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Mixing state of bi-component mixtures under aggregation with a product kernel

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Abstract – We analyze the aggregation of a two-component system with a product kernel, to determine its evolution in time during a progressive mixing. The evolution is governed by the Smoluchowski equation, yielding gelation from a certain time. In the past, equilibrium (or asymptotic) solutions have been used to study mixing of bi-component mixtures for non-gelling kernels. In this letter we show that asymptotic solutions are invalid to describe the mixing behavior for the product kernel case (even before gelation). Besides, an equilibrium concentration is not reached. On the contrary, particles with any composition exist all time.

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Introduction. – Particle aggregation is present in many Physics fields: colloid studies, powders agglomeration, polymerization, aerosols, cloud formation, etc. It is controlled by the multicomponent Smoluchowski equation (see, *v.g.*, [1] for its derivation for aerosols).

Recently, mixing behavior in pharmaceutical agglomeration has been studied by Matsoukas *et al.* [2] and Lee *et al.* [3]. These papers analyze the compositional distribution of the active component as a function of time and particle size, how long does it take to reach a certain blending level, etc., leading to an interesting knowledge of practical interest.

Vigil and Ziff [4] postulated a general scaling law for two-component aggregation with non-gelling kernels. Matsoukas *et al.* [2] based their findings on the bi-component coagulation equation. The latter showed that this equation accepts a Gaussian as the solution to the compositional part of the distribution for non-gelling kernels. If such solution is feasible, the bivariate distribution must be of the form postulated by the asymptotic solutions (AS) of Vigil and Ziff, *i.e.*, an equilibrium solution exists.

Matsoukas *et al.*, identified several cases that conform to this behavior. They also affirm that the degree of mixing between components is controlled by the variance of excess solute, X^2 .

A main hypothesis of the previous cited analysis is the existence of an equilibrium concentration: the system have to accumulate around this concentration. Besides, this fact is tied to the particle size distribution (PSD) form: the number of particles with a given concentration, C , of the first component (solute) must tend to a Dirac δ as $t \rightarrow \infty$.

For conservative mass kernels the equilibrium concentration is C_0 , the overall (global) concentration. The use of an equilibrium solution to analyze long time behavior is adequate for some kernels, as the constant one, but it is not always justified. For the additive kernel case, as shown in [5], the mass PSD fulfills the cited conditions, but the number PSD does not: an asymptote exists at C_0 , but the curve is not a Dirac δ .

For cases with negligible values of the kernel for small particles the asymptotic solution is not valid to describe the overall number PSD, because for large times minute particles (grit) remain in the system. Gelling kernels present more difficulties, due to the lack of mass conservation for time after gelation.

In [2] and [3] gelling kernels are not considered. Can we extend their useful methods for non-gelling cases to gelling cases, even before gelation when mass is still conserved? Does an equilibrium concentration (or some similar) exist? What does the mass and number distribution as a function of solute concentration look like?

Asymptotic solutions for several kernels (*v.g.*, constant, additive and product ones) are known for the discrete

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multicomponent case, but we shall see that these cannot be used in general to obtain the mixing state.

For the continuous multicomponent case, asymptotic solutions for constant and additive kernels are known. However, for gelling kernels (as the product one) they are not known. Nevertheless, for the product kernel, the posed problem can be treated directly from the exact solution [6].

The structure of this paper is as follows. First, we present the Smoluchowski equation, which governs this problem. After that, we demonstrate that the mixing behavior of a discrete bi-component mixture for product kernel cannot be obtained by using asymptotic solutions. Then, using the exact solution of a bi-component exponential initial PSD case, we derive the correct expressions for the total number and mass that correspond to a given value of solute concentration (already used by Lushnikov [7]). Finally, we analyze the mixing state, both before and after gelation, comparing it with the constant and additive kernel cases.

Smoluchowski equation. – In this paper we work only with the bi-component case (the conclusions for multicomponent ones are similar). Then, the PSD is defined through the concentration $c(m, n)$, such that $c(m, n)dm dn$ is the number of particles with masses of each component in the bi-dimensional region $[m, m + dm) \cap [n, n + dn)$.

