Mixing of Components in Two-Component Aggregation

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The problem of binary component aggregation with kernels that are independent of composition is considered. The bivariate distribution as the product of two distributions is studied, one that refers to the size of the aggregates, and one that describes the distribution of the component of interest (solute), and obtain the governing equations for all three. The distribution of solute within aggregates of size v has a steady-state solution, that is independent of the size distribution: it is a Gaussian function whose mean and variance are both proportional to the aggregate size v. To quantify the degree of blending, the sum-square X^2, of the deviation of the amount solute from its mean, is studied. Two cases are identified for which X^2 is constant during aggregation: (a) "partially mixed" seeds regardless of kernel; and (b) sum-type kernels regardless of seed distribution. Simulations confirm the results for these two cases, and further indicate that in the general case, X^2 is nearly constant. The degree of mixing is determined solely by the initial distribution of components, but does not depend on the kernel. Optimum initial conditions that minimize the time required to reach a desired level of homogeneity between components are identified. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 3088–3099, 2006
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Introduction

The binary attachment of particles to form larger particles is one of the most ubiquitous physical mechanisms of size enlargement, encompassing as diverse phenomena as the aggregation of colloids, agglomeration of powders, and polymerization of reactive molecules. While the large majority of studies has focused on the size evolution of chemically homogeneous particles, in most systems of practical interest, the aggregating particles are inhomogeneous in composition. For example, in atmospheric aerosols, in chemical precipitation of colloids, or in copolymerization, components react and mix, as well as aggregate. The most basic problem to consider is that of bicomponent aggregation. In this case, there is no chemical reaction, only blending of components mediated by aggregation. We refer to this process as *aggregative mixing.* One instance where the mixing and uniform distribution of components is a critical processing step, is in the granulation of pharmaceutical powders. Here component A is the drug, and component B the excipient, and the two components are granulated to form larger aggregates with expectation that, with sufficient processing time, composition shall become uniform in all granules. The question we want to address is this: what is the distribution of components in aggregates of a given size, and how long does it take for the components to mix to a desired level?

The first theoretical analysis of bicomponent aggregation was given by Lushnikov[1] who considered the aggregation of

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two components with composition-independent kernels, and showed that if the two components are initially present as monodisperse particles, the compositional distribution is given by the binomial distribution. Vigil and Ziff[2] reviewed Lushnikov's solutions and conjectured that in the scaling limit, regardless of kernel or initial state, the bivariate distribution (in size and composition) is the product of the scaling solution for the size distribution of the homogeneous (one-component) problem, and a Gaussian function that gives the distribution of components within each size class. The conjecture was demonstrated for all special cases for which analytic solutions are known, namely: all composition-independent kernels with monodisperse initial conditions; constant kernel with exponential initial conditions, and for one compositionally dependent kernel of the sum type with monodisperse initial conditions.[2] Others in the past thirty years have studied various aspects of this problem. Gelbard and Seinfeld[3] obtained solutions for constant kernel, and a variety of initial conditions both for pure aggregation, and in the presence of surface growth. The problem of binary aggregation with constant kernel was considered by Krapivsky and Ben-Naim[4] who pointed out the Gaussian nature of the compositional distribution. Pen'kov[5] presented a procedure for obtaining the solution to multicomponent aggregation for kernels that are linear combinations of binary-sum and -product terms. More recently, Trautmann[6] and Merkulovich[7] considered this problem in discrete, finite systems. In terms of general scaling predictions, however, the work of Lushnikov, as summarized by the Vigil-Ziff conjecture, remains the most relevant work to our study. The appeal of the conjecture is that, if true, mixing and aggregation become *decoupled* problems and can be solved independently.

In this article, we formulate the problem of bicomponent aggregation for composition-independent kernels and seek the evolution of the size and compositional distributions. Our motivation arises from the perspective of blending of components: given an initial distribution of two components we seek to obtain rate and degree of mixing as a function of aggregate size and time. Our approach differs from previous work in this area in that we seek the governing equation—and its solution—for the distribution of components among aggregates. Using this approach we are able to prove the Vigil-Ziff conjecture for a wider class of compositionally independent kernels and initial conditions, and show that the distribution of components within aggregates is essentially determined entirely by the state of mixing at the beginning. This article is organized as follows: first we define the parameters of the bivariate distribution. We show that it can be expressed as the product of a size distribution and a compositional distribution, we develop the governing equations for each distribution separately, and discuss conditions under which the solutions are decoupled. To demonstrate the predictions of the theory, and to explore cases that cannot be treated rigorously by theory, we present simulations of aggregative mixing using Monte Carlo. Finally, we discuss the practical implications of our results, and suggest ways to improve the blending of components by manipulating the initial state of mixing.

Definitions

We consider a population of particles that is made out of two components, A (solute) and B (solvent) in which the mass fraction of solute is ϕ. We refer to ϕ as the overall mass fraction of solute to distinguish it from the amount of solute found within aggregates of a given size, a quantity which we introduce later. The state of a particle is determined by the mass of the particle v, and the mass of the solute m, within the particle. We adopt this asymmetric treatment of the two components because the size of an aggregate, and the amount of solute it carries represent quantities of practical interest and form a natural set of variables that describe the system. The bicomponent population is characterized by the bivariate distribution function $F(v, m)$, such that $F(v, m)dvdm$ is the number concentration of particles (aggregates) in the size range $v \pm dv/2$ that contain a mass of solute in the range $m \pm dm/2$.

We define the mixed moment M_{ij}, of order i in v and j in m

$$M_{ij} = \int_0^\infty dv \int_0^v dm(v^i m^j) F(v, m) \tag{1}$$

It follows that M_{00} is the total number of particles, M_{10} is their mass, and M_{01} is the total amount of solute. We adopt the normalization $M_{10} = 1$, by which the total-particle mass is unity. This normalization leads to the following expressions for the mean size (mass), and the overall fraction of solute

$$\bar{v} = \frac{M_{10}}{M_{00}} = \frac{1}{M_{00}} \tag{2}$$

and

$$\phi = \frac{M_{01}}{M_{10}} = \int_0^\infty dv \int_0^v dm(m) F(v, m) \tag{3}$$

where $\bar{v}$ is the average particle mass. Using Eq. 2 the integral of $F(v, m)$ over its entire domain is

$$\int_0^\infty dv \int_0^v dmF(v, m) = 1/\bar{v} \tag{4}$$

Equation 4 will provide the normalization factor in the calculation of various ensemble averages introduced later.

