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Kinetic Study of the Aggregation of Colloids Immersed in a Binary Mixture of Polymers

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Summary: We consider an assembly of colloidal particles, which are immersed in a binary mixture of polymers. At temperatures close to the critical point of the free mixture, the fluctuations of the composition induce a critical Casimir force between colloids. This force naturally depends on their distance and it is responsible for the colloidal aggregation. In this paper, we propose to study the kinetics of such a transition leading colloids from a dispersed phase (gas) to a dense one (liquid). This kinetics is studied through the relaxation rate, which is a function of the transfer wave-vector.

Keywords: colloids; phase separation; polymerization; relaxation; transition

Introduction

Let us consider a low-density assembly of colloidal particles, immersed in a critical mixture of two polymers A and B, of different chemical nature, as illustrated in Figure 1.

We assume that, near the critical temperature T_c, the colloids preferentially adsorb one polymer, saying A. Then, we are in the presence of a *critical adsorption*. Consequently, the particles aggregate in the non-preferred B-rich phase. For instance, the system could be a hydrogenated polyolefin-deuterated polyolefin mixture incorporating silicones particles, as considered in many recent experiments by Wendlandt and coworkers.[1] The computed Casimir force[2–4] decays with the interparticle distance r, according to r^{-3}.

In this paper, we study the kinetics of the colloidal aggregation which is a phase transition driving colloids from dispersed to dense phases, like the gas-liquid transition for fluids. The kinetics is especially concerned with the variation with time of the order parameter or other quantities varying slowly near the critical point. As result, we determine the time dependence of the shift of the order parameter from the equilibrium state.

The Model

To study thermodynamics of colloidal aggregation, we need the introduction of an order parameter φ. The latter is nothing else but the difference between the composition and its critical value that is $\frac{1}{2}$. The starting point is the Landau free energy of colloids[4,5]

$$\frac{F[\varphi]}{k_B T} = \frac{F_0}{k_B T} + \frac{a}{2}\varphi^2 + \frac{b}{4}\varphi^4 \tag{1}$$

With the notations

$$a = \frac{2-u}{2}, \quad b = \frac{1}{3} \tag{1a}$$

Here, u is the interaction parameter, which is simply the integral over space of the effective pair-potential between particles. This writes as[4]

$$u = -\frac{1}{V}\int \frac{U(r)}{k_B T} dr, \tag{1b}$$

where V is the volume of the colloidal solution, and $U(r)$ the effective pair-potential

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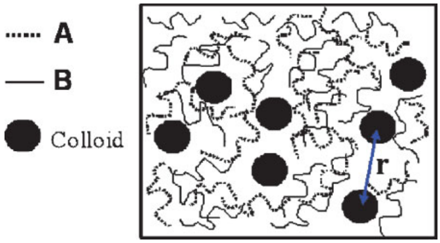

Figure 1.
An assembly of colloidal particles, immersed in a critical mixture of two polymers A and B, of different chemical nature.

between particles. The latter reads[4]

$$\frac{U(r)}{k_B T} = -\frac{32\pi^2}{27} N \left(\frac{d_0}{r}\right)^2 e^{-r/\xi_t} \tag{1c}$$

In this formula, N is the polymerization degree, $d_0 = 2R$ is the particle diameter, and ξ_t the thermal correlation length

The equilibrium order parameter $\overline{\varphi}$ can be obtained minimizing the above free energy, i.e.

$$\left.\frac{\delta F}{\delta \varphi}\right|_{\varphi=\overline{\varphi}} = 0. \tag{2}$$

This gives

$$\overline{\varphi} = \begin{cases} \sqrt{-\frac{a}{b}}, & (a < 0), \\ 0 & (a > 0). \end{cases} \tag{3}$$

The Relaxation Time

Assume that, in the beginning, the mixture in an equilibrium state at an initial temperature T_i different from T_c. Suppose that this temperature is changed to a final value T_f very close to the critical point T_c. In this temperature range, the order parameter, $\varphi(t)$, vary with time t. We are interested in how this order parameter relaxes from the initial value to a final one. The time necessary for the passage $\overline{\varphi_i} \to \overline{\varphi_f}$ is called "relaxation time", denoted τ.

