



On equilibrium solutions of aggregation–fragmentation problems

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ABSTRACT

A characteristic feature of particulate systems that evolve due to competition between aggregation and breakage is that they sometimes produce non-trivial steady-state particle size distributions. If such solutions satisfy detailed balance conditions, then they are equilibrium solutions. The conditions that must be satisfied by aggregation and fragmentation rate kernels in order for equilibrium solutions to be produced are elaborated, and it is shown that the rate kernels are uniquely determined by the aggregation and breakage rate constants for the reactions involving monomers. Consequently, for equilibrium systems there is a significant reduction in the amount of information needed in order to infer the general form for aggregation or breakage kernels, and we explore implications for constructing rate kernels by using atomistic simulations such as molecular dynamics.

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1. Introduction

Population balance equations (PBEs) describing processes in which particles undergo growth and decay through aggregation and breakage have long been studied in connection with a variety of physical phenomena, such as polymerization and the growth of colloidal particles. Not surprisingly, these aggregation–fragmentation PBEs can exhibit the same kinetic behavior that is displayed by more restrictive population balance models of either irreversible aggregation or breakage, such as gelation, shattering, and self-preserving size distributions [1]. However, aggregation–fragmentation PBEs differ fundamentally from irreversible aggregation or irreversible fragmentation PBEs in at least one important respect. Namely, the possibility exists that non-trivial steady-state particle size distributions can be produced by a balance in the competition between growth of particles by aggregation and degradation due to breakage.

The possibility that steady-state solutions are produced by competition between aggregation and breakage leads naturally to the question of what conditions must be satisfied in order for this to occur. For example, consider a system of well-mixed particles that undergoes aggregation and binary fragmentation (two fragments produced when a cluster undergoes fission). If the system is closed to mass exchange, the relevant population balance equation can be expressed as

$$\frac{dc_k}{dt} = \frac{1}{2} \sum_{i+j=k} (K_{ij}c_i c_j - F_{ij}c_{i+j}) - \sum_{j=1}^{\infty} (K_{kj}c_k c_j - F_{kj}c_{k+j}), \quad (1)$$

where c_k is the concentration of particles with mass k at time t . The symmetric matrix K_{ij} (aggregation kernel) specifies rate constants for aggregation of i -mers with j -mers. Similarly, F_{ij} is a symmetric matrix of rate constants for breakage of $i + j$ -mers into i -mers and j -mers. The long-time behavior of (1) therefore will depend upon the choice of K_{ij} and F_{ij} , and possibly also on initial conditions. For aggregation and breakage rate kernels that obey the homogeneity relations

$$\begin{aligned} K_{ai,aj} &\sim a^2 K_{ij}, \\ F_{ai,aj} &\sim a^\beta F_{ij}, \quad \text{as } a \rightarrow \infty, \end{aligned} \quad (2)$$

several investigators have used scaling arguments to show that a necessary condition for the system to always (irrespective of initial conditions) attain a steady-state solution is given by [1–4]:

$$\beta - \lambda + 2 > 0. \quad (3)$$

Eq. (3) is useful for anticipating the existence or absence of steady-state solutions for arbitrary homogeneous kernels K_{ij} and F_{ij} without the need to analytically or numerically solve Eq. (1), but it does not provide information concerning the nature of any steady-state solutions produced, such as whether or not they are also equilibrium solutions.

The contrast between equilibrium and non-equilibrium steady states can be explained as follows. Time-independent solutions of Eq. (1), \bar{c}_k , must satisfy

$$\frac{1}{2} \sum_{i+j=k} (K_{ij}\bar{c}_i \bar{c}_j - F_{ij}\bar{c}_{i+j}) = \sum_{j=1}^{\infty} (K_{kj}\bar{c}_k \bar{c}_j - F_{kj}\bar{c}_{k+j}). \quad (4)$$

As has been observed many times previously (e.g. [5–7]), Eq. (4) will be satisfied if the steady-state solution \bar{c}_k also obeys

$$K_{ij}\bar{c}_i \bar{c}_j = F_{ij}\bar{c}_{i+j} \quad (5)$$

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for all pairs of particle masses i and j . The condition (5) is a statement of microscopic detailed balance that requires each aggregation or breakage pathway to be reversible and in dynamic equilibrium at steady state. Therefore, solutions of Eq. (4) that satisfy Eq. (5) are equilibrium steady states. For a given set of aggregation and breakage kernels, however, there may exist steady-state solutions that satisfy Eq. (4) but not Eq. (5), and it follows that any such steady-state solutions are non-equilibrium solutions.