Bi-component Smoluchowski equation gives us the evolution of $c(m, n, t)$ with time:

$$\begin{aligned} \frac{\partial c(m, n, t)}{\partial t} = & \frac{1}{2} \int_0^m \int_0^n K(m - m', n - n' | m', n') \\ & \times c(m - m', n - n', t) c(m', n', t) dm' dn' \\ & - c(m, n, t) \int_0^\infty \int_0^\infty K(m, n | m', n') \\ & \times c(m', n', t) dm' dn'. \end{aligned} \quad (1)$$

K is the coagulation coefficient or kernel, which in the present case is

$$K(m, n | m', n') = b_2(m + n)(m' + n'), \quad (2)$$

being b_2 a constant. This kernel appears, *i.e.*, in branched-chain polymerization of RA_f type (in the large f limit) [8].

The product kernel gives gelation: particles with sizes approaching infinity pass to other phase (gel), which can or cannot interact with other particles (sol phase) [9]. In this letter we assume there is no interaction —model S of Stockmayer. This phenomenon leads to a decrease of the total mass present in sol phase.

For homogeneous kernel fulfilling $K(am | am') = a^\lambda K(m | m')$, gelation is produced for homogeneity constant $\lambda > 1$ (see, *v.g.*, [9]). In our case it is $\lambda_{\text{prod}} = 2$. The additive kernel is just at the boundary: $\lambda_{\text{add}} = 1$.

Lushnikov [7] introduces two interesting macroscopical magnitudes that characterize the time evolution of the

aggregating mixture. Naming $C' = m/(m + n)$ the solute concentration in a generic particle, then

$$N(C, t) = \int_0^\infty dm \int_0^\infty dn c(m, n, t) \times \delta(C - C')$$

is the total number of particles with solute concentration C . On the other hand

$$M(C, t) = \int_0^\infty dm \int_0^\infty dn (m + n) c(m, n, t) \times \delta(C - C')$$

is the total mass of particles with solute concentration C .

With the change of variables:

$$m = \chi C, \quad n = \chi(1 - C) = \chi \tilde{C}, \quad (3)$$

being $\chi = m + n$ the total mass in the particle, the Jacobian is $|J| = \chi$, and we obtain

$$N(C, t) = \int_0^\infty \chi c(m(\chi, C), n(\chi, C), t) d\chi, \quad (4)$$

$$M(C, t) = \int_0^\infty \chi^2 c(m(\chi, C), n(\chi, C), t) d\chi. \quad (5)$$

These expressions will be used in what follows.

Mixing state from asymptotic solutions. – Let us start from the discrete case. We assume an initial PSD formed by two types of monomers, with an initial number M_{10} for the first and M_{01} for the second. We name $M_T = M_{10} + M_{01}$.

In general, the PSD is described through the concentration, c , of particles that contain m type-1 monomers and n type-2 monomers. For large times and large particles, for non-gelling kernels, Vigil and Ziff [4] conjecture that $c(m, n, t)$ is expressed as the product of a Gaussian times the scaling solution of the homogeneous case (both monomers would be indistinguishable), regardless of the initial condition.

Following [7], for the discrete case and kernels independent of the composition, the temporal evolution is

$$c(m, n, t) = P(m, n) c_{\text{homo}}(m + n, t),$$

being c_{homo} the concentration corresponding to the homogeneous case, and

$$P(m, n) \approx \frac{M_T}{\sqrt{2\pi M_{10} M_{01}}} \exp\left(-\frac{M_T^2}{2M_{10} M_{01}} (C - C_o)^2 \chi\right),$$

being $C = m/(m + n)$ the solute concentration in a particle and $C_o = M_{10}/M_T$ the mean concentration of the solute in the whole system. This approximation, which is a Gaussian (continuous) is obtained in the limit from a binomial distribution (discrete), and it is accordingly the Vigil and Ziff conjecture.

Time is normally transformed into other equivalent variable, a critical particle size (named sometimes maximum

cluster size) that increases with time, and depends on the initial PSD and on the kernel parameters.