Size and Solute Distribution. Integrating out the compositional variable m, we obtain the distribution of sizes $f(v)$, irrespectively of solute concentration

$$f(v) = \int_0^v F(v, m)dm \tag{5}$$

Function $f(v)$ is the familiar size distribution of the homogeneous (one-component) problem. It can be easily verified that all moments of v (that is, of zero order in m) can be obtained directly from the size distribution $f(v)$

$$M_{i0} = \int_0^\infty v^i f(v)dv \tag{6}$$

Let $g(m|v)$ be the fraction of particles in the size class v with solute content $m \pm dm/2$. This makes $g(m|v)$ the conditional probability to find a particle with solute content m, given that the particle has size v. By its definition, the compositional distribution is equal to the bivariate distribution normalized by the number of particles in the size range $v \pm dv/2$

$$g(m|v) = \frac{F(v, m)}{\int_0^v F(v, m)dm} \tag{7}$$

Using Eqs. 5 and 7, the bivariate distribution is expressed as the product of the unconditional size distribution f, and the conditional solute distribution g

$$F(v, m) = f(v)\,g(m|v) \tag{8}$$

This result has a simple interpretation: the probability to find an aggregate of size v that contains amount of solute m is equal to the probability to find a particle of size v, multiplied by the probability to find solute m given the size of the aggregate. We note, however, that only $g(m|v)$ is a properly normalized probability density function, while both $F(v, m)$, and $f(v)$ produce on integration, the total number of particles in the system. The moments of the solute distribution are of interest, especially those relating to the mean and variance of the solute in aggregates of a given size. Let $\mu_k(v)$ be the k-order moment of $g(m|v)$ with respect to m

$$\mu_k(v) = \int_0^v m^k g(m|v)dm \tag{9}$$

By definition $\mu_0(v) = 1$ for all v, $\mu_1(v)$ is the mean amount of solute in the size class v and $\mu_2(v)$ is the second moment. The relationship between the moments of the solute distribution and those of the bivariate distribution is easily established to be

$$M_{ij} = \int_0^\infty v^i \mu_j(v)\,f(v)dv \tag{10}$$

Concentration. It is convenient to express composition in terms of the concentration (mass fraction), c, which we define as

$$c = m/v \tag{11}$$

The probability density function of the mass fraction c, is obtained from that of m

$$G(c|v) = g(m|v)\left(\frac{\partial m}{\partial c}\right)_v = vg(vc|v) \tag{12}$$

In our analysis we will employ the solute mass, since is it a conserved quantity, but the results can be appreciated more clearly if expressed in terms of the mass fraction c.

Excess Solute. If the components were perfectly mixed among all aggregates, the amount of solute in an aggregate of size v would be ϕv. If the actual amount of solute in the aggregate is m, the difference $m - \phi v$ defines the *excess solute* x

$$x = m - \phi v = v(c - \phi) \tag{13}$$

It follows that the mean value of x in the population is zero; accordingly, the variance of the excess solute is equal to $\langle x^2 \rangle$

$$\langle x^2 \rangle = \bar{v} \int_0^\infty dv \int_0^v dm(m - \phi v)^2 F(v, m) = \text{var}(x) \tag{14}$$

This is the variance of excess solute over the entire population. We may also define the size-specific variance, $\text{var}(x|v)$, within aggregates of size v

$$\text{var}(x|v) = \int_0^v (m - \phi v)^2 g(m|v)dm \tag{15}$$

The size-specific and the overall variance of excess solute are related as follows

$$\langle x^2 \rangle = \bar{v} \int_0^\infty \text{var}(x|v) f(v)dv \tag{16}$$

This is obtained by integrating Eq. 15 over the size distribution $f(v)$, followed by normalization with the total number of particles $M_{00} = 1/\bar{v}$. For a perfectly mixed system, both variances are zero; conversely, if the total variance is zero, then $\text{var}(x|v)$ is zero for all v—or more precisely, for all v in the range, where $f(v)$ is significant. A related parameter that will prove useful in the subsequent analysis is the sum-square, or total variance, of excess solute

$$X^2 = \int_0^\infty dv \int_0^v dm(m - \phi v)^2 F(v, m) = \frac{\langle x^2 \rangle}{\bar{v}} \tag{17}$$

The overall variance $\langle x^2 \rangle$, or, equivalently, the total variance X^2, represents a convenient single-point measure of the degree of mixing between the two components.

Population Balance

To simplify the notation of the population balance equations, we introduce the state vector $\mathbf{r}$, which we define as

$$\mathbf{r} = (v, m) \tag{18}$$

as a shorthand notation for aggregates of mass v that contain solute m. In this convention the aggregation kernel is

$$K_{12} = K(\mathbf{r}_1, \mathbf{r}_2) \tag{19}$$

In this study, we are concerned exclusively with kernels that do not depend on composition. For notational simplicity, however, we will use the notation in Eq. 19, even though K does not depend on m, m'. As a further simplification in notation, we do not show time explicitly in the argument list of the distributions, with the understanding that F, f and g are all time dependent.

Since both v and m are conserved upon aggregation, the constitutive equation for the aggregation of particles 1 and 2 is

$$\mathbf{r}_1 + \mathbf{r}_2 = \mathbf{r} \tag{20}$$

With this observation, the evolution of the bivariate distribution, $F(\mathbf{r})$, can be written by analogy to the one-component problem as

$$\frac{\partial F(\mathbf{r})}{\partial t} = \frac{1}{2}\int_0^{\mathbf{r}} F(\mathbf{r}-\mathbf{r}')F(\mathbf{r}')K(\mathbf{r}-\mathbf{r}',\mathbf{r}')d\mathbf{r}' - \int_0^{\infty} F(\mathbf{r})F(\mathbf{r}')K(\mathbf{r},\mathbf{r}')d\mathbf{r}' \tag{21}$$

Before we proceed, a brief comment on the integration limits is in order. The notation $d\mathbf{r}$ is used as a shorthand for $dvdm$. The integration domain for the solute mass m, is from zero to v, but if we adopt the convention $F(v, m) = 0$ for $m > v$, the upper limit can be replaced by infinity. We adopt this convention in all equations written in terms of the particle vector $\mathbf{r}$; when writing integrals explicitly in terms of v and m, we will use the natural limits for m.

We note here a useful equation that can be used to obtain the time evolution of various moments. If $A(v, m) = A(\mathbf{r})$ is an extensive scalar property of the particle state, the corresponding total property over the population, which we will denote as $[A]$, is

$$[A] = \int_0^{\infty} A(\mathbf{r})F(\mathbf{r})d\mathbf{r} \tag{22}$$

and the average value of A over the population is

$$\langle A \rangle = \bar{v}[A] \tag{23}$$

We obtain the time evolution of $[A]$ by multiplying Eq. 21 by $A(\mathbf{r})$ followed by integration over $\mathbf{r}$. The result, as shown in the Appendix, is

$$\frac{d[A]}{dt} = \frac{1}{2}\int_0^{\infty} d\mathbf{r}\int_0^{\infty} d\mathbf{r}'[A(\mathbf{r}+\mathbf{r}') - A(\mathbf{r}) - A(\mathbf{r}')]F(\mathbf{r})F(\mathbf{r}')K(\mathbf{r},\mathbf{r}') \tag{24}$$

This gives the time evolution of $[A]$ and implicitly, via Eq. 23, the evolution of $\langle A \rangle$. The time evolution of the mixed moment of order i, k can now be obtained from Eq. 24 with $A = v^i m^k$. For $k = 0$, in particular, we find

$$\frac{dM_{00}}{dt} = -\frac{1}{2}\int_0^{\infty} d\mathbf{r}\int_0^{\infty} d\mathbf{r}' F(\mathbf{r})F(\mathbf{r}')K(\mathbf{r},\mathbf{r}') \tag{25}$$

which gives the total number of aggregates. It is a simple matter to show, starting with Eq. 24, that $dM_{10}/dt = dM_{01}/dt = 0$, in agreement with the conservation of the total mass and solute mass in the system. The same procedure allows us to obtain the evolution of sum-square of excess solute, X^2. Using $A(\mathbf{r}) = x(\mathbf{r}) = (m - \phi v)^2$ in Eq. 24 we obtain,

$$\frac{dX^2}{dt} = \int_0^{\infty} d\mathbf{r}\int_0^{\infty} d\mathbf{r}' x(\mathbf{r})x(\mathbf{r}')F(\mathbf{r})F(\mathbf{r}')K(\mathbf{r},\mathbf{r}') \tag{26}$$

where $x(\mathbf{r}') = m' - \phi v'$. This is the governing equation of the total variance of excess solute.

