$$

Combining with Eq. (37) we arrive at scaling relationships for the mass, x:

$$\frac{\sigma_x^2}{x_1^2} \sim \begin{cases} x_1^{-1}, & 0 \leqslant a < 1/2, \\ x_1^{-2(1-a)}, & 1/2 < a \leqslant 1. \end{cases} \tag{40}$$

In the discrete treatment with $a=0$ we found that the distribution at long times is a Gaussian function with $\sigma_x^2/x_1^2 \sim 1/x_1$. Here we find that the variance obeys the same scaling in the entire range $0 \leqslant 1 < 1/2$. This result prompts us to examine whether the Gaussian character of the distribution also persists in this range of growth exponents. Indeed, it does. Since distributions are narrow, $k(z) \approx k(z_1)$, and Eq. (25) becomes

$$\frac{\partial g}{\partial t} \approx -\frac{\partial g}{\partial z} + \frac{1}{2k(z_1)}\frac{\partial}{\partial z}\left(\frac{\partial g}{\partial z}\right). \tag{41}$$

Noting that $dz_1 = dt$ from Eq. (28), the above result is analogous to the diffusion equation with time-dependent diffusivity. Its solution is a Gaussian function with mean z_1 and variance

$$\sigma_z^2 = \int_{z_{1,0}}^{z} \frac{dz_1}{k(z_1)} \sim z_1^{1-\beta}. \tag{42}$$

This result is in agreement with Eq. (33). Thus we conclude that in the range $0 \leqslant a < 1/2$, the distribution at long-time goes over to a Gaussian function independently of the initial conditions. The distribution in x is also approximately Gaussian, since both $f(x)$ and $g(z)$ become sharply peaked functions.

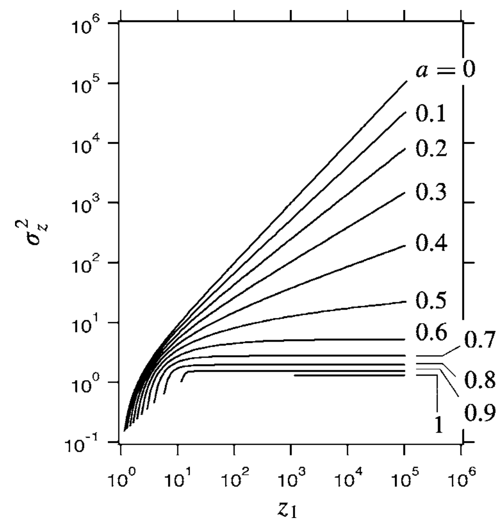

FIG. 1. Variance of transformed size z as a function of the mean based on the solution of Eq. (31).

IV. RESULTS AND DISCUSSION

To compare our results to the complete solution of the population balance equation we have conducted Monte Carlo simulations with growth exponents in the range 0 to 1. The algorithm used has been described in detail elsewhere [15] and is briefly outlined here. A population of N particles is followed during growth in the presence of a concentration of monomer. At each step, a particle is selected and its mass is incremented by 1 if the following condition is met:

$$\text{RND} \leqslant \left(\frac{M_i}{M_{\max}}\right)^a, \tag{43}$$

where RND is a random number from a uniform distribution in the range 0 to 1, M_i is the mass of the selected particle, and $M_{\max}$ is the maximum mass in the population. The process is then repeated until the desired final size has been reached. This algorithm simulates growth under an unlimited supply of monomer. Since the mean size x_1 serves as the growth coordinate, it is not necessary to account for time explicitly, though this may be done, as discussed in Ref. [15]. The simulations are conducted with $N=10^5$ simulation particles using monodisperse initial conditions with $x_{1,0}=1$ (i.e., the initial particle size is equal to the size of the monomer).