As a starting point we take the AS obtained by Vigil and Ziff [4] for constant kernel for the discrete case. For constant $K = b_0$ the critical size is $\sigma = b_0 t / 2$. With the known asymptotic solution of the homogeneous case [10] we set

$$c_{\text{cons}}(\chi, C, \sigma) \approx \frac{M_T^2}{\sqrt{2\pi M_{10} M_{01}}} \sigma^{-2} \chi^{-1/2} \exp(-\chi E_0(C, \sigma)),$$

being the exponent term:

$$E_0(C, \sigma) = \frac{M_T^2}{2M_{10}M_{01}} (C - C_o)^2 + \log \left(1 + \frac{1}{\sigma} \right).$$

By using expression (5) we obtain

$$M_{\text{cons}}(C, \sigma) \approx \frac{3M_T}{4\sqrt{2M_{10}M_{01}}} \sigma^{-2} [E_0(C, \sigma)]^{-5/2}. \quad (6)$$

This equation (and the similar one for N not present for brevity) has the proper form, which matches with the obtained in [5] directly from the exact solution given in [7]: both are Dirac δ as time goes to infinity.

For the additive kernel case, we start with the AS obtained by Vigil and Ziff [4] from the discrete case. In this case the critical size is $\sigma = \exp(2tb_1 M_T)$ (being b_1 the proportionality constant in the kernel). The known solution of the homogeneous case [4] leads us to

$$M_{\text{addi}}(C, \sigma) \approx \frac{M_T}{2\pi\sqrt{M_{10}M_{01}}} \sigma^{-1/2} [E_1(C, \sigma)]^{-1}, \quad (7)$$

being

$$E_1(C, \sigma) = \frac{M_T^2}{2M_{10}M_{01}} (C - C_o)^2 + \frac{1}{2\sigma}.$$

This equation has also the proper form (see [5]): For $C = C_o$ a maximum with value proportional to $\sigma^{1/2}$ appears.

However, by using (4) an improper integral appears for N . Therefore, with asymptotic tools it is impossible to obtain N with this method for the additive kernel. The exact solution must be used (see [5]). Even with better approximations for the asymptotic solution we cannot obtain N in this case, because that solution does not describe well the solution for large times in the small-size particles region.

For product kernel, before gelation, the critical size is $\sigma = (1 - b_2 M_T t)^{-2}$. The known AS of the homogeneous case [6] leads to

$$M_{\text{prod}}^{\text{pre-gel}}(C, \sigma) \approx \frac{M_T}{8\sqrt{\pi M_{10} M_{01}}} [E_1(C, \sigma)]^{-1/2}. \quad (8)$$

This equation does not make sense physically, because it encloses an infinite area under the curve between abscissae 0 and 1 when $\sigma \rightarrow \infty$. The equation corresponding to N is increasing towards 0 and 1 (without physical sense).

We believe that asymptotic solutions are good enough to substitute the exact PSD in the cases in which aggregation eliminates small particles with time (*i.e.*, Brownian kernel). However, obtaining the mixing behavior for the product kernel needs an exact solution, as we shall show now.

Analysis of the bi-component exponential PSD for product kernel. – In what follows, back in the continuous case, we name m the solute mass and n the solvent mass in a particle. We take an initial exponential PSD:

$$c(m, n, 0) = ab \exp(-am - bn),$$

already used by Lushnikov [7] to analyze the mixing state of bi-component mixtures for the constant kernel case.

This PSD has first- and second-order moments:

$$\varphi = \frac{1}{a} + \frac{1}{b}, \quad \psi = \frac{2}{a^2} + \frac{2}{ab} + \frac{2}{b^2}, \quad (9)$$

respectively. Then, the unitary mass to make dimensionless the Smoluchowski equation is (see [6]):

$$\omega = \frac{\psi}{\varphi} = \frac{2(a^2 + ab + b^2)}{ab(a + b)}. \quad (10)$$

The initial amount of the solute is $1/a$ and of the solvent is $1/b$, values that must be conserved until gelation. The total initial number of particles is 1.

By applying the method shown in [6] the solution is

$$\begin{aligned} c(m, n, \tau) &= \frac{ab}{m+n} \exp \left(-am - bn - \frac{m+n}{\omega} T \right) \\ &\times \sum_{k=0}^{\infty} \left(\frac{a^3 b^3 mn(m+n)\tau}{2(a^2 + ab + b^2)} \right)^k \\ &\times \sum_j^{k+1} \frac{m^j n^{k+1-j}}{j!(k+1-j)!(k+j)!(2k+1-j)!}, \end{aligned}$$

being

$$\tau = b_2 \psi t, \quad T = \int_0^\tau \mathcal{M}(\tau) d\tau.$$

$\mathcal{M}(\tau)$ is the total dimensionless mass present, which after gelation (for $\tau = 1$) diminishes with time.