A separate equation can be obtained for the evolution of the size distribution $f(v)$. This is done by integrating out the compositional component in Eq. 21. Noting that $K(\mathbf{r}, \mathbf{r}')$ is independent of the amount of solute, the result is

$$\frac{\partial f(v)}{\partial t} = \frac{1}{2}\int_0^{v} f(v-v')f(v')K(v-v';v')dv' - \int_0^{\infty} f(v)f(v')K(v;v')dv' \tag{27}$$

In Eq. 27 we have recovered the familiar one-component aggregation equation. This result, pointed out previously by Lushnikov[1] and by Vigil and Ziff,[2] is easily understood: since the rate of aggregation does not depend on composition, the system aggregates as a one-component system. It follows that the size distribution, as well as its various moments, can be solved for independently of composition.

A separate equation can be now be obtained for the compositional distribution $g(m|v)$. Differentiation of Eq. 8 with respect to time gives

$$f\frac{\partial g}{\partial t} = \frac{\partial F}{\partial t} - g\frac{\partial f}{\partial t} \tag{28}$$

Using Eqs. 21 and 27 for the time derivatives of F and f, respectively, and after some manipulation (see the Appendix for more details) the final result is

$$f(v)\,\frac{\partial g(m|v)}{\partial t} = \frac{1}{2}\int_0^v \Omega(v,\, v-v')\left[-g(m|v) + \int_0^m g(m-m'|v-v')\,g(m'|v')dm'\right]dv' \tag{29}$$

where

$$\Omega(v,\, v-v') = K(v-v',\, v')\,f(v-v')\,f(v') \tag{30}$$

is the aggregation rate between sizes v' and $v - v'$. Having obtained the evolution of the compositional distribution we may now write expressions for the moments. The governing equation for the k-order moment is obtained by multiplying Eq. 29 by m^k, and integrating over m. This procedure leads to the following general result (see the Appendix for details)

$$f(v)\,\frac{d\mu_k}{dt} = \frac{1}{2}\int_0^v \Omega(v-v',\, v')\left[-\mu_k(v) + \sum_{i=0}^{k}\frac{k!}{i!(k-i)!}\,\mu_i(v')\mu_{k-i}(v-v')\right]dv' \tag{31}$$

The evolution of the average $\mu_1(v)$, and variance, $\sigma^2(v) = \mu_2(v) - \mu_1^2(v)$, follows from Eq. 31, with $k = 1, 2$

$$f(v)\,\frac{d\mu_1(v)}{dt} = -\frac{1}{2}\int_0^v \Omega(v-v',\, v')(\Delta\mu_1)dv' \tag{32}$$

$$f(v)\,\frac{d\sigma^2(v)}{dt} = -\frac{1}{2}\int_0^v \Omega(v-v',\, v')\{\Delta\sigma^2 - (\Delta\mu_1)^2\}dv' \tag{33}$$

where

$$\Delta\mu_1 = \mu_1(v) - \mu_1(v-v') - \mu_1(v') \tag{34}$$

$$\Delta\sigma^2 = \sigma^2(v) - \sigma^2(v-v') - \sigma^2(v') \tag{35}$$

Equations 32 and 33 give the evolution of the mean and variance of the amount of solute found within aggregates of size v. If the system initially well mixed ($\mu_1(v) = \phi v$, $\sigma^2(v) = 0$ for all v at $t = 0$), it will remain well mixed at all times because the righthand side of Eqs. 32 and 33 is zero. This is precisely what is expected when the aggregation kernel is independent of composition.

Stationary-solute distribution

From Eq. 29 we note that the compositional distribution is stationary if the following condition is met

$$g(m|v) = \int_0^m g(m-m'|v-v')\,g(m'|v')dm' \tag{36}$$

Here, on the righthand side we have the solute distribution in the size range v, and on the lefthand we have the solute distribution that emerges via all aggregations that produce that size v. Equation 36 states, therefore, that if the distribution of solute in the size class v is equal to the distribution produced via binary aggregation events from all smaller sizes, then the compositional distribution in size class v is stationary. To determine this stationary distribution, we note that the Gaussian function

$$g(m|v) = \frac{1}{\sqrt{2\pi a_2 v}}\exp\left[-\frac{(m-a_1 v)^2}{2a_2 v}\right] \tag{37}$$

with a_1, a_2, constants, satisfies Eq. 36 provided that the lower and upper integration limits are replaced by $-\infty$, $+\infty$, respectively. For sufficiently large v, namely, $v \gg a_2/a_1^2$, Eq. 37 is sharply peaked about the mean, and the shift of integration limits is inconsequential. In this limit, therefore, Eq. 37 satisfies the stationary condition.

We now seek to determine the parameters a_1 and a_2. To obtain a_1 we apply the conservation of solute in the system

$$\phi = \int_0^\infty dv f(v)\int_0^v dm\, m\, g(m|v) = a_1\int_0^\infty v f(v)dv = a_1 \tag{38}$$

Therefore, the mean concentration of solute is $\bar{c} = \phi$ in all particles, or, the mean excess solute is zero in all size classes. To determine a_2, we evaluate the second moment of excess solute over the entire population and find

$$X^2 = \int_0^\infty dv f(v)\int_0^v dm(m-\phi v)^2 g(m|v) = a_2 \tag{39}$$

Therefore, a_2 is equal to the sum-square of the excess solute over the population; since a_2 is constant, we conclude that the sum-square of excess solute in the stationary state is also constant.

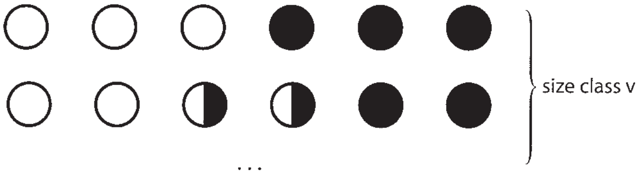
Partial mixing

Suppose the initial condition is such that the mean concentration of solute in all size classes is equal to the overall solute fraction ϕ

$$t = 0: \quad \mu_1(v) = \phi v, \text{ for all } v \tag{40}$$

This situation is illustrated pictorially in Figure 1 by contrast to perfect mixing: In a perfectly mixed system, all particles (in all size classes) contain the desired mass fraction of solute ϕ, that is, $\mu_1(v) = v$ and $\sigma^2(v) = 0$. Equation 40, on the other hand, represents a weaker condition that requires all size

(a) complete mixing in size class v, $\phi = 0.5$



(b) partial mixing in size class v, $\phi = 0.5$

Figure 1. Illustration of perfect and partial mixing at ϕ = 0.5: (a) perfectly mixed system, all particles contain ϕ mass fraction of solute; (b) partial mixing, the mass fraction of solute in the entire size class is v, but individually particles contain varying amounts of solute.

classes to contain the mean solute fraction ϕ, but places no constraints on the distribution of solute among the particles. We refer to this condition as *partial mixing.* A special case of partial mixing is a population of monodisperse particles that are either pure solvent, or pure solute (the so-called *monodisperse* initial condition). In this case the size class of monomers contains the overall fraction ϕ of solute, but solute and solvent are completely segregated.