For example, consider the kernels $K_{ij} = i + j$ and $F_{ij} = 2$, which have homogeneity exponents $\lambda = 1$ and $\beta = 0$, and therefore satisfy the steady-state condition (3). The fact that these kernels always produce a steady state can be verified by deriving analytical solutions for the moments of the size distribution, $M_n = \sum_{k=1}^{\infty} k^n c_k$. The general expression for the moments is easily obtained by multiplying Eq. (1) by k^n and summing over all k , which yields

$$\frac{dM_n}{dt} = \frac{1}{2} \sum_{i=1}^{\infty} \sum_{j=1}^{\infty} (K_{ij} c_i c_j - F_{ij} c_{i+j}) [(i+j)^n - i^n - j^n]. \quad (6)$$

By choosing $n = 0$ and substituting $K_{ij} = i + j$ and $F_{ij} = 2$ into Eq. (6), it is not difficult to show that the steady-state mean particle size $\bar{S}_1 = M_1/\bar{M}_0$ is given by

$$\bar{S}_1 = M_1 + 1, \quad (7)$$

independent of the initial conditions. Thus, the mean particle size depends only on the first moment, M_1 , which represents the total particle mass density and is time-independent, as can be seen from Eq. (6). Although there is no known analytical solution for the particle size distribution $c_k(t)$ for this combination of aggregation and breakage kernels, the steady-state solutions \bar{c}_k for small values of k can be found by solving Eq. (4):

$$\begin{aligned} \bar{c}_1 &= \frac{2M_1}{M_1^2 + 4M_1 + 2}, \\ \bar{c}_2 &= \frac{1}{2} \frac{(M_1^3 + 6M_1^2 + 12M_1 + 6)}{M_1^2 + 6M_1 + 3} \bar{c}_1^2, \\ \bar{c}_3 &= \frac{1}{4} \frac{(M_1^6 + 14M_1^5 + 83M_1^4 + 248M_1^3 + 380M_1^2 + 272M_1 + 72)}{(M_1^2 + 8M_1 + 4)(M_1^2 + 6M_1 + 3)} \bar{c}_1^3. \end{aligned} \quad (8)$$

Substitution of the above expressions into the detailed balance relations required by Eq. (5), such as $K_{11}\bar{c}_1^2 = F_{11}\bar{c}_2$ and $K_{12}\bar{c}_1\bar{c}_2 = F_{12}\bar{c}_3$, shows that microscopic reversibility is not satisfied and we therefore conclude that the steady-state solution produced by this particular combination of aggregation and breakage kernels is a non-equilibrium solution.

The foregoing example gives rise to the question of how to select a combination of kernels K_{ij} and F_{ij} that will produce an equilibrium steady-state particle size distribution. In the remainder of this paper, we review and expand on the answer to this question and explore some ramifications for constructing kernels for physically-relevant problems. We also consider how detailed balance requirements might be used to better understand the link between aggregation–fragmentation population balance equations and atomistic descriptions of aggregation–fragmentation processes, such as molecular dynamics simulations.

2. Existence of equilibrium solutions

As others have observed previously [6], equilibrium solutions of Eq. (1) (should they exist) can be derived by using the recurrence property of Eq. (5). For example, the equilibrium concentrations, \bar{c}_k , can be expressed as