Without loss of generality, we assume that $a \geq b$, and we name $\eta_0 = b/a$, then $0 \leq \eta_0 \leq 1$.

For each time, τ , the total dimensionless mass, \mathcal{M} , the modified time, T , and the total dimensionless number of particles, \mathcal{N} , should be known.

For $\tau \leq 1$ we have

$$T = \tau, \quad \mathcal{M}(\tau) = 1, \quad \mathcal{N}(\tau) = \frac{2(\eta_0^2 + \eta_0 + 1)}{(\eta_0 + 1)^2} - \frac{1}{2}\tau.$$

For $\tau > 1$, from eq. (63) of [6] we have

$$\begin{aligned} &\left(\frac{\frac{1}{a}}{\frac{s}{\omega a} + 1} + \frac{\frac{1}{b}}{\frac{s}{\omega b} + 1} \right)^2 + \frac{\frac{1}{a^2}}{\left(\frac{s}{\omega a} + 1 \right)^2} + \frac{\frac{1}{b^2}}{\left(\frac{s}{\omega b} + 1 \right)^2} = \\ &\frac{(a+b)^2 + a^2 + b^2}{a^2 b^2 \tau} \left(\frac{s}{\omega a} + 1 \right) \left(\frac{s}{\omega b} + 1 \right). \end{aligned} \quad (11)$$

By setting

$$\eta = \frac{s + \omega b}{s + \omega a}, \quad (12)$$

we get

$$\left(\frac{1}{\eta} - 1\right)^3 (1 - \eta^3) = \left(\frac{1}{\eta_0} - 1\right)^3 (1 - \eta_0^3) \frac{1}{\tau}. \quad (13)$$

By solving numerically this equation for η , we can obtain $\mathcal{M}(\tau)$ by using:

$$\mathcal{M}(\tau(\eta)) = \frac{(1 + \eta)(1 - \eta)^3 \eta_0^2}{(1 + \eta_0)(1 - \eta_0)^3 \eta^2}.$$

From this equation we can calculate $\mathcal{N}(\tau)$ by numerical integration and $T(\tau)$ taking into account that [6]:

$$T = s + \mathcal{M}\tau = \frac{a\eta - b}{1 - \eta} \omega + \mathcal{M}\tau.$$

Analysis of the number and mass of particles with a given concentration of solute. – From expressions (4) and (5), after making the integrals, by setting $\tilde{C} = 1 - C$, and naming:

$$A = aC + b\tilde{C} + \frac{T}{\omega}, \quad D = \frac{a^3 b^3 C \tilde{C} \tau}{2(a^2 + ab + b^2)}, \quad (14)$$

we have

$$N(C, \tau) = \frac{ab}{A^2} \sum_{k=0}^{\infty} (4k + 1)! \left(\frac{D}{A^4}\right)^k v(C, \tilde{C}, k), \quad (15)$$

$$M(C, \tau) = \frac{ab}{A^3} \sum_{k=0}^{\infty} (4k + 2)! \left(\frac{D}{A^4}\right)^k v(C, \tilde{C}, k), \quad (16)$$

being v the function:

$$v(x, y, k) = \sum_j^{k+1} \frac{x^j y^{k+1-j}}{j!(k+1-j)!(k+j)!(2k+1-j)!}. \quad (17)$$

Except for $\eta_0 = 0$ and $\eta_0 = 1$, N and M must be obtained numerically.

In the previous equations, D/A^4 is invariant up to a global change in the time scale (it does not change when a and b are both multiplied by the same constant).

As shown in [5] for the additive kernel, it is better to work with N divided by the total number of particles present at each time, and the same with M divided by the total mass at each time. In that case the area under the curves that represent these new functions in $[0, 1]$ must be unity. Therefore, the new magnitudes are

$$N^*(C, \tau) = \frac{\omega N(C, \tau)}{\varphi \mathcal{N}(\tau)}, \quad (18)$$

$$M^*(C, \tau) = \frac{M(C, \tau)}{\varphi \mathcal{M}(\tau)}, \quad (19)$$

as functions of C for each τ value.