If the system obeys partial mixing initially, Eq. 26 for the evolution of X^2 leads to

$$\left.\frac{dX^2}{dt}\right|_{t=0} = \int_0^\infty dv \int_0^\infty dv'\,\Omega(v, v') \int_0^v dm(m - \phi v)\, g(m|v) \int_0^{v'} dm'(m' - \phi v')\, g(m'|v') = 0 \quad (41)$$

noting that its righthand side is zero by virtue of Eq. 40 (the integrals with respect to m and m' are both equal to $\mu_1(v) - \phi v = 0$). Therefore, the initial condition of partial mixing implies $dX^2/dt = 0$ at $t = 0$. According to Eq. 34, if the condition of partial mixing is satisfied by all sizes at a one time, it will be satisfied at all subsequent times because aggregates formed by partially mixed particles are also partially mixed. We conclude that $dX^2/dt = 0$, at all times, that is, X^2 is constant and equal to its value at time zero

$$X^2 = X_0^2 = \text{constant} \quad (42)$$

From Eq. 39, then, $a_2 = X_0^2$ from which it follows that

$$\sigma^2(v) = vX_0^2 \quad (43)$$

Partial mixing encompasses the monodisperse initial condition, as a special case. For this initial condition, Lushnikov found that the distribution of components is given by the binomial distribution[1]

$$g(m|v) = \frac{v!}{m!(v-m)!}\,\phi^m(1-\phi)^{v-m} \quad (44)$$

Notice that this solution satisfies the discrete version of Eq. 36

$$g(m|v) = \sum_{m'=0}^{m} g(m - m'|v - v')\, g(m'|v') \quad (45)$$

For large v the binomial distribution goes over to a normal distribution with mean $\mu_1(v) = \phi v$ and variance $\sigma^2(v) = v\phi(1 - \phi) = vX_0$. Thus, we obtain full agreement between our solution and Lushnikov's. We point out, however, that our solution is valid not only for monodisperse condition but for the more general case of partial mixing.

Kernels of the sum type

If the kernel is of the sum-type

$$K(v_1, v_2) = k(v_1) + k(v_2) \quad (46)$$

Eq. 26 can be rearranged in the form

$$\frac{dX^2}{dt} = 2\int_0^\infty dv \int_0^v dm(m - \phi v)k(v)F(v, m) \int_0^\infty dv' \int_0^{v'} dm'(m' - \phi v')F(v', m') = 0, \quad (47)$$

whose righthand side is zero because the integral in m' is equal to the mean excess solute $\langle x \rangle$, which by definition is zero. This result is independent of the solute/size distribution. We conclude that in this case too, the sum-square of excess solute X^2, is constant at all times, regardless of the initial distribution of seeds. This type of kernel encompasses the constant kernel, $K(v, v') = 1$, as well as the sum kernel $K(v, v') = v + v'$.

A special case of this type is aggregation under constant kernel with initial condition given by the exponential distribution

$$F_0(v, m) = \frac{1}{(1-\phi)\phi}\exp\left(-\frac{m}{\phi} - \frac{v-m}{1-\phi}\right) \quad (48)$$

whose total variance of excess solute is

$$X_0^2 = 2\phi^2(1-\phi)^2 \quad (49)$$

Lushnikov obtained the exact solution to this problem and Vigil and Ziff showed that the solute distribution for large v is a normal distribution with mean $\mu_1(v) = \phi v$, and variance $\sigma^2(v) = 2\phi^2(1 - \phi)^2 v$. With $a_1 = \phi$, and $a_2 = X_0^2$, this is in full agreement with our prediction for kernels of the sum type.

General case

The two special cases, (1) arbitrary kernel with initially partial mixed conditions, and (2) sum-type kernel with arbitrary initial conditions, were shown above to lead to strict invariance of X^2. This in turn implies, via Eq. 43, that the degree of blending between components is entirely determined by the initial state of mixing. It is possible to explain these results in a qualitative manner: If we assume that aggregates of sufficiently large size consist of a random mix of seeds, the variance of excess solute must be equal to the variance of the seeds $\langle x_0^2 \rangle$, multiplied by the number of seeds that make up the aggregate. As the average number of seeds in v is $v/\bar{v}_0$, where $\bar{v}_0$ is the mean size initially, the variance becomes

$$\mathrm{var}(x|v) = \frac{v}{\bar{v}_0}\langle x_0^2 \rangle = vX_0^2 \tag{50}$$

with the result on the far right obtained by noting that $\langle x_0^2 \rangle / \bar{v}_0 = X_0^2$. For the sum-square of excess solute it follows

$$X^2 = \int_0^\infty dvf(v) \int_0^v dm\ \mathrm{var}(x|v) = X_0^2 \int_0^\infty vf(v)dv = X_0^2 \tag{51}$$

Therefore, the assumption that aggregates are formed of random mixture of seeds can explain why the overall variance X^2, remains constant during aggregation. This assumption can be invoked for sufficiently large aggregates, but does not necessarily hold true during the earlier stages of the process, a demonstrated by counterexample: Suppose that the initial seeds consist of, say, solvent in the form of monomers and solute in the form of decamers in number ratio one-to-one. Clearly, all aggregates in the range $v = 2$ to 9 contain solute, but no solvent; and while 11-mers produced from 10-mers, and monomers contain both components, those produced through the aggregation of 9-mer or smaller particles will consist of pure solute. Such transient behavior may result in segregation of components or even in preferential mixing, if for example the aggregation rate between unequal sizes is favored (see the appendix for examples of such cases). Eventually, the population reaches a state of partial mixing at which point X^2 reaches a value that no longer changes. How different this value is from its value at time zero is matter that cannot be addressed theoretically. We examine this question by simulation.