$$\begin{aligned} \bar{c}_2 &= \phi_{11} \bar{c}_1^2, \\ \bar{c}_3 &= \phi_{12} \bar{c}_1 \bar{c}_2 = \phi_{11} \phi_{12} \bar{c}_1^3, \\ \bar{c}_4 &= \phi_{13} \bar{c}_1 \bar{c}_3 = \phi_{22} \bar{c}_2^2 = \phi_{11}^2 \phi_{22} \bar{c}_1^4 = \phi_{11} \phi_{12} \phi_{13} \bar{c}_1^4, \\ \bar{c}_5 &= \phi_{14} \bar{c}_1 \bar{c}_4 = \phi_{23} \bar{c}_2 \bar{c}_3 = \phi_{11}^2 \phi_{12} \phi_{23} \bar{c}_1^5 = \phi_{11} \phi_{12} \phi_{13} \phi_{14} \bar{c}_1^5, \\ \bar{c}_6 &= \phi_{15} \bar{c}_1 \bar{c}_5 = \phi_{24} \bar{c}_2 \bar{c}_4 = \phi_{33} \bar{c}_3^2 = \phi_{11}^2 \phi_{12} \phi_{13} \phi_{24} \bar{c}_1^6 = \phi_{11}^2 \phi_{12}^2 \phi_{33} \bar{c}_1^6 \\ &= \phi_{11} \phi_{12} \phi_{13} \phi_{14} \phi_{15} \bar{c}_1^6, \\ &\vdots \end{aligned} \quad (9)$$

where $\phi_{ij} = K_{ij}/F_{ij}$. By induction, it becomes immediately obvious that the equilibrium particle size distribution is given by

$$\bar{c}_k = \left(\prod_{n=1}^{k-1} \phi_{1n} \right) \bar{c}_1^k \quad k \geq 2, \quad (10)$$

so that all \bar{c}_k depend on the equilibrium monomer concentration, \bar{c}_1 . The latter quantity must be determined independently by solving the overall mass balance

$$M_1 = \sum_{k=1}^{\infty} k \bar{c}_k = \sum_{k=1}^{\infty} \left(\prod_{n=1}^{k-1} \phi_{1n} \right) k \bar{c}_1^k, \quad (11)$$

subject to the physical constraint

$$0 < \bar{c}_1 < M_1. \quad (12)$$

Eqs. (10) and (11) provide a general solution for equilibrium particle size distributions in aggregation–fragmentation systems, and this solution depends only on the ratios of corresponding terms in the aggregation and breakage kernels that involve monomers, ϕ_{1n} , where $n \geq 1$, and not on the ϕ_{ij} generally. However, the existence of an equilibrium particle size distribution does depend critically upon the other elements of the matrix ϕ_{ij} , because these must satisfy an infinite set of constraints (not all of which are independent) implied by the detailed balance criterion Eq. (9), such as

$$\begin{aligned} \phi_{12} \phi_{13} &= \phi_{11} \phi_{22}, \\ \phi_{13} \phi_{14} &= \phi_{11} \phi_{23}, \\ \phi_{14} \phi_{15} &= \phi_{11} \phi_{24}, \\ \phi_{13} \phi_{24} &= \phi_{12} \phi_{33}, \\ \phi_{13} \phi_{14} \phi_{15} &= \phi_{11} \phi_{12} \phi_{33}, \\ &\vdots \end{aligned} \quad (13)$$

Although it has been suggested [8] that the ϕ_{ij} are overdetermined by (13), these relationships can in fact be collapsed dramatically by expressing ϕ_{ij} , where $i, j \neq 1$, in terms of the ϕ_{1n} . The first few terms, for example, can be written as

$$\begin{aligned} \phi_{22} &= \frac{\phi_{12} \phi_{13}}{\phi_{11}}, \\ \phi_{23} &= \frac{\phi_{13} \phi_{14}}{\phi_{11}}, \\ \phi_{24} &= \frac{\phi_{14} \phi_{15}}{\phi_{11}}, \\ \phi_{33} &= \frac{\phi_{13} \phi_{24}}{\phi_{12}} = \frac{\phi_{13} \phi_{14} \phi_{15}}{\phi_{11} \phi_{12}}, \\ &\vdots \end{aligned} \quad (14)$$

Continuing in this way, by induction it follows that for an equilibrium solution to exist, the ϕ_{ij} must obey

$$\phi_{ij} = \frac{\prod_{n=j}^{i+j-1} \phi_{1n}}{\prod_{n=1}^{i-1} \phi_{1n}}. \quad (15)$$

Eq. (15) demonstrates that for equilibrium systems, once the functional form of $\phi_{1n} = K_{1n}/F_{1n}$ has been chosen, then the remaining terms ϕ_{ij} and the equilibrium particle size distribution (10) are uniquely determined. This observation may have important applica-

tions for certain physical problems, because it suggests that for systems that produce equilibrium particle size distributions, physically accurate expressions for the rate constants of reactions involving monomers (i.e. K_{1n} and F_{1n}) and knowledge of the general expression for either K_{ij} or F_{ij} is sufficient to compute the other kernel. This significant reduction in the amount of information needed to infer the functional form of either the aggregation or breakage kernel may be particularly useful for facilitating the use of atomistic simulations such as molecular dynamics to develop rate kernels.

