A new approach to the theory of Brownian coagulation

M.S. Veshchunov, I.B. Azarov

Nuclear Safety Institute (IBRAE) of Russian Academy of Sciences,
Moscow, 115191, Russia
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Presenting author email: vms@ibrae.ac.ru

The new approach to the Brownian coagulation theory developed in the authors papers (Veshchunov, 2010) and (Veshchunov and Azarov, 2011), is overviewed. The traditional diffusion approach to calculation of the collision frequency function for coagulation of Brownian particles is critically analyzed. In particular, it is shown that the diffusion theory (Smoluchowski, 1917), (Chandrasekhar, 1943) is applicable only to the special case of coalescence between large and small particles, $R_1 >> \bar{r} >> R_2$ (where $\bar{r} \approx n^{-1/3}$ is the mean inter-particle distance), and becomes inappropriate to calculation of the coalescence rate for particles of comparable sizes, $R_1, R_2 << \bar{r}$.

In the latter, more general case of comparable size particles, coalescences occur mainly in the kinetic regime (rather than in the diffusion one) characterized by random (homogeneous) spatial distribution of particles (rather than by their concentration profiles), owing to their rapid diffusion mixing in-between collisions. This kinetic regime is realized in a wide range of the particles concentrations, obeying the basic assumption of the theory $n^{1/3}R << 1$, this allows calculation of the collision rate in various modes of the kinetic regime (continuum, free molecular and transition) within the same approach.

In the kinetic regime the original multi-particle problem is rigorously reduced to consideration of two-particle collisions. This justifies the phenomenological form of the pair-wise kernel $\beta(R_1, R_2)$ in the Smoluchowski kinetic equation, derived for spatially homogeneous systems.

In the continuum mode of the kinetic regime, corresponding to $a << R$, where a is the particle persistent length, the calculated coalescence rate formally (and, in fact, fortuitously) coincides with the expression $\beta_{dif}(R_1, R_2) = 4\pi(D_1 + D_2)(R_1 + R_2) \equiv 4\pi D_{12} R_{12}$ derived by Smoluchowski (1917) for the diffusion regime that is relevant only in the particular case of large and small particles coalescences. This formal coincidence apparently explains a reasonable agreement of predictions of the kinetic equation derived in the traditional approach with experimental measurements of the Brownian particles coalescence rate.

In the opposite range $a >> R$, the standard free molecular expression for the collision frequency function β_{fm} is valid. Since the transition interval $a \approx R$ also belongs to the kinetic regime characterized by homogeneous spatial distribution of particles, it can be described by the interpolation formulas derived within the new analytical approach with fitting parameters that can be specified numerically, avoiding semi-empirical assumptions of the existing models.

Numerical calculations of the coalescence rate β/β_{fm} as a function of a_{12}/R_{12} are performed using the Monte Carlo method (by evaluation of the sweeping rate $\beta/\beta_{fm} = (\delta V/\delta t)/(\delta V_0/\tau_{12})$ of randomly distributed immobile point markers by migrating Brownian particle), generalizing the analytical approach applied to the limiting cases $a << R$ and $a >> R$, in two subsequent approximations of the random walk theory. The calculated points can be approximated by analytical expressions with 2 and 4 fitting parameters, Figure 1.

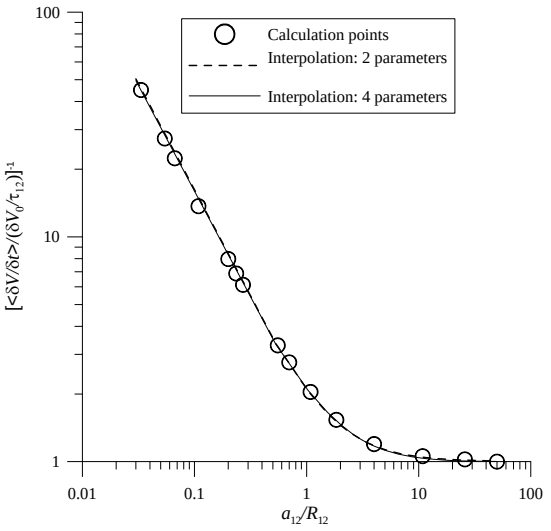

Figure 1. Dependence of the steady-state values of the inverse coalescence rate on the parameter a/R using interpolation curves, in comparison with the calculated points (centers of circles).

References

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