Simulations

To demonstrate the previous findings and explore the general case we have performed simulations of bicomponent aggregation for various kernels and initial conditions. The simulation method is based on the constant-number Monte-Carlo algorithm, which we have previously applied to several population balance problems in one-component systems.[8,9,10,11] The adaptation of the constant-number method to multicomponent aggregation is straightforward and briefly outlined below. The simulation begins with N particles, each represented by a vector $\mathbf{r} = (v, m)$, which gives the mass of the particle and the amount of solute. At each step of the algorithm, a pair of particles is selected to undergo aggregation. The selection is made with probability $P_{ij} \propto K_{ij}$, where K_{ij} is the aggregation kernel between the particles. In the simulations described here, we implement the acceptance/rejection method according to which pairs are randomly chosen until the acceptance condition is met: rnd $\leq K_{ij}/K_0$; here rnd is a random number uniformly distributed between 0 and 1, and K_0 is a normalization constant that ensures probabilities satisfy the condition $0 \leq P_{ij} \leq 1$. In the simulation we choose K_0 to be the maximum kernel in the simulation box, because this choice leads to fewer rejections and speedier execution of the algorithm. Once a pair is selected, a new particle is formed whose mass and amount of solute is obtained by adding those of the aggregating particles. Since this process results in the net loss of one particle from the simulation box, a new particle is added by randomly picking and duplicating one of the existing particles. This procedure ensures that the number of particles remains constant, and allows us to reach the scaling limit even with a finite number of simulation particles. Upon implementing an aggregation event, the time is advanced according to[9]

$$\Delta t = \frac{2\bar{v}}{N\bar{v}_0\langle K_{ij} \rangle} \tag{52}$$

where $\langle K_{ij} \rangle$ is the mean value of the aggregation kernel in the simulation box, and $\bar{v}$ is the mean size. This procedure may be extended to any number of components. For the simulations presented here we have used 30,000 particles. We have previously tested this algorithm with 15,000 particles against known solutions to coagulation, and breakup problems and confirmed its accuracy.[8,9] Since the constant-N method adds randomly selected particles to the simulation box, the amount of solute in the simulation is not constant but fluctuates. To ensure accuracy, we monitor the fraction of solute during simulation and have confirmed that its fluctuations remain within less than 1% of the desired value.

We present results for two kernels, the constant kernel $K_{12} = 1$, and the Brownian coagulation kernel, which in dimensionless form is given by

$$K_{12} = 2 + \left(\frac{v_1}{v_2}\right)^{1/3} + \left(\frac{v_1}{v_2}\right)^{-1/3} \tag{53}$$

Both kernels are homogeneous with degree 0, but while the constant kernel is of the sum type, the Brownian kernel is not. For each kernel we run two mass fractions of solute $\phi = 0.5$ and $\phi = 0.1$. For each of these cases we use two different initial conditions, one monodisperse, and one bidisperse. In the monodisperse case all particles initially have the same size, that is, $v_A = v_B = 1$, and consist of pure solute or pure solvent. In the bidisperse case, the solute particles have size $v_A = 1$ and the solvent particles $v_B = 10v_A$. The parameters of the distribution at the initial conditions are summarized in Table 1.

Figure 2 shows the normalized variance, $\langle x^2 \rangle / \bar{v}^2$ plotted against the mean size, $\bar{v}$, for the eight combinations of kernels, mass fractions, and initial conditions. The results collapse into

Table 1. Initial Conditions for the Simulations (“A” = solute, “B” = solvent)

Case	Size Distr.	ϕ	v_A	v_B	$f_0(v_A)$	$f_0(v_B)$	$\bar{v}_0$	$\langle x_0^2\rangle/\bar{v}_0^2 = X_0^2/\bar{v}_0$
(a)	Monodisperse	0.1	1	1	0.1	0.9	1	0.09
(b)	Monodisperse	0.5	1	1	0.5	0.5	1	0.25
(c)	Bidisperse	0.1	1	10	0.5263	0.4737	5.26	0.0325
(d)	Bidisperse	0.5	1	10	0.9091	0.0909	1.82	0.7563

four distinct groups according to the initial variance but independently of the kernel type or overall mass fraction of solute. All data are described by the equation

$$\frac{\langle x^2\rangle}{\bar{v}^2} = \frac{\langle x_0^2\rangle/\bar{v}_0^2}{\bar{v}/\bar{v}_0} = \frac{X_0^2}{\bar{v}} \tag{54}$$

which implies that in all cases X^2 remains constant during aggregation. This result is anticipated for all initial conditions of the constant kernel (a special case of kernel of the sum type), as well as for all cases with monodisperse initial conditions (which satisfy partial mixing). The interesting observation is that this behavior is also confirmed for the Brownian kernel with bidisperse initial conditions. Since the theory cannot predict the evolution of X^2 for this case, we analyze this situation by examining the conditions at the initial state more closely.

With bidisperse conditions with $v_A/v_B = \beta$, Eq. 26 gives (see Appendix)

$$\left(\frac{dX^2}{dt}\right)_{t=0} = v_A^2 \frac{(1-\phi)^2\phi^2}{(\beta+\phi-\phi\beta)^2}[K(v_A, v_A) - 2K(v_A, v_B) + K(v_B, v_B)] \tag{55}$$

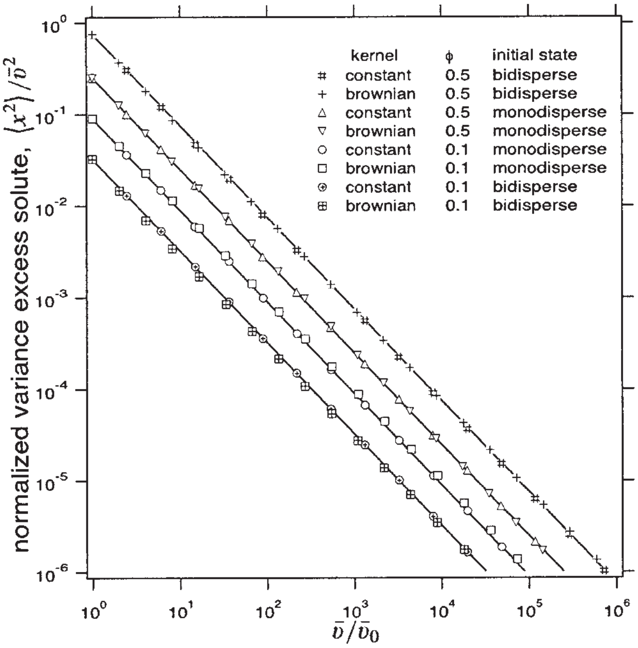


Figure 2. Normalized variance of excess solute, $\langle x^2\rangle/\bar{v}_0^2$, against mean size.

The slope is −1 for all cases, demonstrating Gaussian dynamics of mixing.

The sign of the derivative depends on the quantity $K(v_A, v_A) - 2K(v_A, v_B) + K(v_B, v_B)$: for $v_A = v_B$, it is zero regardless of kernel (recall that $v_A = v_B$ in this case implies partial mixing); for kernels of the sum type it is zero regardless of v_A and v_B. For the general kernel, the sign of the derivative dX^2/dt at time 0 can be either positive or negative. For the Brownian kernel in particular it is *negative,* implying that the variance of the excess solute *decreases* during the early stages of aggregation. This is because this kernel favors aggregation among unequal sizes leading to preferential aggregation between monomers (solute) and decamers (solvent). As pointed out in the discussion of the general case, this preferential mixing is an indirect result which arises from the discreteness of the initial state, even though the kernel itself is independent of composition. As a result, the scaling form of $\langle x^2\rangle/\bar{v}^2$ in Figure 2 extrapolated to time zero, must be smaller than the value of $\langle x^2\rangle/\bar{v}^2$ at $t = 0$. The magnitude of this shift depends on the volume fraction and the size ratio v_A/v_B. With a solute fraction of $\phi = 0.5$, the number of solvent particles is less than 10% of the total with the result that the effect of cross-aggregation becomes minimized. With $\phi = 0.1$, the number of solute and solvent particles is more nearly equal, and a stronger effect is expected. To see this behavior more clearly, we plot the evolution of the sum-square of the excess solute during aggregation in Figure 3. As we see, the sum-square X^2, for the Brownian kernel at $\phi = 0.1$ with bidisperse conditions shows a small decrease of about 10%. This shift is small and in Figure 2 it is hardly noticeable. Conceivably, other kernels may amplify this effect more strongly, but our view is that, at least for nongelling kernels, the effect of transient mixing/segregation of secondary importance. Kernels that lead to gelation[12,13] might lead to different behavior, but this class of kernels is beyond the scope of the present study.