Eq. (15) may also be used to exclude kernel combinations that do not lead to equilibrium, even if they lead to a steady state. For example, using the aggregation and breakage kernels discussed earlier, $K_{ij} = i + j$ and $F_{ij} = 2$, we find that $\phi_{1j} = (j + 1)/2$. Substitution of the latter expression into Eq. (15) shows that for an equilibrium solution to exist, the remaining elements of ϕ_{ij} are related to the binomial coefficients according to

$$\phi_{ij} = \frac{1}{2} \frac{(i+j)!}{i!j!}, \quad i, j > 1, \quad (16)$$

which is obviously inconsistent with $\phi_{ij} = K_{ij}/F_{ij} = (i+j)/2$, and hence the choice of $K_{ij} = i + j$ and $F_{ij} = 2$ cannot produce an equilibrium particle size distribution.

We conclude this section by noting that if any corresponding elements i, j of the rate kernels are null so that $K_{ij} = F_{ij} = 0$, then not all of the detailed balance constraints given by Eq. (15) are operative. For example, in Ostwald ripening only monomer addition and breakage is allowed so that the only non-zero elements of the symmetric rate kernels are K_{1n} and F_{1n} , and therefore Eq. (15) does not apply at all. In the remainder of this paper we limit our considerations to aggregation–fragmentations processes described by fully populated kernels so that there are no zero elements in K_{ij} and F_{ij} .

3. Examples of equilibrium kernels

3.1. Blatz–Tobolsky model

Perhaps the best-known aggregation–fragmentation population balance model was studied by Blatz and Tobolsky in the context of reversible polymerization of linear polymers [9]. They derived a complete time-dependent solution to Eq. (1) by assuming constant aggregation and breakage kernels such that $K_{ij}/F_{ij} = \alpha$, where α represents the relative strength of aggregation to breakage. It is well known that the Blatz–Tobolsky model produces a steady-state particle size distribution identical to the distribution predicted by Eqs. (10) and (11), and it is therefore also an equilibrium solution. Notice that if we substitute $\phi_{1n} = \alpha$ into Eq. (15), we find that $\phi_{ij} = \alpha$ for all values of i and j (consistent with constant aggregation and breakage kernels), and therefore an equilibrium solution for this case is correctly anticipated by the equilibrium criterion (15). Since the equilibrium criterion only requires that the ratios ϕ_{ij} be constant and equal, one can conclude that any pair of aggregation and breakage kernels $K_{ij} = \alpha f(i, j)$, $F_{ij} = f(i, j)$, where $f(i, j)$ is an arbitrary function of i and j , will produce the same equilibrium solution as the Blatz–Tobolsky model, even though the kinetic behavior may depend upon the specific form of $f(i, j)$. Also notice that Eq. (3) will always be satisfied since the homogeneity exponents of the kernels (assuming that $f(i, j)$ obeys the homogeneity relation) for this case are equal, $\lambda = \beta$.

3.2. Separable aggregation kernel

Gueron and Levin [10] have significantly expanded the known sets of kernels that produce equilibrium steady states by observing that if the aggregation kernel can be factored such that $K_{ij} = \alpha g_i g_j$,

where g_i is a function of i alone, then the microscopic reversibility conditions (5) will be satisfied if $F_{ij} = g_{i+j}$. This can be demonstrated by substituting the monomer kernel ratios