We begin by first examining the behavior of the analytic solution for the variance in z. Figure 1 shows a plot of σ_z^2 against the mean size z_1 for values of the growth exponent in the range 0 to 1. This variance is computed from the analytic solution of Eq. (31), given by Eq. (A26) in the Appendix. The behavior predicted by theory is clearly observed: for growth exponents in the interval $0 \leqslant a < 1/2$, the variance increases in power-law form while for $1/2 < a \leqslant 1$ it reaches a steady-state value. The special case $a=1/2$ gives rise to a slow logarithmic increase.

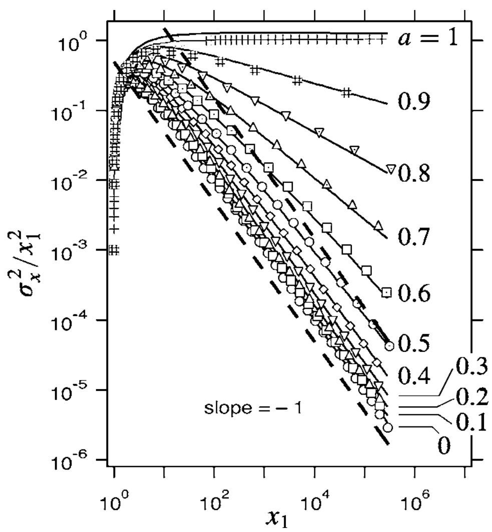

FIG. 2. Normalized variance σ_x^2/x_1^2 vs average mass with initial size $x_{1,0=1}$. Solid lines are calculated from the solution of Eq. (31); points are from Monte Carlo simulation with 10^5 particles and monodisperse initial conditions with $x_{1,0}=0$. The dashed lines are drawn with slope −1.

The normalized variance σ_x^2/x_1^2 is shown in Fig. 2. Lines are from the theoretical solution, obtained from the approximate solution, Eq. (31), in combination with Eqs. (38) and (39), and are compared with results obtained by Monte Carlo simulation. The scaling predicted by theory is seen clearly. For all growth exponents in the range $0 \leqslant a < 1/2$, the normalized variance decays as $1/x_1$. For $1/2 < a < 1$, the decay is slower until, for $a=1$, the normalized polydispersity becomes constant. The analytic results are in excellent agreement with the Monte Carlo results in the region $a < 1/2$ and note that for $a=0$ the difference between simulations and theory is less than 0.1%. Deviations are observed as a is increased above 1/2 and at $a=1$ we find that the analytic result overestimates the variance by about 25%. These deviations are due to the approximations involved in the analytic result. Specifically, the derivation of Eq. (31), which provides the theoretical calculation for this graph, assumes the distribution to be narrow. This assumption is certainly very good for small a but less accurate near $a=1$, where the mass distribution is in fact exponential. On the other hand, Eq. (16), which is the exact solution for $a=1$, is in agreement with Monte Carlo but this comparison is not shown to avoid clutter.

The size distributions obtained by MC simulation are shown in Fig. 3. We recall that for growth exponents below 1/2 the distribution is predicted to be Gaussian with variance that is proportional to the mean size x_1. Accordingly, by plotting the distributions in the normalized size coordinate, y, defined

$$y = 2(x^{1/2} - x_1^{1/2}), \tag{44}$$

size distributions obtained at different times must all collapse onto a single shape that has Gaussian form. This is indeed observed in Fig. 3. The Gaussian fits, shown by solid lines, are in very good agreement with the data. At the critical value $a=1/2$, the distribution does not reach a stationary state, as demonstrated by the imperfect collapse of the data. Still, the Gaussian form seems to provide a good description of the size distribution.

