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Brownian coagulation in dense systems: Thermal non-equilibrium effects

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ABSTRACT

Non-equilibrium effects in Brownian coagulation at particle number densities that are large in comparison to that of the background gas are analysed theoretically and through computer experiments. With increasing rarefaction of the suspending gas there is a point, when the particle relaxation time becomes longer than the characteristic coagulation time. At that point the average velocity of particles will decrease due to mutual inelastic collisions and will fall below the value predicted by the energy equipartition theorem for there is insufficient time between the collisions to restore the thermal equilibrium. This reduced particle velocity results in a lower coagulation rate than predicted by the classical coagulation theory and this effect is shown through first principle computer experiments using the Langevin dynamics methodology developed in our previous studies on the particle crowding effects, as well as through the novel application of the kinetic Monte Carlo method with the majorant kernel proposed in this work. A theoretical model quantifying the effect of the coagulation rate suppression is formulated by introducing the concept of a thermalization number, which is defined as the reduced mean kinetic energy of particle motion. An expression for this quantity is derived and used to extend the classical coagulation theory to this new non-equilibrium regime of coagulation by following, and extending further, the methodology that we proposed previously to describe the concentration enhancement effects in coagulation. A closed-form, analytical formula for the coagulation kernel is obtained and shown to be applicable for all particle sizes and a wide range of concentrations. Close agreement is demonstrated between the predictions from this formula and the results from first principle simulations in the monodisperse case and this agreement can be improved further still, as well as extended to the polydisperse case, if a single model parameter is allowed to be adjusted from its theoretically derived value.

1. Introduction

Brownian coagulation is one of the most important physical processes governing mechanics of aerosols and colloids. The classical theory of Brownian coagulation rests firmly on the assumptions that the particle system remains in the thermal equilibrium with the suspending fluid and that this system is sufficiently diluted to neglect many-particle effects, i.e., the macroscopic dynamics of the system can be deduced from behaviour of an isolated particle pair. Recently, the authors

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investigated coagulation kinetics under concentrated conditions in the continuum, free-molecule and transition regimes by performing Langevin dynamics simulations of colliding Brownian particles. A novel computational algorithm was proposed to determine the coagulation kernel by keeping the coagulating system under monodisperse and thermal equilibrium conditions at all times (Trzeciak, 2012; Trzeciak et al., 2004, 2006). Through these simulations it was found that the kinetic coefficient of the coagulation rate (the coagulation kernel) becomes in general dependent on the volumetric particle concentration, i.e., the classical assumption of pairwise only influences breaks for high enough concentrations.

Heine & Pratsinis (2007) employed a more traditional Langevin dynamics algorithm to investigate concentration enhancement of the coagulation kernel in a polydisperse system of coalescing particles in the continuum regime and found good agreement with results of Trzeciak et al. (2006). Buesser et al. (2009) extended their approach to the transition and free-molecule regimes. They found slower coagulation rates than predicted by the classical theory, which were explained through the kinetic energy loss in inelastic particle–particle collisions together with short collision times in highly concentrated systems.

In this paper we extend the classical theory of Brownian coagulation to account for the effect of kinetic energy dissipation in inelastic collisions and we derive a closed-form, analytical formula for the overall coagulation kernel. The ability to make accurate, quantitative predictions with this formula is then verified by comparison with first principle calculations for a variety of conditions using Langevin dynamics and kinetic Monte Carlo simulation methods. Comparison with recently published results of Buesser et al. (2009) is also made together with critical assessment of that work, in particular their choice of non-dimensional parameters governing the process and some of the conclusions being drawn regarding applicability of the classical coagulation theory.

2. Brownian motion and energy dissipation in collisions

Due to the fact that particle collisions in the coagulation process are perfectly inelastic, part of particles' kinetic energy is dissipated into internal heat. With increasing rarefaction of the suspending gas there is a point, where the particle relaxation time becomes longer than the period between the collisions experienced by such a particle. At that point the average velocity of particles will decrease below the value predicted by the energy equipartition theorem for there is insufficient time between the collisions to restore the thermal equilibrium. The particle velocity will steadily decay until a steady state is reached, where the kinetic energy lost in collisions is on average regained back from the bombardment of gas molecules on particles during the inter-collision period. As a result of this reduced particle velocity, the coagulation rate will be reduced as well (Buesser et al., 2009).

The actual effect of the collisional energy dissipation on the particle velocity distribution can be examined from first principles using Brownian dynamics simulations. The simulation methodology developed in our previous work (Trzeciak, 2012; Trzeciak et al., 2004, 2006) is suitable for this purpose, but it needs to be modified slightly to account for the dissipative nature of collisions.

In the original algorithm the thermal equilibrium between the particles and the suspending fluid was forcefully maintained at all times by sampling particle post-collision velocities from the Maxwellian distribution. Instead, these velocities can be calculated from the law of momentum conservation. For two particles a and b of mass m_a and m_b and of velocity $\mathbf{v}_a$ and $\mathbf{v}_b$, their post-collision velocity $\mathbf{v}_{ab}$ will be

$$(m_a+m_b)\mathbf{v}_{ab} = m_a\mathbf{v}_a + m_b\mathbf{v}_b \tag{1}$$

With the above change in the simulation algorithm, particles are no longer artificially constrained to the thermal equilibrium with the background fluid and their velocity can develop in a physically driven manner.

In Fig. 1 velocity distributions are shown that were obtained for platinum particles (density $\rho_p = 21.45\ \mathrm{g\ cm^{-3}}$) coagulating at 10% volume fraction and in air at standard conditions (1 atm, 20 °C). With decreasing particle diameter d_p, the velocity distributions become increasingly more narrow as compared to a reference, thermally equilibrated system. This is indeed consistent with the forgoing argumentation of particles slowing down when the characteristic coagulation time $\tau_K = (KC)^{-1}$ becomes shorter than the particle relaxation time $\tau_p = \beta^{-1}$, where $\beta = \zeta/m_p$ is the mass specific friction coefficient, i.e., the friction coefficient ζ per particle mass m_p, K is the coagulation coefficient and C is the particle number concentration. The characteristic bell shape of the Maxwell distribution is approximately retained, however, despite this decrease in the distribution width.

One can expect that the reduction in average particle velocity due to the non-equilibrium thermal state should depend somehow on the ratio of the characteristic times $\tau_K/\tau_p = \beta/KC$. Let us consider the motion of a single particle in the time period between collisions. This motion is governed by the Langevin equations, which can be integrated to obtain the particle velocity (Chandrasekhar, 1943; Ermak & Buckholz, 1980; Podgórski, 2001):

$$\mathbf{v} = \mathbf{v}_0 e^{-\beta t} + \mathbf{G}_v \sqrt{\frac{k_B T'}{m_p}\left(1 - e^{-2\beta t}\right)} \tag{2}$$

where t denotes the time counted from the last collision, $\mathbf{v}_0$ is the initial particle velocity, k_B is the Boltzmann constant, T' is the gas temperature increased due to the energy dissipated in collisions and G_v is a vector of independent random numbers drawn from the standard normal distribution.