$$\phi_{1n} = \alpha \frac{g_1 g_n}{g_{n+1}} \quad (17)$$

into Eq. (15), which leads to

$$\phi_{ij} = \alpha \frac{g_i g_j}{g_{i+j}}. \quad (18)$$

Therefore, the Blatz–Tobolsky model discussed above is a special case of the Gueron–Levin Kernel with $g_i = 1$. Another simple example of a system with kernel ratios obeying (18) is obtained by selecting $g_i = i$, which leads to $\phi_{ij} = \alpha ij/(i+j)$. Lowe and Thorlacius [11] have provided an analytical solution for the continuous analog of Eq. (1) using the aggregation and breakage kernels $K_{ij} = \alpha ij$ and $F_{ij} = i + j$, and it can be shown that at steady state their solution is equivalent to the continuous analog of the equilibrium solution predicted by Eq. (10). Although in principle many other examples of kernel combinations of the form (18) could be generated by choosing arbitrary functions g_i , the steady-state criteria Eq. (3) implies that not all choices for g_i produce an equilibrium solution. In particular, if we define the homogeneity exponent ν using the expression

$$g_{ai} \sim a^\nu g_i, \quad \text{as } a \rightarrow \infty, \quad (19)$$

it follows from Eqs. (3) and (18) that

$$\nu = \lambda - \beta < 2 \quad (20)$$

for the system to reach a steady-state particle size distribution for arbitrary initial conditions.

Eq. (18) imposes other limitations that may not be immediately obvious. Specifically, the requirement that the breakage kernel is of the form $F_{ij} = g_{i+j}$ implies that the fragments produced by breakage events are governed by a uniform probability distribution function. This can be shown by factoring F_{ij} so that

$$F_{ij} = a_{i+j} b_{i|i+j}, \quad (21)$$

where a_{i+j} is the overall rate coefficient for breakage of particles with mass $i + j$, and $b_{i|i+j}$ is the conditional probability of producing an i -sized fragment upon breakage of an $i + j$ -sized particle. Because the rate of breakage of $i + j$ -sized particles depends linearly on c_{i+j} , a_{i+j} is simply the sum over all the F_{ij} ,

$$a_{i+j} = \frac{1}{2} \sum_{i=1}^{i+j-1} F_{ij} = \frac{1}{2} g_{i+j} (i+j-1). \quad (22)$$

Substitution of Eq. (22) into Eq. (21) shows that the conditional distribution function is given by

$$b_{i|i+j} = \frac{2}{i+j-1}. \quad (23)$$

Since Eq. (23) depends only upon the sum $i + j$ (mass of the particle undergoing breakage) and not on i independently, we conclude that choosing $F_{ij} = g_{i+j}$ implies a uniform distribution of fragments. Despite this limitation, as well as the requirement given by Eq. (20), Eq. (18) encompasses many possible kernel combinations that lead to an equilibrium particle size distribution.

3.3. Brownian aggregation

The aggregation and breakage of particles undergoing Brownian motion is relevant to many problems, including the manufacture of nanoparticles. For diffusion-limited aggregation of spheres, the kernel first derived by Smoluchowski is given by the non-separable expression

$$K_{ij} = \alpha \left[2 + \left(\frac{i}{j} \right)^{1/3} + \left(\frac{j}{i} \right)^{1/3} \right], \quad (24)$$

where in this case $\alpha = 2k_B T / 3\mu$, k_B is Boltzmann's constant, T is temperature, and μ is the viscosity of the solvent. Far more elusive, however, is the functional form of a physically-realistic breakage kernel that, when coupled with the Brownian aggregation kernel (24), will lead to an equilibrium solution. With few exceptions (e.g. some relatively simple polymerization problems), the derivation of general analytical expressions for F_{ij} to describe physical problems is exceedingly difficult because the rate of breakage and distribution of fragments depends upon many microscopic details such as aggregate morphology and connectivity, as well as the responsible breakage mechanisms (e.g. thermal fluctuations, shear-induced breakage, aggregate-wall collisions, etc.). However, in systems that are thermodynamically isolated, such as in an unstirred adiabatic batch reactor, any steady-state particle size distribution that develops due to the competition between Brownian aggregation and breakage must also satisfy the microscopic detailed balance conditions (15). Hence, if the functional form for the elements of the breakage kernel involving monomers, F_{1n} , is known or assumed, then the remaining elements of F_{ij} can be computed from Eq. (15) and by using (24).