Implications for Mixing

The conclusion of the preceding sections is that the sum-square of excess solute remains constant during aggregation regardless of initial conditions or kernel. This is strictly true for partially mixed states and kernels of the sum type; it is true to a good approximation in all other cases examined here. If X_0^2 is constant, the compositional distribution, expressed in terms of the concentration c, becomes

$$G(c|v) = \frac{1}{\sqrt{2\pi(X_0^2/v)}}\exp\left[-\frac{(c-\phi)^2}{2(X_0^2/v)}\right] \tag{56}$$

The result states that the concentration in all aggregates goes over to the overall mass fraction of solute and that the variance decreases as $1/v$. Therefore, compositional fluctuations die out as aggregates increase in size, and the system approaches a state of homogeneous distribution of its components. Signifi-

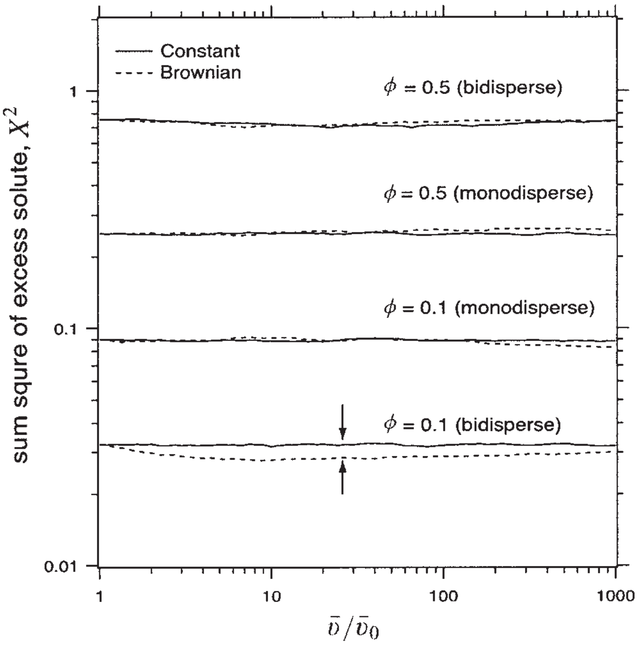


Figure 3. Evolution from the sum-square of excess solute.

Solid lines refer to the constant kernel, dashed lines to the Brownian kernel. The arrow highlight the small decrease in X^2 for the Brownian kernel with bidisperse conditions at $\phi = 0.1$.

cantly, the degree of mixing among components is independent of the kernel and is solely a function of the initial state of mixing, as expressed by X_0^2. For the overall variance of excess solute we obtain

$$\frac{\langle x^2 \rangle}{\bar{v}^2} = \frac{\text{const.}}{\bar{v}} \approx \frac{X_0^2}{\bar{v}} \tag{57}$$

The normalized variance, $\langle x^2 \rangle / \bar{v}^2$, a measure of the overall degree of mixing between components, decreases as $1/\bar{v}$. Therefore, in the limit of long times the population as a whole becomes well mixed regardless of initial conditions. Using Eq. 57 it is possible to predict the point during aggregation that the normalized variance, $\langle x^2 \rangle / \bar{v}^2$, reaches a predetermined value. Suppose that the desired variance is σ_*^2. Solving Eq. 57 for the corresponding mean size, we obtain

$$\bar{v}_* = \frac{X_0^2}{\sigma_*^2} \tag{58}$$

Notice that the average size $\bar{v}_*$, corresponding to the point at which the desired variance is reached, does not depend on the kernel; of course the *time* required to reach this size, does. As one might expect, the smaller the desired variance, the larger is the target size $\bar{v}_*$, thus, requiring longer aggregation times. The target size also depends on X_0^2, the sum-square of excess solute at time zero. This suggests that the blending of components will be reached faster if X_0^2 is minimized. The condition that minimizes X_0^2 can be easily obtained if the initial distribution is bidisperse. Suppose that the solvent is present in size v_B and the solute in size $v_A = \beta v_B$. With solute fraction ϕ, the sum-square of excess solute, X_0^2, is (see also the Appendix)

$$\frac{X_0^2}{\bar{v}_0^2} = \frac{\phi(1-\phi)(\beta + \phi - \phi\beta)^2}{\beta} \tag{59}$$

Minimizing X_0^2 with respect to the size ratio $\beta = v_A/v_B$ at constant $\bar{v}_0$ we obtain

$$\left(\frac{v_A}{v_B}\right)_{\text{opt}} = \frac{\phi}{1-\phi} \tag{60}$$

and the corresponding minimum value of X_0^2 is

$$\left(\frac{X_0^2}{\bar{v}_0^2}\right)_{\text{opt}} = 4\phi^2(1-\phi)^2 \tag{61}$$

Equation 60 gives the optimum solute-to-solvent size ratio among all bidisperse distributions with the same mean, such that such system has the minimum total excess solute X_0^2. The graphical interpretation is that the system has the lowest-lying intercept in Figure 3. It follows that such system reaches any predetermined value of the variance $\langle x^2 \rangle / \bar{v}^2$ sooner compared to all other initial conditions. The optimum size ratio and the corresponding value of X_{opt}^2 are plotted in Figure 4 against the solute volume fraction. For $\phi = 0.5$, the optimum bidisperse condition consists of equal size particles. If the solute fraction is small, then the solute particles must be smaller than the

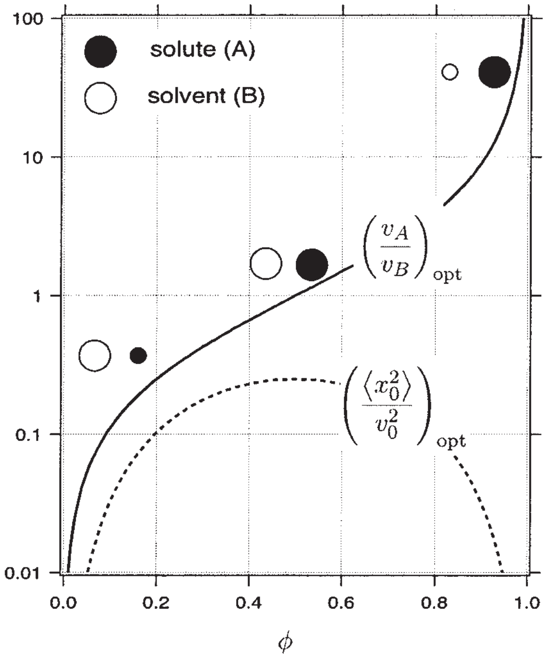


Figure 4. Optimum solute-to-solvent size ratio for minimizing blending time, as a function of solute fraction ϕ.