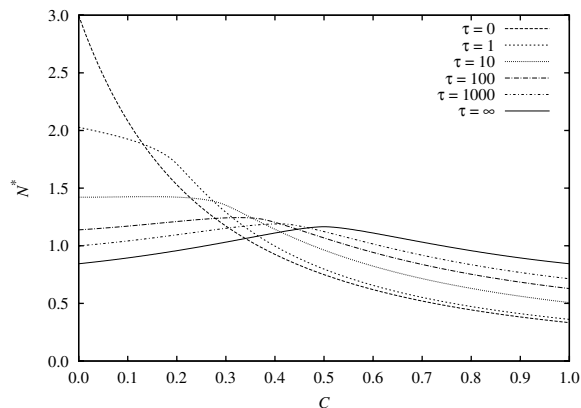


Fig. 1: Evolution of $N^*(C, \tau)$ for several values of τ , $a=3$, $b=1$. For $\tau \rightarrow \infty$ this function tends to the solution when $a=b$ (continuous line).

For $\tau \rightarrow 1$ we can use the critical size instead of τ . Following Ziff *et al.* [11] that size is defined from the initial second- and third-order moments and the gelation time. Its dimensionless value, σ , is related to τ :

$$\tau = 1 - \sigma^{-1/2}. \quad (20)$$

In the gelation $\sigma \rightarrow \infty$, and after it σ is infinite forever [11]. Then, σ cannot be used instead of the time after gelation.

The form of N^* and M^* is general for any values of a and b . As an example, a case with $a=3$, $b=1$, is used in the figures.

In fig. 1 the particle number evolution is shown. Independently of the specific values of a and b , finite values for N^* always appear. The curve tends to the curve obtained for $a=b$ (symmetric case) as time goes on (continuous curve in the fig. 1). Therefore, for product kernel an equilibrium concentration does not exist, but a maximum at $C_m = 0.5$ for $\tau \rightarrow \infty$ exists. This signifies that the main component (solvent in the present case) passes preferably to the gel phase with time, tending to a sol phase with equal amount of both components.

Figure 2a shows the evolution of M^* for the same case $a=3$, $b=1$, for time until gelation. Here, an asymptote for $\tau=1$ appears at $C_i \approx 0.192$.

Figure 2b shows the evolution of M^* after gelation. The asymptote is present but it displaces towards $C_m = 0.5$ with time.

We have analyzed the place C_i where the asymptote appears for $\tau=1$ as a function of η_0 . In fig. 3 the results for several values of η_0 are shown. If a and b are similar the value of C_i approaches 0.5. On the other hand when $a \rightarrow \infty$ we have $C_i = 0$ (the solute does not exist).

It is important to determine C_i as a function of η_0 when $\tau=1$. This is a difficult task in an analytical form (due to the series character of our solutions). Therefore, we opted for a heuristic method: calculating M^* as a function of C by summing the series for several values of η_0 for $\tau=1$, and determining by inspecting the place of the asymptote.

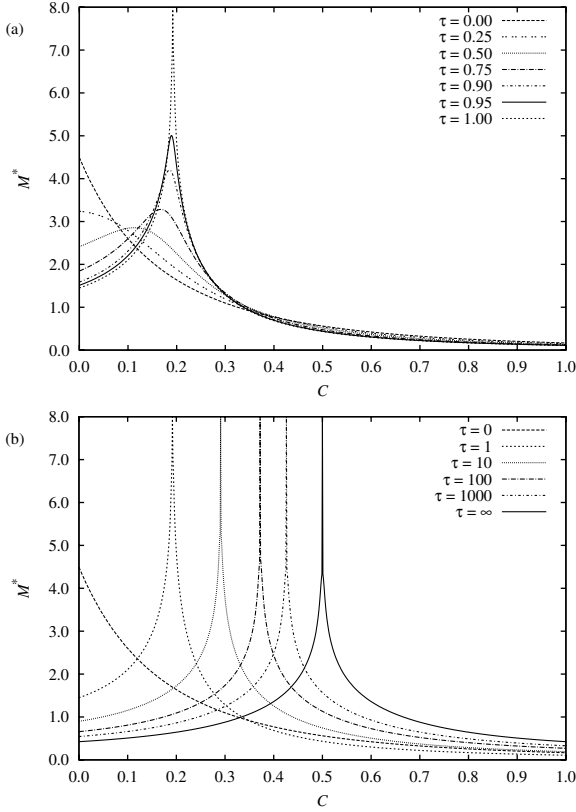


Fig. 2: Evolution of $M^*(C, \tau)$ for several values of τ , $a = 3$, $b = 1$. (a) Before gelation. At this time the function has a logarithmic singularity at C_i (see its definition in the text). (b) After gelation. The function tends with time to the solution for the symmetrical case $a = b$, with a displacement of the asymptote towards $C_m = 0.5$.