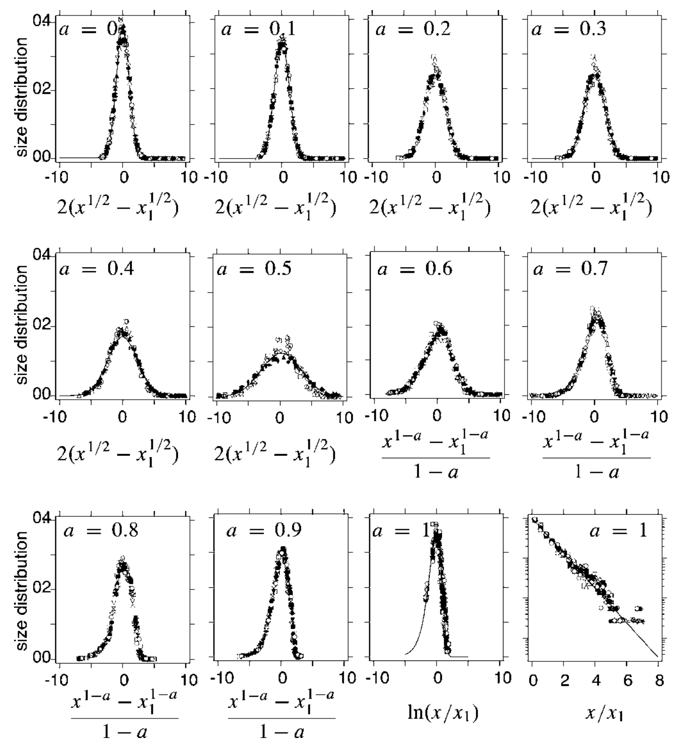

FIG. 3. Distributions by Monte Carlo simulation with monodisperse initial conditions and $x_{1,0}=1$. Symbols represent distributions obtained for different times during growth. The size coordinate is defined so as to collapse all data at long times onto a single distribution that depends only on the growth exponent a.

For growth exponents larger than 1/2, the size transformation that collapses all distributions is given by the transformed size z, translated to zero mean:

$$y = (z - z_1)/(1 - a) \approx (x^{1-a} - x_1^{1-a})/(1 - a). \tag{45}$$

With increasing a, the distribution attains a pronounced tail in small sizes and a sharper front above the mean. In the special case $a=1$ the transformed size coordinate is $z=\ln x$ and the corresponding distribution in x is exponential. To demonstrate the latter point, the distribution for $a=1$ is also shown in the semilog coordinates. We note that the apparent narrowing of the size distribution in the range $a=1/2$ to 1 is an artifact of the transformed coordinate in the abscissa. In terms of the particle mass, x, distributions become wider as the growth exponent increases.

The scaling behavior that emerges from the above results establishes $a=1/2$ as the characteristic growth exponent that separates two distinct regimes. This distinction was noted earlier in Matsoukas and Gulari [7] who used the terms *weak* ($a<1/2$) and *strong* kernels ($a>1/2$) to refer to the two regimes. This distinction is formalized here on the basis of the Fokker-Planck truncation of the population balance equation. This truncation, which retains the diffusive term, correctly accounts for the effects of dispersion that is intrinsic to

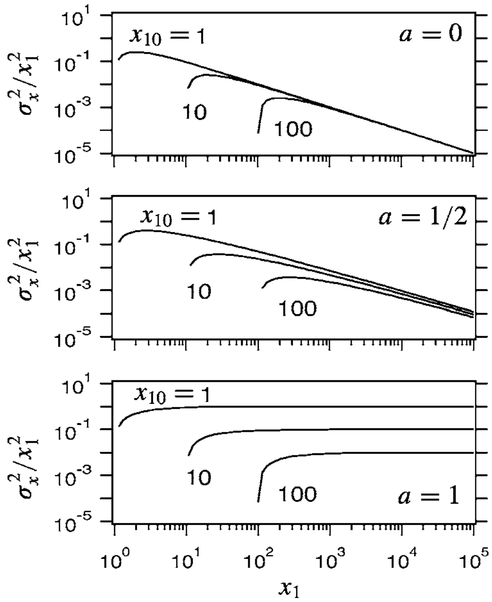

FIG. 4. Effect of initial size on polydispersity. Initial conditions are monodisperse with $x_{1,0}=1,10,100$.