The solid line shows the optimum value of the size ratio v_A/v_B; the dashed line shows the corresponding minimum value of X_0.

solvent particles to produce a sufficient population, that such small amount may mix with the majority component. Yet, the size of the solute particle should not be too small because an over-abundance of solute particles will cause some segregation via solute/solute aggregation. These conclusions are demonstrated in Figure 3. Among all cases with $\phi = 0.5$, the lowest-lying curve is the one corresponding to monodisperse initial conditions, that is, $v_A = v_B$. By contrast, among all cases with $\phi = 0.1$ the lowest-lying is that for $v_A/v_B = 10$, which is closest to the optimum value $v_A/v_B = 9$ calculated from Eq. 60. These results suggest that pregrinding the minority component to the right size before the two components are mixed should lead to shorter mixing times.

Conclusions

We have shown that the bivariate distribution is the product of the size distribution $f(v)$, with a Gaussian compositional distribution $g(m|v)$

$$F(v, m) = f(v)\, g(m|v) \tag{62}$$

We have further shown that for large aggregates the compositional distribution is Gaussian, a result which formalizes the validity of the Vigil-Ziff conjecture for composition-independent kernels with arbitrary initial conditions. The size distribution $f(v)$, is governed by the familiar, one-component coagulation equation, and can be solved independently of composition. The governing equation for the compositional component is given by Eq. 29 and its solution for large v is a Gaussian function in the amount of solute with mean and variance that are both proportional to the aggregate size v. The proportionality constant in the relationship between variance of solute and aggregate size is $a_2 \approx X_0^2$, where X_0^2 is the sum-square of the excess solute over the population at time zero. Aggregation always produces a mixed system that with the solute concentration approaching the well-mixed state with variance that decreases as $1/v$. The scaling of the variance indicates that the mixing of components is not characterized by a time scale, but rather by a size scale: for aggregates whose size is much larger than that of the initial seeds, the solute variance in aggregates of size v scales as $1/v$ and the overall variance scales with the mean size as $1/\bar{v}$. The time to reach this point is entirely dependent on the kernel and reaching a desired value for the compositional variance is merely a matter of waiting long enough until the corresponding size is reached.

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Notation

c = mass fraction of solute within a particle; ($c = m/v$)
$F(v, m)$ = concentration of particles with size (mass) v containing amount of solute m
$f(v)$ = size distribution (irrespective of composition)
$g(m|v)$ = conditional probability density that a particle contains mass m of solute given that the particle mass is v
$G(c|v)$ = conditional probability density that a particle contains solute mass fraction, c, given that the particle mass is v
$K(v, v'; m, m')$ = aggregation kernel between particles (v, m) and (v', m')
M_{ij} = mixed moment of $F(v, m)$ of order i, j, with respect to v, m, respectively
m = mass of solute within a particle
$\mathbf{r}$ = vector of particle state, $\mathbf{r} = (v, m)$
v = mass of particle
$\bar{v}$ = average size over all compositions
$var(x|v)$ = variance of excess solute in size class v
x = excess amount of solute per particle, $x = m - v\phi$
X^2 = sum of x^2 over all aggregates
β = size ratio of solute particles to solvent particles in bidisperse initial conditions
$\mu_i(v)$ = moment of $g(m|v)$ of order i with respect to m
$\sigma^2(v)$ = variance of solute within particles of size v ($\sigma^2(v) = \mu_2(v) - \mu_1(v)^2$)
ϕ = overall volume fraction of solute
$\Omega(v, v')$ = overall aggregation rate between sizes v and v' ($\Omega(v, v') = f(v)f(v')K(v, v')$)

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Appendix

Evolution of total property

Here we derive Eq. 24 for the time evolution of total property $[A]$. If $A(\mathbf{r})$ is a property of the population, the total property $[A]$ is defined as

$$[A] = \int_0^\infty A(\mathbf{r})\, F(\mathbf{r}) d\mathbf{r} \tag{A1}$$

We take the time derivative and use Eq. 21 for $\partial F(\mathbf{r})/\partial t$ to obtain

$$\frac{d[A]}{dt} = \frac{1}{2}\int_0^\infty d\mathbf{r}\int_0^{\mathbf{r}} d\mathbf{r}' A(\mathbf{r}) F(\mathbf{r}-\mathbf{r}') F(\mathbf{r}') K(\mathbf{r}-\mathbf{r}', \mathbf{r}') - \int_0^\infty d\mathbf{r}\int_0^\infty d\mathbf{r}' A(\mathbf{r}) F(\mathbf{r}) F(\mathbf{r}') K(\mathbf{r}, \mathbf{r}')$$

Changing the integration variables of the first integral to $\mathbf{r}_1 = \mathbf{r}'$, $\mathbf{r}_2 = \mathbf{r} - \mathbf{r}'$, that integral becomes

$$\frac{1}{2}\int_0^\infty d\mathbf{r}\int_0^{\mathbf{r}} d\mathbf{r}' A(\mathbf{r}_1 + \mathbf{r}_2) F(\mathbf{r}_1) F(\mathbf{r}_2) K(\mathbf{r}_1, \mathbf{r}_2) \qquad \text{(A2)}$$

For the second integral, we use $\mathbf{r}_1 = \mathbf{r}$, $\mathbf{r}_2 = \mathbf{r}'$, and noting the symmetry between $\mathbf{r}_1$ and $\mathbf{r}_2$, we obtain

$$\int_0^\infty d\mathbf{r}_1 \int_0^\infty d\mathbf{r}_2 A(\mathbf{r}_1) F(\mathbf{r}_1) F(\mathbf{r}_2) K(\mathbf{r}_1, \mathbf{r}_2) = \int_0^\infty d\mathbf{r}_1 \int_0^\infty d\mathbf{r}_2 \frac{A(\mathbf{r}_1) + A(\mathbf{r}_2)}{2} F(\mathbf{r}_1) F(\mathbf{r}_2) K(\mathbf{r}_1, \mathbf{r}_2) \qquad \text{(A3)}$$

Combining these results we obtain

$$\frac{d[A]}{dt} = \frac{1}{2}\int_0^\infty d\mathbf{r}\int_0^\infty d\mathbf{r}'[A(\mathbf{r}_1 + \mathbf{r}_2) - A(\mathbf{r}_1) - A(\mathbf{r}_2)] F(\mathbf{r}_1) F(\mathbf{r}_2) K(\mathbf{r}_1, \mathbf{r}_2) \qquad \text{(A4)}$$

which is Eq. 24 of the text.

Derivations Relating to Compositional Distribution

Time evolution of compositional distribution

The time evolution of the compositional distribution $g(m|v)$ is obtained from Eq. 28 along with Eqs. 21 and 27. We combine these equations, group terms into two terms, a formation and a depletion term, factor the volume terms and write the result in the form

$$f(v)\frac{\partial g(m|v)}{\partial t} = \frac{1}{2}\int_0^\infty f(v-v') f(v') K(v-v', v')\left\{-g(m|v) + \int_0^v g(m-m'|v-v') g(m'|v') dm'\right\} dv' - f(v)\int_0^\infty f(v') K(v, v') g(m|v)\left\{1 - \int_0^v g(m'|v') dm'\right\} dv' \qquad \text{(A5)}$$

The second term is zero by virtue of the normalization

$$\int_0^v g(m'|v') dm' = 1 \qquad \text{(A6)}$$

leading to Eq. 29 of the text.

