

Mixing state of bi-component mixtures under coagulation from scaling solutions

J.M. Fernández-Díaz, G. Gómez-García, M.A. Rodríguez-Braña, M. Domat, I.A. SanJuan

Department of Physics, University of Oviedo, C/Calvo Sotelo, s/n, E-33007 Oviedo, SPAIN

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Smoluchowski coagulation equation gives a mean field description of many aggregation processes: aerosol and cloud physics, polymer chemistry, colloidal chemistry, etc. This equation describes the evolution of the particle size distribution (PSD). For mono-component systems one size variable is needed (particle diameter or mass). However, when several species are necessary to the description of the system, a multicomponent approach has to be used: the independent variables are the masses of every species in the particles.

The simplest multicomponent system is a bi-component mixture: each particle is described by the mass of the first (m) and the second (n) component. Apart from the PSD, $c(m, n, t)$ (t is time) some others (derived) properties can be analysed in the evolution. Among these, Lushnikov (1976) introduced two important magnitudes to characterise coagulation mixtures: the total number, N , of particles having a given concentration $C = m/(m + n)$ of the first component, and the total mass, M , with the same concentration (expressions for M not shown for brevity). By putting $\chi = m + n$, the total mass in a particle, it is obtained:

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

In the evolution of the systems we are often interested in their long time (asymptotical) behaviour. This leads to the so called scaling solutions, which describe approximately the system, and are sometimes obtained from a discrete case: i.e., the PSD is composed by two kind of monomers, with an initial number M_{10} of the first component and M_{01} of the second one ($M_T = M_{10} + M_{01}$). For coagulating systems with kernel independent from the composition of the colliding particles, Lushnikov showed that:

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

being c_{homo} the PSD corresponding to the homogeneous case (if we were not able to distinguish the monomers). For long time and large particles, Vigil and Ziff (1998) showed (expressed with our nomenclature) that:

$$P(m, n) \approx \frac{M_T}{\sqrt{2\pi M_{10} M_{01}}} \exp\left(-\frac{M_T^2 (C - C_0)^2 \chi}{2M_{10} M_{01}}\right),$$

being $C_0 = M_{10}/M_T$ the overall concentration of the first component.

We will use the scaling solutions and previous equations to study the values of N (and M) for long

time, for the cases with constant, additive and product kernel, for which c_{homo} are known. Time t is normally expressed in function of other equivalent variable: a critical cluster size (s), increasing with time, and depending on the initial PSD and the kernel.

For the constant kernel, $s = b_0 t / 2$, by using the known homogeneous case solution, we obtain:

$$N_{\text{cons}}(C, s) \approx \frac{M_T}{2\sqrt{2M_{10}M_{01}}} s^{-2} [E_0(C, s)]^{-3/2},$$

$$E_0(C, s) = \frac{M_T^2}{2M_{10}M_{01}} (C - C_0)^2 + \log(1 + 1/s).$$

This expression has the adequate form: the total area between $C = 0$ and $C = 1$ under N is the total number of particles (variable with time) (For M the area is the total mass—constant.) Moreover, curves for N and M tend to a Dirac- δ : particles with concentration away from C_0 are removed from the system.

For the additive kernel (with the proper s definition) M obtained through the exposed methodology is good. However, N cannot be obtained because an improper integral appears. For the product kernel the problem is greater: it shows gelation, and the total mass in the system is no more conserved from certain instant. For time tending to gelation time the scaling solution is known, and from this we obtain M and N as before. Both expressions show bizarre behaviour: N increases as C tends to 0 and 1, and M (with an apparently correct form) encloses an infinite area. In both cases non-physical behaviour is found.

In conclusion, we think that scaling solutions are good enough to analyse the mixing state of mixtures for PSDs that have not grit (small particles) for long time (i.e., constant and Brownian kernels). On the contrary, if small particles remain in the system mixing states could be only obtained from the actual (and not approximate) solutions.

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