the growth process. This dispersion can be thought to arise from two sources. The first source is due to statistical fluctuations which grow in time and give rise to Gaussian dispersion. These fluctuations are further amplified by the growth law. For growth exponents $a<1/2$ this amplification does not interfere with the Gaussian nature of the dispersion. On the other hand, growth with strong size dependence, i.e., $a>1/2$, is dominated by the convective part of the PBE and leads to size distributions that are not universal but depend on the initial conditions. We refer to this type of broadening as "convective" dispersion because it arises from the different rates at which the low and high ends of the distribution grow. After a transient broadening that depends on the initial seed population the variance in z remains constant. This amounts to dropping the diffusive term from the PBE—although such simplification leaves us without the means to quantify this variance. We note that the size coordinate z was introduced in a semiquantitative way by Overbeek [16] who observed that the growth rate of the moment x^{1-a} is independent of size. Overbeek thus concluded that the distribution of z merely translates along the size axis from which it follows that the variance must be constant. This conclusion, which is based on the convective term of the PBE alone, is indeed correct if $a>1/2$, but not if $a<1/2$.

A further difference between the two growth regimes is with respect to the effect of the initial conditions. With weak growth exponents $(a<1/2)$ the memory of the initial state is lost and the scaling form of the variance is independent of the initial conditions. With strong growth exponents the variance at long times is a function on the initial state and, as shown in Eq. (35), it depends on both the variance and mean size at time zero. This behavior is demonstrated in Fig. 4 in which we plot the normalized variance as a function of time for monodisperse initial conditions and initial size ranging from 1 to 100. In our normalization this refers to the size of the seeds relative to the size of the attaching unit. For $a=0$ the effect of seed size is transient and all lines at long times collapse onto the predicted scaling form. With $a=1$, the normalized variance decreases as the seed size is increased. The borderline case $a=1/2$ leads to long-time behavior such that the normalized polydispersity is logarithmically spaced in $x_{1,0}$. Therefore with strong growth exponents, the steady-state polydispersity has an inverse relationship to the initial seed size. Maximum dispersion is obtained when the size of the seeds is equal to the size of the depositing unit, leading to the distributions shown in Fig. 3. In fact, dispersion is predicted to increase even further when $x_{0,1}<1$, however, we are not aware of any physical system in which the seed particles are *smaller* than the attaching unit.

V. CONCLUSIONS

Our analysis has elucidated the relationship between the rigorous (discrete) population balance equation and the various truncations of its continuous representation. We have shown that the Fokker-Planck truncation tracks the variance exactly and have provided analytic solutions for the variance for power-law growth rates with exponents in the range 0 to 1. Although the simple PBE that consists of the convective term alone is incapable of tracking the spread of the distribution, this failing is not always a serious limitation in practice. For growth exponents in the natural range $0\leqslant a\leqslant 1$, the evolution of the distribution is self-sharpening, indicating that in the long run dispersion can be ignored. This is even more so when the population balance equation includes coagulation or other processes that result in substantial broadening of the distribution, masking the more subtle effects of diffusive dispersion. Dropping the diffusive term in such case, as commonly done in the aerosol literature, is generally acceptable [17–19]. On the other hand, the simple PBE fails to properly account the evolution of narrow distributions of small seeds, especially if growth does not advance substantially beyond the size of the monomer. Thus, in modeling the synthesis of nanoparticles, or the assembly of building blocks into small clusters, the simple PBE is inadequate and the diffusive term needs to be incorporated.

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APPENDIX: DERIVATIONS

1. Relationships between moments in the narrow-distribution approximation

Consider the random variable z and its probability density function, $g(x)$. We define the deviation variable $\delta = z - z_1$ where z_1 is the first moment of x. Obviously, $\mathrm{var}(\delta)=\sigma_z^2$. To obtain an expansion for the k-order moment we first write

$$(z_1+\delta)^k = z_1^k\left[1+\frac{\delta}{z_1}+\frac{k(k-1)}{2}\left(\frac{\delta}{z_1}\right)^2+\cdots\right]. \quad \text{(A1)}$$