However, not all choices for F_{1n} will produce equilibrium solutions when coupled with the Brownian aggregation kernel, as can be illustrated by the following example. Choosing $K_{1n} = \alpha(2 + n^{-1/3} + n^{1/3})$ and $F_{1n} = 1$, we find from Eq. (11) that \bar{c}_1 must satisfy

$$M_1 = \frac{1}{\alpha} \sum_{k=1}^{\infty} \left(\prod_{n=1}^{k-1} (2 + n^{-1/3} + n^{1/3}) \right) k (\alpha \bar{c}_1)^k. \quad (25)$$

The sum on the right hand side of (25) does not converge for any value of $\bar{c}_1 > 0$ and therefore no equilibrium solution exists for Brownian aggregation with $F_{1n} = 1$. It does not follow from this conclusion, however, that a steady-state solution does not exist for a system described by the Brownian aggregation kernel and $F_{ij} = 1$. Indeed, the steady-state criterion (3) is satisfied for these choices of kernels, and therefore a non-equilibrium steady-state solution will be produced.

Lacking specific information concerning breakage mechanisms and aggregate morphology, it could be hypothesized that the breakage rate coefficients for monomer reactions scale according to a power law,

$$F_{1n} \sim n^\tau. \quad (26)$$

By using this assumption for F_{1n} and the Brownian aggregation kernel, we find that the product term in the mass balance equation (11) obeys

$$\prod_{n=1}^{k-1} \phi_{1n} \sim (\Gamma(k))^{\frac{1}{3}-\tau} \quad \text{as } k \rightarrow \infty. \quad (27)$$

Because the gamma function (even when raised to a fractional power) diverges faster than the exponential function, the summation in Eq. (11) will not converge for any value of \bar{c}_1 if $\tau < 1/3$, and therefore no equilibrium solution will exist. A maximal value of τ can be inferred from the following considerations. Aggregates comprised of constituent monomers arranged so that they have very low coordination numbers would seem to maximize F_{1n} , because such arrangements require the fewest disruptions of nearest neighbor contacts in order to separate monomers from the parent cluster. Taken to the extreme, every monomer in an aggregate would be accessible for breakage so that $F_{1n} \sim n$. In view of the foregoing observations, we conclude that $1/3 < \tau < 1$. The resulting steady-state size distributions obtained from Eqs. (10) and (11) are plotted in Fig. 1 for these minimum and maximum values of

τ . When $\tau = 1/3$, dimers are the most abundant species, independent of the value of α . Furthermore, for $k \geq 2$, the size distribution \bar{c}_k decays exponentially as $k \rightarrow \infty$, as can easily be shown from a log-normal plot. This result is reminiscent of the Blatz–Tobolsky model, which is known to exhibit an exponential particle size distribution. The similarity of the two models can be explained by the fact that for $\tau = 1/3$, it follows that the kernel ratio becomes constant, $\phi_{1n} \sim \alpha$, in the limit $n \rightarrow \infty$. In contrast, Fig. 1 shows that for $\tau = 1$ the equilibrium size distribution is marked by a relatively narrow unimodal distribution, and the peak cluster size does depend on the parameter α .

4. Rate kernels, equilibrium, and atomistic simulations

Mean-field population models such as Eq. (1) provide the mathematical framework for a macroscopic description of aggregation phenomena, but their usefulness for obtaining quantitatively accurate predictions depends upon the availability of accurate rate kernels that correctly describe the microscopic mechanisms of aggregation and breakup. Although it is possible, by invoking sweeping assumptions, to derive kernels for some problems (e.g. diffusion-limited Brownian aggregation or branched polymerization) using analysis alone, the application of such kernels for computing particle size distributions of real systems may still require empiricism (for example determining sticking coefficients for aggregation). As was mentioned earlier, fragmentation kernels are even more difficult to construct from first principles analyses, and consequently empirical or semi-empirical approaches must often be employed.