After that, we fitted the solution with rational functions, by searching integer coefficients. The solution

$$C_i(\eta_0) = \frac{\eta_0^2 + \eta_0/2}{\eta_0^2 + \eta_0 + 1} = \frac{2b^2 + ab}{2(a^2 + ab + b^2)}, \quad (21)$$

fits very well, and this is drawn with the “experimental” points in fig. 3.

Not only the integral character of the obtained coefficients, but also the term $a^2 + ab + b^2$ (already present in other analytical parameters of the problem) support the goodness of expression (21). The previous function also verifies the symmetry condition:

$$C_i(a, b) = 1 - C_i(b, a),$$

as theoretically should be. Therefore, although the validity of (21) is not rigorously proved, we think it is correct.

After we know the vertical asymptote location for any value of η_0 we can determine the asymptotical behavior of $M^*(\tau = 1)$ at C_i . The problem is difficult because $v(C_i, \tilde{C}_i, k)$ cannot be easily obtained. However, we can determine its asymptotic value for $k \rightarrow \infty$.

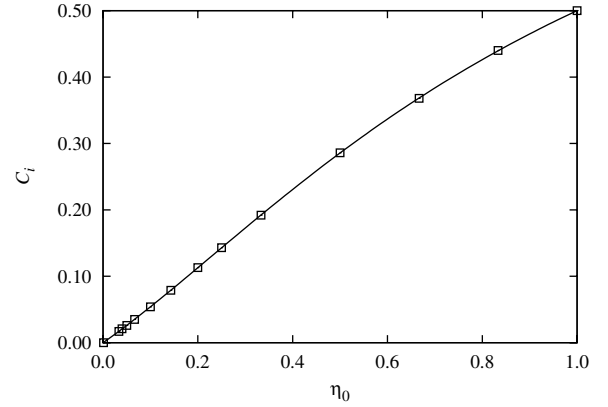


Fig. 3: Maxima of $M^*(C, \tau = 1)$. Marks are the “experimental” locations of the vertical asymptote for $\tau = 1$. The curve shows $C_i(\eta_0) = (\eta_0^2 + \eta_0/2)/(\eta_0^2 + \eta_0 + 1)$.

Starting with (16), (17) and (19), in the limit when $\sigma \rightarrow \infty$, we arrive at

$$M^*(C_i, \sigma \rightarrow \infty) = \frac{(a^2 + ab + b^2)^3}{8ab(a+b)^4} \times \sum_{k=0}^{\infty} (4k+2)! \left(1 - \frac{3}{8\sigma}\right)^k \times d^k v(C_i, \tilde{C}_i, k), \quad (22)$$

with

$$d = (2a^2 + 5ab + 2b^2)(a^2 + ab + b^2)/(a+b)^4/128.$$

We can assume that, in the limit when $k \rightarrow \infty$,

$$v(C_i, \tilde{C}_i, k) \approx v(C_{\#}, C_{\#}, k)$$

is fulfilled, being $C_{\#}$ an auxiliary “concentration” to be determined (expected not much different from 0.5). The calculation of $v(C_{\#}, C_{\#}, k)$ is straightforward:

$$v(C_{\#}, C_{\#}, k) = \frac{C_{\#}^{k+1} (4k+2)!}{(k+1)! [(2k+1)!]^2 (3k+1)!}.$$

In this case, approximating the factorials we get

$$v(C_i, \tilde{C}_i, k) \approx \frac{64}{\pi\sqrt{27}(4k+2)!k} \left(\frac{4096}{27}\right)^k C_{\#}^{k+1}. \quad (23)$$

By taking into account the logarithmic series, we have

$$M^*(C_i, \sigma \rightarrow \infty) = -\frac{(a^2 + ab + b^2)^3}{ab(2a^2 + 5ab + 2b^2)} \times \log \left[1 - G \left(1 - \frac{3}{8\sigma} \right) \right], \quad (24)$$

being

$$G = \frac{32(2a^2 + 5ab + 2b^2)(a^2 + ab + b^2)C_{\#}}{27(a+b)^4}.$$

G cannot be greater than unity, because in this case the logarithm is complex. If $G < 1$ then we have not an asymptote (we should have a finite value). Therefore, the unique possibility is $G = 1$, which leads to

$$C_{\#} = \frac{27(a+b)^4}{32(2a^2 + 5ab + 2b^2)(a^2 + ab + b^2)}. \quad (25)$$

Then, a logarithmic singularity appears:

$$M^*(C_i, \sigma \rightarrow \infty) = \frac{\sqrt{27}}{4\pi} \frac{(a^2 + ab + b^2)^3}{ab(2a^2 + 5ab + 2b^2)} \log \sigma. \quad (26)$$