Upon integration over the distribution of δ we obtain

$$z_k = z_1^k\left[1 + \frac{k(k-1)}{2}\frac{\sigma_z^2}{z_1^2} + \cdots\right]. \tag{A2}$$

Consider now the transformation

$$x = Cz^n. \tag{A3}$$

We wish to obtain a relationship between the variance in z and the variance in x. First we note an exact relationship between the moments of z and those of x:

$$x_k = C^k z_{nk}, \tag{A4}$$

from which

$$x_1 = Cz_n = Cz_1^n\left[1 + \frac{n(n-1)}{2}\frac{\sigma_z^2}{z_1^2} + \cdots\right], \tag{A5}$$

$$x_2 = C^2 z_{2n} = C^2 z_1^{2n}\left[1 + n(2n-1)\frac{\sigma_z^2}{z_1^2} + \cdots\right]. \tag{A6}$$

Combining these and expressing the results as a series expansion in σ_z^2/z_1^2 around $\sigma_z^2/z_1^2=0$ we find

$$\frac{\sigma_x^2}{x_1^2} = n^2\left(\frac{\sigma_z^2}{z_1^2}\right)\left[1 - O\left(\frac{\sigma_z^2}{z_1^2}\right)^2\right]. \tag{A7}$$

For narrow distributions, therefore

$$\frac{\sigma_z^2}{z_1^2} = n^2\frac{\sigma_x^2}{x_1^2}. \tag{A8}$$

For the transformation defined in Eq. (24), $C=(1-a)^{1/(1-a)}$ and $n=1/(1-a)$, and Eq. (A8) gives

$$\frac{\sigma_x^2}{x_1^2} = (1-a)^2\frac{\sigma_z^2}{z_1^2}. \tag{A9}$$

The relationship is valid provided that the distribution in z is narrow.

2. Moments in x

In this section we derive the moments of the full PBE in Eq. (18). We begin by deriving the following general result for any k, a (not necessarily integer):

$$\int_0^\infty x^k\frac{\partial x^a f(x)}{\partial x}dx = x^{k+a}f(x)\big|_0^\infty - \int_0^\infty kx^{k-1+a}f(x)dx = kx_{k+a-1}, \tag{A10}$$

where we have assumed that $f(x)$ at $x=0$ and $x\to\infty$ goes to zero faster than any power of x. Using the above result, integration of the second derivative yields

$$\int x^k\frac{\partial^2 x^a f(x)}{\partial x^2}dx = k(k-1)x_{k+a-2}. \tag{A11}$$

It can be seen now that in the term of order m, the result is

$$\int x^k\frac{\partial^m x^a f(x)}{\partial x^m}dx = (-1)^m k(k-1)\cdots(k-m+1)x_{k+a-m}$$
$$= (-1)^m\frac{\Gamma(k+1)}{\Gamma(k-m+1)}x_{k+a-m}, \tag{A12}$$

which leads to Eq. (20) of the text.

3. Derivation of the PBE in other size coordinates

For the arbitrary size transformation, $z=z(x)$, the corresponding size distribution is

$$g(x;t) = f(x;t)\frac{dx}{dz}. \tag{A13}$$

We use the above equation to express the derivatives of $f(x;t)$ in terms of $g(x;t)$ and its derivatives, and substitute the result into Eq. (22). This results in the following equation for g:

$$\frac{\partial g}{\partial t} = -\frac{\partial}{\partial z}\left(k\frac{dz}{dx}g\right) + \frac{1}{2}\frac{\partial}{\partial z}\left[\frac{dz}{dx}\frac{\partial}{\partial z}\left(gk\frac{dz}{dx}\right)\right]. \tag{A14}$$