Atomistic simulations, such as molecular dynamics, could potentially provide the microscopic details needed to develop accurate kernels (assuming that reasonably accurate pairwise interaction

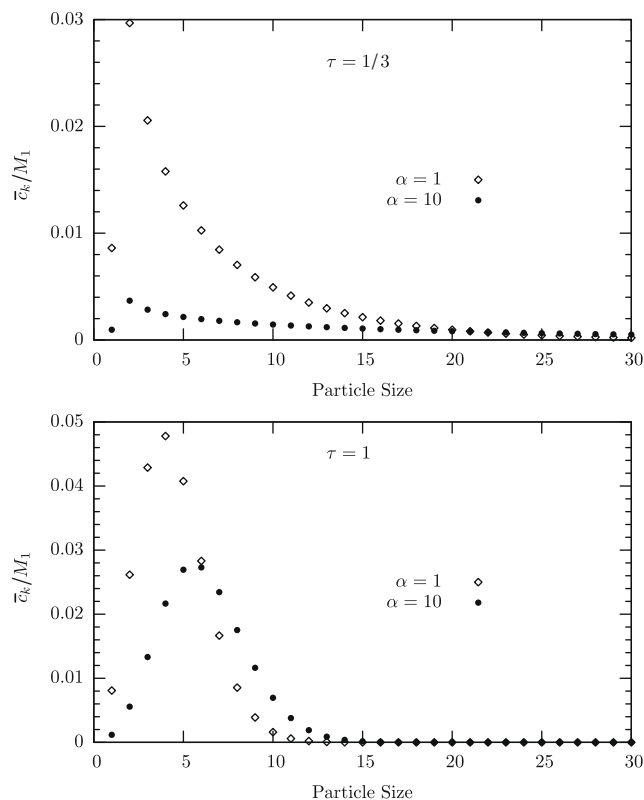


Fig. 1. Normalized equilibrium particle size distributions \bar{c}_k/M_1 computed from Eqs. (10) and (11) using $K_{1n} = \alpha(2 + n^{-1/3} + n^{1/3})$ and $F_{1n} = n^\tau$. Top panel: $\tau = 1/3$. Bottom panel: $\tau = 1$.

potentials are available for the system constituents). However, these methods are not well-suited for evolving fully developed particle size distributions because the time and length scales accessible are far smaller than the characteristic time and length scales of aggregation in physically-realistic systems. Hence, there is a strong motive for developing a means for distilling microscopic information produced by atomistic simulations in order to construct accurate aggregation and breakage kernels without having to carry out simulations using astronomically large numbers of particles and time scales that are practically unachievable. In this section, we outline a possible approach for overcoming this problem by making use of a statistical mechanical analysis of reversible aggregation.

By constructing a partition function and minimizing Gibbs free energy, Cohen and Benedek [7] derived an equilibrium particle size distribution for reversible polymerization given by

$$\bar{c}_k = D_k e^{-G_k/k_B T} \bar{c}_1^k, \quad (28)$$

which bears striking resemblance to Eq. (10). In the above expression, the function D_k is a degeneracy factor that describes the number of distinct ways of assembling k monomers into a k -mer (and therefore it depends upon factors that affect cluster structure, such as monomer functionality), and G_k is the local standard free energy change associated with removing k monomers from the system and adding a k -mer, which in turn depends upon bond strength, solvent interactions, etc. Two important assumptions were used to derive Eq. (28). First, it was assumed that the solute phase is sufficiently dilute so that non-specific interactions between aggregates are negligible. Second, Cohen and Benedek assumed that clusters comprised of k monomers are held together by $k - 1$ bonds. The first assumption is consistent with the dilute approximation implicit in mean-field population balance descriptions of aggregation–fragmentation such as Eq. (1). The second assumption is more restrictive, but it appears to manifest itself only by limiting the functional forms of D_k , and therefore Eq. (28) should be applicable to any dilute reversible aggregation process even if the second assumption is relaxed.