Comparison with the constant and additive kernels. – In [5] it is shown that the behavior of the exponential PSD during its time evolution for constant and additive kernels are somewhat similar: both hold asymptotic solutions (as Vigil and Ziff [4] conjecture and also show from some specific cases). However, in [5] it is shown that the asymptotic solution for additive kernel has a limited use to study the PSD for large time values.

For constant kernel (see [5]), the maxima of N^* and M^* are proportional to $\sigma^{1/2}$ as time goes on. In this case an equilibrium concentration exists with a value of $C_o = b/(a+b)$. All particles present tend to have this concentration as time increases. Also, the number and mass PSDs have the same shape (see fig. 1 of [5]).

For additive kernel (see fig. 2 of [5]), the maximum of M^* is proportional to $\sigma^{1/2}$ as time evolves, tending the M^* curve to a Dirac δ . However, N^* does not have this shape, because the maximum of the curve is proportional to $\log \sigma$, having the asymptotic PSD an asymptote at C_o . Therefore, the number PSD does not have an equilibrium concentration.

As we have demonstrated here, for product kernel (see figs. 1 and 2) equilibrium concentrations do not exist in any case (*a fortiori* for the number PSD), even before gelation. Rather, a “critical concentration”, C_i , appears for the mass PSD.

We conjecture that mixing behaviors mainly depend on the homogeneity constant of the kernel, λ , which is 0 for both the constant kernel and the Brownian one, which is

$$K(m|m') = 2 + (m/m')^{1/3} + (m'/m)^{1/3}.$$

The results for constant and Brownian kernels shown by Matsoukas *et al.* [2] are very enlightening, regarding the evolution of the excess variance of solute, X^2 : both cases behave similarly, by maintaining X^2/\mathcal{M} constant.

The case with ‘free molecular regime’ kernel (with $\lambda = 1/6$, a small value) is analyzed numerically in [3]: its behavior is similar to the other two previous cases, although X^2/\mathcal{M} decreases slowly with time.

For gelling cases, the typical handling of the moments evolution equations are not allowed. For example, the masses of each component in the system have non-zero derivatives, and some other moments have infinite values. Therefore, we think that the use of X^2 in cases without

Dirac δ as asymptotic solution is risky and probably invalid (*i.e.*, gelation cases).

Conclusions. – We have shown that asymptotic solutions cannot be used to analyze the mixing state of a bi-component mixture as $t \rightarrow \infty$ in all cases. This also yields to the non-existence of an equilibrium concentration.

When kernel values are small for minute particles, these particles remain a long time in the system, invalidating the asymptotic solutions (obtained for large particle sizes) to analyze the mixing state. Gelling kernels are of this kind, and the problem is even worse, due to the lack of mass conservation for times after gelation.

In the specific case of the product kernel, the number of particles, N^* , with a given solute concentration, is always finite (different from the constant and additive kernels: for infinite time some concentration has $N^* \rightarrow \infty$ in both cases). Therefore, an equilibrium concentration, in which particles “accumulate”, does not exist for product kernel.

The evolution in time of the particles mass, M^* , with a given solute concentration has an asymptote from gelation time at a concentration C_i , which depends on initial PSD parameters. Besides, the shape of the function is not a Dirac δ because particles with $C = 0$ and $C = 1$ always exist.

After gelation, particles pass to gel phase in an asymmetrical way: the component in excess passes faster to the gel phase, tending the sol phase to have the same amount of both components.

Finally, the conclusions presented in [2] and [3] regarding bi-component mixing behavior for non-gelling kernels cannot be generalized to kernels with gelation. Nonetheless, some of those conclusions could still be approximately valid.

Obviously, the present conclusions do not invalidate the interesting analysis of non-gelling cases in [2] and [3]. Besides, the numerical method used there (constant Monte Carlo method) is very useful to analyze the mixing state for cases with or without gelation.

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