The coefficient of the convective term can be made constant if we choose z such that

$$k\frac{dz}{dx} = 1. \tag{A15}$$

Using Eq. (A15), Eq. (A14) simplifies to

$$\frac{\partial g}{\partial t} = -\frac{\partial g}{\partial z} + \frac{1}{2}\frac{\partial}{\partial z}\left(\frac{dz}{dx}\frac{\partial g}{\partial z}\right), \tag{A16}$$

and by further of Eq. (A15), to

$$\frac{\partial g}{\partial t} = -\frac{\partial g}{\partial z} + \frac{1}{2}\frac{\partial}{\partial z}\left(\frac{1}{k}\frac{\partial g}{\partial z}\right), \tag{A17}$$

which is Eq. (25) of the text. The transformation that removes the size dependence of the convective term is given by Eq. (A15). For the power-law kernel in particular, integration leads to

$$z = \begin{cases} x^{1-a}/(1-a) - c & \text{if } a \neq 1, \\ \ln x - c & \text{if } a = 1, \end{cases} \tag{A18}$$

where c is an integration constant. With $c=0$ we obtain Eq. (24) of the text.

We note that the procedure to transform the Fokker-Planck equation into a form with constant convective term via Eq. (A15) is possible for any functional form of the growth law, not only the power-law form adopted here.

4. Moments in z

The moments of the z coordinate are obtained in analogous manner from Eq. (25) by multiplying by z^k followed by integration over z. Using Eq. (26) for k, the result is

$$\frac{dz_k}{dt} = -\int z^k\frac{\partial g}{\partial z}dz + \frac{(1+\beta)^\beta}{2}\int z^k\frac{\partial}{\partial z}z^{-\beta}\frac{\partial g}{\partial z}dz, \tag{A19}$$

where

$$\beta = \frac{a}{1-a}. \tag{A20}$$

The integrals in Eq. (A19) are obtained from Eq. (A12) with $m=1$, $a=0$, and $m=2$, $a=-\beta$, respectively, leading to the general result,

$$\frac{dz_k}{dt} = kz_{k-1} + \frac{k(k-1)}{2}(1+\beta)^{\beta} z_{k-\beta-2}. \tag{A21}$$

With $k=0,1$, and 2 we obtain

$$\frac{dz_0}{dt} = 0, \tag{A22}$$

$$\frac{dz_1}{dt} = 1, \tag{A23}$$

$$\frac{dz_2}{dt} = 2z_1 + (1+\beta)^{\beta} z_{-\beta}. \tag{A24}$$

Applying these results to the variance, $\sigma_z^2 = z_2 - z_1^2$, and using $dt = dz_1$, we find

$$\frac{d\sigma_z^2}{dz_1} = (1+\beta)^{\beta} z_{-\beta}. \tag{A25}$$

With $a=0$ (i.e., $\beta=0$, $z=x$) we obtain $d\sigma_z^2/dz_1 = 1$ and thus we retrieve the scaling obtained from the solution of the discrete PBE.

5. Solution for σ_z^2

To resolve the closure problem in Eq. (A25) we express $z_{-\beta}$ using Eq. (A2) with $k=-\beta$. This leads to Eq. (30) of the text and finally to Eq. (31) for the variance. Using MATHEMATICA (Wolfram Research, version 5.2) the solution of Eq. (31) for monodisperse initial conditions and initial size $z_{1,0}$ is

$$\sigma_z^2 = \frac{2z_{1,0}^2 e^{C(z^{-\beta-1} - z_{1,0}^{-\beta-1})}}{\beta(\beta+1)} - \frac{2z^2}{\beta(\beta+1)} + \frac{4e^{Cz^{-\beta-1}}[z^2 E_{(\beta+3)/(\beta+1)}(Cz^{-\beta-1}) - E_{(\beta+3)/(\beta+1)}(Cz_{1,0}^{-\beta-1}) z_{1,0}^2]}{\beta(\beta+1)^2}, \tag{A26}$$

where

$$C = -\frac{1}{2}\beta(1+\beta)^{\beta}, \tag{A27}$$

and $E_n(z)$ is the exponential integral, defined as

$$E_n(z) = \int_1^{\infty} \frac{e^{-zt}}{t^n} dt. \tag{A28}$$

This equation was used to obtain Fig. 1.

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