Combining Eqs. (28) and (10), which were derived by completely different methods, provides the crucial relationship between the macroscopic (ϕ_{1n}) description of aggregation and breakage events and the microscopic description represented by G_k and D_k :

$$\prod_{n=1}^{k-1} \phi_{1n} = D_k e^{-G_k/k_B T}. \quad (29)$$

Atomistic simulations are well-suited for computing G_k and D_k , at least for sufficiently small cluster sizes k , and therefore the kernel ratios for monomer interactions ϕ_{1n} could in principle be computed sequentially using Eq. (29) until the functional form of ϕ_{1n} is inferred. Subsequently, Eq. (15) could be used to find the general expression for ϕ_{ij} . The practical usefulness of this approach remains to be demonstrated, but its validity seems to be supported by considering a simple example leading to a known solution. In particular, Cohen and Benedek [7] demonstrated that if one assumes that the standard free energy of bond formation is independent of cluster size or position within the cluster, then $G_k = (k - 1)E$, where E is the bond strength. In addition, for the special case of reversible polymerization of linear polymers, the degeneracy factor is given by $D_k = 1$ and it follows from Eq. (29) that $\phi_{1n} = \alpha$, where $\alpha = e^{-E/k_B T}$. Substituting ϕ_{1n} into Eq. (15) gives the expected result that $\phi_{ij} = \alpha$, which is the Blatz–Tobolsky model for reversible polymerization of linear polymers. Notice that α , which represents the relative strength of aggregation compared to breakage, depends only on the reduced bond energy $E/k_B T$, and this suggests that at

equilibrium the particle size distribution depends not on the particular details of the pairwise particle interaction potential used in an atomistic simulation of this process, but only on the depth of the potential energy well for the bonded state.

5. Discussion and summary

As a consequence of the detailed balance criterion (5), equilibrium solutions of aggregation–fragmentation population balance are given by Eqs. (10) and (11), which depend only upon the ratios $\phi_{1n} = K_{1n}/F_{1n}$. Although the equilibrium solution does not depend explicitly on the other elements of the matrix $\phi_{ij} = K_{ij}/F_{ij}$ where $i, j \neq 1$, the detailed balance criterion imposes restrictions on these terms in order for an equilibrium solution to exist, and it has not generally been appreciated that these restrictions establish a relationship between ϕ_{ij} and ϕ_{1n} given by Eq. (15). Hence, the specification of the ratio of monomer reaction rate constants ϕ_{1n} alone is sufficient to determine both the equilibrium particle size distribution and the kernel ratios ϕ_{ij} . However, as was shown in Section 3, the ϕ_{1n} cannot be chosen arbitrarily, because the steady-state criterion (3) must also be satisfied in order for an equilibrium solution to exist.

The fact that aggregation and breakage kernels for equilibrium systems must obey Eq. (15) also potentially simplifies the construction of kernels suitable for quantitatively describing specific physical problems, particularly if either an appropriate aggregation or breakage kernel is already known, such as in the case of Brownian aggregation. Furthermore, the significant reduction in the amount of information required to find ϕ_{1n} rather than ϕ_{ij} may also play a crucial role in making it feasible to use atomistic simulations to construct rate kernels for specific chemical systems, as was outlined in the previous section. However, complete validation of this approach will require carrying out atomistic simulations for a specific physical system in order to compute ϕ_{1n} , and comparing the resulting prediction for the equilibrium particle size distribution \bar{c}_k using Eqs. (10) and (11) to the equilibrium size distribution obtained from experiments. Subsequently, if the functional forms of either K_{ij} or F_{ij} are known or assumed, then the other kernel can be determined from Eq. (15). The population balance (1) could then be used to predict the kinetic behavior of the size distribution and the results compared with experimental observations.

Although significant simplifications occur in the analysis of processes that produce equilibrium size distributions due to competition between aggregation and fragmentation, questions remain concerning the applicability of these results to real problems. In particular, limitations concerning the physical circumstances and the aggregation and breakage mechanisms that produce steady states that obey the detailed balance requirements (5) have not been fully elaborated. For example, is true microscopic reversibility only possible for thermodynamically isolated systems in which the aggregation and fragmentation mechanisms are driven by thermal fluctuations, such as in the case of reversible polymerization in an adiabatic unstirred batch reactor, or could other processes such as aggregation and breakage driven by fluid shear also satisfy detailed balance constraints? Are droplet systems inherently non-equilibrium because coalescence results in loss of distinguishability of the original droplets, which appears to violate the detailed balance criterion? Further work is needed to resolve these questions and also to establish the limitations of invoking microscopic detailed balance as an approximation for systems that may not satisfy the assumption exactly. Despite these remaining problems, the equilibrium analysis of aggregation–fragmentation systems may yet prove to be a useful tool for developing better models for these processes.

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