To study the kinetics, one uses the Langevin equations (without noise)[6]

$$\frac{d\varphi}{dt} = -\Gamma \frac{\partial F}{\partial \varphi}, \tag{4}$$

where Γ is some positive constant and F the static free energy, relation (1). We use the following decomposition

$$\varphi = \overline{\varphi} + \delta\varphi. \tag{5}$$

Here, $\delta\varphi$ is the fluctuation of the order parameter from its equilibrium value $\overline{\varphi}$. The shift of the order parameter then satisfies the linear equation

$$\frac{d\delta\varphi}{dt} = -\Gamma \left.\frac{\partial^2 F}{\partial \varphi^2}\right|_{\varphi=\overline{\varphi}} \delta\varphi. \tag{6}$$

The solution to this linear equation is

$$\delta\varphi(t) = A e^{-t/\tau}, \tag{7}$$

where A is a known amplitude, and τ the relaxation time we find to be given by

$$\tau^{-1} = \Gamma(a + 3b\overline{\varphi}^2) \tag{8}$$

Combining relations (3) and (8), we find

$$\tau^{-1} = \Gamma \frac{1}{V} \frac{64}{27} \pi^2 N d_0^2 (\xi_t^2 - \xi_{t^*}^2), \tag{9}$$

with ξ_{t^*} the correlation length at the critical temperature T^* of the colloidal aggregation (different from T_c).

This relation shows the explicit dependence the relaxation time upon colloid geometry, through their radius R, and the chains characteristics through the polymerisation degree N.

Thus, the relaxation time diverges at the spinodal temperature T^* of the colloidal aggregation, i.e.

$$\tau \propto |T - T^*|^{-y_0}, \quad y_0 = 1. \tag{10}$$

It is noted that the divergence of the relaxation time is a signature a phase transition.

Spatial Fluctuations Effects

We note that the above considerations ignore the spatial fluctuations of the order parameter. The purpose, now, is to show how these can affect the relaxation time. The kinetics will be described in term of the relaxation rate. To this end, we first replace the Landau free energy (1) by the Ornstein-

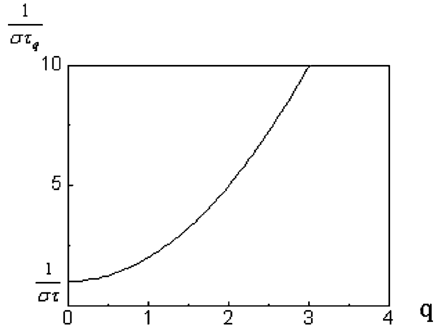

Figure 2.
The inverse of the relaxation rate (characteristic frequency) upon wave –vector.

Zernike one, defined as usual by[7,8]

$$\frac{F[\varphi(r)]}{k_B T} = \int dr \left\{ \frac{1}{2}(\nabla\varphi)^2 + \frac{a}{2}\varphi^2 + \frac{b}{4}\varphi^4 \right\}(r). \tag{11}$$

The gradient term traduces the spatial variation of the order parameter. There, r is the d-dimensional position vector.

The equilibrium order parameter can be obtained by minimizing the above free energy. The result reads

$$-\Delta\varphi + a\varphi + b\varphi^3 = 0. \tag{12}$$

By using the decomposition (5), the equation of composition fluctuation is

$$\frac{d\delta\varphi}{dt} = -\Gamma\left[-\Delta + a + 3b\overline{\varphi}^2\right]\delta\varphi. \tag{13}$$

This equation can be easily solved in reciprocal apace. The expression of the Fourier transform of the composition fluctuation reads

$$\delta\varphi_q(t) = \delta\varphi_q(0)e^{-t/\tau_q}, \tag{14}$$

With the relaxation rate τ_q

$$\tau_q^{-1} = \Gamma q^2 + \tau^{-1}, \tag{15}$$

Where τ is the relaxation time, relation (8). The relaxation rate upon wave-vector is depicted in Figure 2

Conclusion

In this work, we developed a kinetic study of the colloidal aggregation, which is a phase transition driving colloids from a dispersed phase to a dense one, when the temperature is changed from an initial value T_i towards a final one T_f very close to the critical point of the free polymer mixture. We have derived the time dependence of the shift of the order parameter from its equilibrium state. We found that this function exponentially decreases in time, with a relaxation time τ diverging at the critical temperature T^* of the colloidal system trapped in a critical polymer blend.

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