Moments of compositional distribution

The governing equation for $\mu_k(v)$ is obtained from Eq. 29 by multiplying both sides by m^k and carrying out the integration with respect to m. Exchanging the order of integration and keeping in mind that the kernel does not depend on m we obtain

$$f(v)\frac{d\mu_k}{dt} = \frac{1}{2}\int_0^v dv' \Omega(v-v', v')\left[\int_0^v dm \int_0^m dm' m^k g(m - m'|v-v') g(m'|v') - \int_0^v m^k g(m|v) dm\right]$$
$$= \frac{1}{2}\int_0^v dv' \Omega(v-v', v')\left[\int_0^v dm \int_0^m dm' m^k g(m - m'|v - v') g(m'|v') - \mu_k(v)\right] \qquad \text{(A7)}$$

We make the variable transformation $m_1 = m'$, $m_2 = m - m'$ noting that in the transformed plane the integration domain for m_1 is 0 to v', while for m_2 it is from 0 to $v - v'$, since $g(x|y)$ is zero if $x > y$. For inner double integral we now have

$$\int_0^{v'} dm_1 \int_0^{v-v'} dm_2 (m_1 + m_2)^k g(m_1|v') g(m_2|v-v') = \sum_{i=0}^{k} \frac{k!}{i!(k-i)!} \mu_i(v') \mu_{k-i}(v-v') \qquad \text{(A8)}$$

Using this result, the equation for the k-order moment is

$$f(v)\frac{d\mu_k}{dt} = \frac{1}{2}\int_0^v \Omega(v-v', v')\left[-\mu_k(v) + \sum_{i=0}^{k} \frac{k!}{i!(k-i)!} \mu_i(v') \mu_{k-i}(v-v')\right] dv' \qquad \text{(A9)}$$

With $k = 0, 1, 2$ we now obtain the following results

$$\frac{d\mu_0}{dt} = 0 \qquad \text{(A10)}$$

$$f(v)\,\frac{d\mu_1}{dt} = \frac{1}{2}\int_0^v \Omega(v-v',\,v')[\mu_1(v-v') + \mu_1(v') - \mu_1(v)]dv' \tag{A11}$$

$$f(v)\,\frac{d\mu_2}{dt} = \frac{1}{2}\int_0^v \Omega(v-v',\,v')[\mu_2(v-v') + 2\mu_1(v')\mu_1(v-v') + \mu_2(v') - \mu_2(v)]dv' \tag{A12}$$

Equation A10 is in agreement with the normalization $\mu_0(v) = 1$.

Equation for $\sigma^2(v)$. Let $\sigma^2(v)$ be the compositional variance of particles of size v. By definition

$$\sigma^2(v) = \mu_2(v) - \mu_1^2(v) \tag{A13}$$

from which it follows

$$\frac{d\sigma^2(v)}{dt} = \frac{d\mu_2(v)}{dt} - 2\mu_1(v)\,\frac{d\mu_1(v)}{dt} \tag{A14}$$

Combining the above with Eqs. A11 and A12, we obtain the governing equation for σ^2

$$f(v)\,\frac{d\sigma^2(v)}{dt} = \frac{1}{2}\int_0^v \{\sigma^2(v-v') + \sigma^2(v') - \sigma^2(v) + [\mu_1(v-v') + \mu_1(v') - \mu_1(v)]^2\}\Omega(v-v',\,v')dv' \tag{A15}$$

This can be written in the somewhat more compact form

$$f(v)\,\frac{d\sigma^2(v)}{dt} = \frac{1}{2}\int_0^v \{-\Delta\sigma^2 + (\Delta\mu_1)^2\}\Omega(v-v',\,v')dv' \tag{A16}$$

where

$$\Delta\mu_1 = \mu_1(v) - \mu_1(v-v') - \mu_1(v') \tag{A17}$$

$$\Delta\sigma^2 = \sigma^2(v) - \sigma^2(v-v') - \sigma^2(v') \tag{A18}$$

According to these definitions $\Delta\mu_1$ is the difference between the mean composition of new aggregates that enter the size class v, and the mean composition of all aggregates in the size class. The same interpretation applies to $\Delta\sigma^2$.

Steady-State Condition. The steady-state condition for μ_1 is

$$\mu_1(v) = \mu_1(v-v') + \mu_1(v') \tag{A19}$$

which is clearly satisfied by $\mu_1 = a_1 v$, where a_1 is constant. Using Eqs. A16 and A19 the steady-state condition for the variance $\sigma^2(v)$ becomes

$$\sigma^2(v) = \sigma^2(v-v') + \sigma^2(v') \tag{A20}$$

which is satisified if $\sigma^2(v) = a_2 v$, with a_2 constant. Thus, we independently recover the proportionality relationships for the mean and variance required by Eq. 37.

Bidisperse Initial Conditions

Suppose a distribution consists of particles of pure solute (A) and pure solvent (B) with size ratio $\beta = v_A/v_B$, overall solute fraction ϕ, and mean size $\bar{v} = 1$. We express v_A, v_B, and the number of solvent and solute particles in terms of β and ϕ

$$v_A = \beta + \phi - \phi\beta, \quad v_B = \frac{\beta + \phi - \phi\beta}{\beta} \tag{A21}$$

$$f(v_A) = \frac{\phi}{\beta + \phi - \phi\beta}, \quad f(v_B) = 1 - f(v_A) \tag{A22}$$

which satisfies the normalization $v_A f(v_A) + v_B f(v_B) = 1$. The sum-square of excess solute X^2, is calculated as

$$X^2 = x_A^2 f(v_A) + x_B^2 f(v_B) \tag{A23}$$

with $x_A = v_A(1-\phi)$, $x_B = -v_B\phi$. After some algebraic manipulation the result can be written in the form

$$X^2 = \frac{\phi(1-\phi)(\beta + \phi - \phi\beta)^2}{\beta} \tag{A24}$$

For bidisperse conditions, Eq. 26 for dX^2/dt gives

$$\frac{dX^2}{dt} = x_A^2 f^2(v_A)\,K(v_A,\,v_A) + x_A x_B f(v_A)\,f(v_B)\,K(v_A,\,v_B) + x_B^2 f^2(v_B)\,K(v_B,\,v_B) \tag{A25}$$

and from this we finally obtain

$$\frac{dX^2}{dt} = \phi^2(1-\phi)^2(K(v_A,\,v_A) + K(v_B,\,v_B) - 2K(v_A,\,v_B)) \tag{A26}$$

The righthand side can be either positive, negative, or zero. For kernels of the sum type, it is zero. For the Brownian kernel it is always negative while for the product kernel it is always positive (in the special case $v_A = v_B$, it is zero regardless of kernel; recall that in this case the condition of partial mixing is satisfied). Therefore, the sum-square of excess solute at time zero may either increase, decrease, or stay constant depending on the kernel and the initial size distribution of solute and solvent particles.

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