Power-Law Growth of Liquid- and Crystal-Droplets in Highly Charged Colloidal Suspensions

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Brownian coagulation of droplets has been attracting wide attention in various systems, such as emulsions, alloys, and suspensions [1]. Recently, we have performed the simulations on dilute suspensions of highly charged colloids with the effective Tokuyama potential [2] and found that depending on valency of charge, there exist three kinds of phases; a gas phase for lower charges, a liquid-droplet phase for medium charges, and a crystal-droplet phase for higher charges [3]. In this paper, we discuss the dynamics of droplet growth in droplet phases, which is described by a Brownian coagulation. Thus, the average radius $R(t)$ of the droplets is shown to obey the same power-law growth in time as $R(t) \sim t^{1/6}$, while the number $n(t)$ of colloidal droplets decreases in time as $n(t) \sim t^{-1/2}$ since the total volume of droplets is conserved.

We consider a three dimensional suspension, which consists of N colloidal particles with valency of bare charge Z and radius a and N_c counterions with valency of charge q and radius a_c in an equilibrium solvent with a dielectric constant ϵ and a viscosity η at temperature T, where the total volume of the system is given by V. Here $Z \gg q > 0$ and $a \gg a_c$. The global charge neutrality also requires that $NZ - N_c q = 0$. The volume fraction of the colloidal particles ϕ is given by $\phi = \frac{4\pi}{3}a^3(N/V)$. The position vector $\boldsymbol{r}_i(t)$ of colloid i is then described by the Langevin-type equation on the time scale of $t_D(= a^2/D_0)$

$$\frac{d}{dt}\boldsymbol{r}_i(t) = \sum_{j\neq i}^{N} \boldsymbol{F}_T(\boldsymbol{r}_{ij}(t)) + \boldsymbol{R}_i(t), \tag{1}$$

with the effective Tokuyama force between colloidal particles given by [2]

$$\boldsymbol{F}_T(\boldsymbol{r}) \;=\; D_0\Gamma^2 a^2\left[\left(\frac{Z}{q}\right)^2 e^{-r/\lambda_m} - e^{-r/\lambda}\right]\frac{\boldsymbol{r}}{r^4}, \tag{2}$$

where $D_0(= k_BT/6\pi\eta a)$ is a diffusion constant of a single colloid, $\Gamma(= Zql_B/a)$ a coupling parameter, $\lambda(= a/(3\phi\ \Gamma)^{1/2})$ the Debye screening length, $\lambda_m = (q/Z)^{1/2}\lambda$, $\boldsymbol{r}_{ij} = \boldsymbol{r}_i - \boldsymbol{r}_j$, and $r_{ij} = |\boldsymbol{r}_{ij}|$. Here l_B $(= e^2/\epsilon k_BT)$ is the Bjerrum length and k_B the Boltzmann constant, where we choose $a = 55.4$nm and $l_B = 7.29$ Å at room temperature $T = 293$ K here. The random velocity $\boldsymbol{R}_i(t)$ obeys a Gaussian, Markov process with zero mean and satisfies $< \boldsymbol{R}_i(t)\boldsymbol{R}_j(t') >= 2D_0\delta(t-t')\delta_{i,j}\mathbf{1}$, where the brackets denote the average over an equilibrium ensemble.

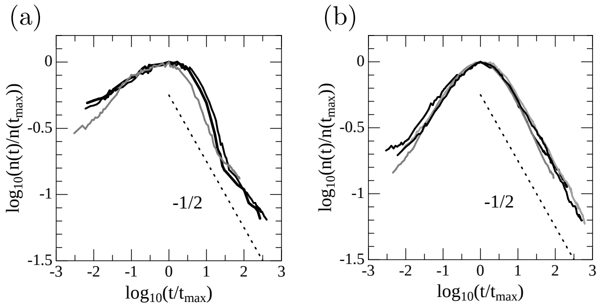

Figure 1: The time dependence of the number of the colloidal droplets. (a) the numerical results for a liquid-droplet phase at $(\phi, Z, q) = (0.003, 400, 2)$, $(0.002, 450, 2)$, and $(0.002, 650, 1)$ (from up to to bottom at the early time stage) and (b) for a solid-droplet phase at $(\phi, Z, q) = (0.001, 850, 1)$, $(0.002, 550, 2)$, $(0.003, 500, 2)$, and $(0, 001, 800, 2)$ (from up to bottom).

In this paper, we assume that the hydrodynamic interactions between colloids can be neglected because of $\phi \ll 1$.

Figure 1 shows a log-log plot of $n(t)$ versus t for two droplet phases. At an initial nucleation stage $n(t)$ increases because the colloids gather to make droplets. After this stage, it starts to decrease because the droplets aggregate each other by a Brownian coagulation, where $n(t)$ behaves differently in both phases because many isolated colloids still exist in a liquid-droplet phase. At the late stage where all isolated colloids disappear, $n(t)$ obeys the power-law decay in time as $n(t) \sim t^{-1/2}$, leading to $R(t) \sim t^{1/6}$. These power laws are different from those obtained in Ostwald ripening, where $R(t) \sim t^{1/3}$ and $n(t) \sim t^{-1}$. The details will be discussed in the meeting.

References

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