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Dynamic study of the aggregation of nanoparticles immersed in a ternary mixture of polymers

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Abstract

The physical system we consider is a ternary polymers solution made by two chemically incompatible polymers and a good solvent. The mixture is assumed to be in the presence of identical nanoparticles. 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 is responsible for the colloidal aggregation. In this paper, we propose to study the dynamics of such transition leading colloids from dispersed phase to dense phase, like the gas-liquid transition for fluids. Using field theory, we compute the relaxation rate of this transition. In the order to understand the solvent role effect on the relaxation rate, we compare the obtained results of the binary polymer mixture and those of the ternary polymer solution.

Keywords: Polymer, colloid, aggregation, transition, relaxation time, solvent, ternary solution, nanoparticles.

1. Introduction

In order to study the kinetic of colloidal aggregation [3,4], the physical system considered by the authors of article [12] is 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 Fig.1

Assume that, in the beginning, the mixture in an equilibrium state at an initial temperature T_i different from T_c. We suppose that this temperature is changed to a final value T_f very close to T_c. In this temperature range, the order parameter, φ(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 $\overline{\varphi_i} \rightarrow \overline{\varphi_f}$ is called "relaxation time", denoted τ.

The starting point is the Landau free energy of colloids [4,5,16, 19]

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

With the notations

$$a = \frac{2-\Gamma}{2} \propto t - t^* , \qquad b = \frac{1}{3}, \qquad t^* = T^* - T_c \qquad (1a)$$

Here, Γ is the interaction parameter, T* is the critical temperature of the aggregation, T_c is the temperature of consolute point of the free mixture.

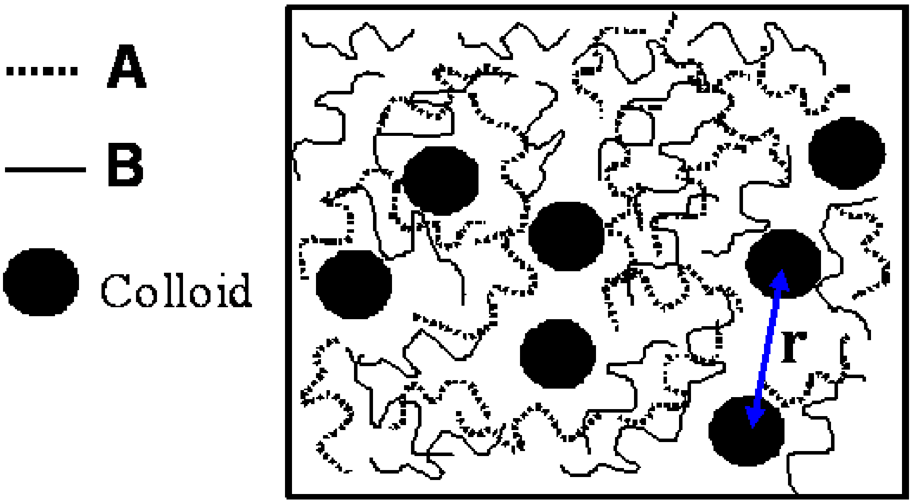


Fig.1: An assembly of colloidal particles, immersed in a critical mixture of two polymers A and B, of different chemical nature

Explicitly the relaxation time is written like below: [9,11, 12]:

$$\boldsymbol{\tau^{-1} = \sigma \frac{1}{V}\frac{64}{27}\pi^2 N d_0^2\left(\xi_t^2 - \xi_{t*}^2\right)} \qquad (2)$$

$\boldsymbol{\sigma}$ is a some positive constant, $\boldsymbol{d_0 = 2R}$ is the particle diameter and $\boldsymbol{V}$ is the volume of the colloidal solution.

With ξ_{t^*} is the correlation length at the critical temperature T* of the colloidal aggregation (different from Tc).
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. [8,17, 21]

$$\tau \propto \left|T - T^*\right|^{-y_0}, \qquad y_0 = 1 \qquad (3)$$

It is noted that the divergence of the relaxation time is a signature of a phase transition.
We note that the above considerations ignore the spatial fluctuations of the order parameter. In this case the dynamic of colloids will be described in term of the relaxation rate.
If we take into account the spatial fluctuations, the relaxation rate τ_q is written as below:

$$\tau_q^{-1} = \sigma q^2 + \tau^{-1} \qquad (4)$$

Where $\boldsymbol{\tau}$ is the relaxation time, relation (2). The inverse of the relaxation rate upon wave-vector is depicted in Fig. 2

2. The blob model

We consider a low-density assembly of colloidal particles immersed in a mixture of two incompatible polymers A and B in a common good solvent, close to the critical point T_k. We assume that, near the critical temperature T_k, the colloids preferentially adsorb one polymer, so called A. Then, we are in the presence of a critical adsorption [20, 21]. Consequently, the particles aggregate in the non-preferred B-rich phase. As shown in Refs. [10, 11], the Casimir force in the absence of solvent is less important than that with solvent. The difference comes from the fact that the solvent leads to an additional fluctuations of the monomer concentration [14,18], which are absent in the molten state.

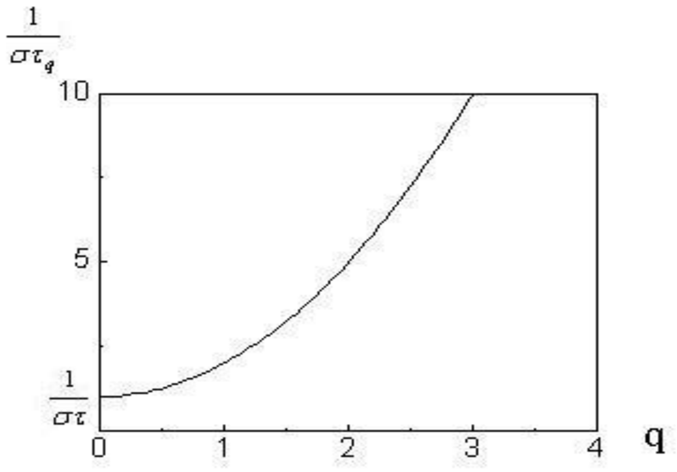


Fig. 2: The inverse of the relaxation rate (characteristic frequency) upon wave –vector

To simplify, we assume that the two polymers A and B have the same polymerization degree N. Thus we are concerned with a monodisperse system. We denote the overall monomer fraction by $\phi = \phi_A + \phi_B$, where ϕ_A and ϕ_B are the respective monomer fractions of A and B-polymers.

In a dilute solution, where the overall monomer fraction ϕ is below the threshold $\phi^* \propto N^{1-d\upsilon}$, $(\upsilon = 0{,}588\,[13]\, in\ d = 3)$, A and B-chains behave like separated swollen coils avoiding completely each other, and in principle no phase separation is expected. In semi dilute solution $(\phi^* \prec\prec \phi \prec\prec 1)$, however, chains overlap and can be viewed as a sequence of uncorrected subunits or blobs of types A and B. Each chain contains $Z(\phi) \propto N\phi^{1/(d\upsilon-1)}$ blobs. The blobs size or screening length, $\xi(\phi)$, depends only on the total monomer fraction ϕ, and scales as [14]: $\boldsymbol{\xi(\phi) \propto l\phi^{\upsilon/(1-d\upsilon)}}$ where l is the monomer size. This model constitutes the so-called blob model who was introduced by de Gennes [14]. We will apply this model to calculate the relaxation time of the colloidal aggregation transition. This is precisely the aim of the next section.

3. Results and discussion

To precise the role of the solvent effect on the relaxation rate, we consider here an assembly of colloidal particles immersed in a ternary polymer solution made of two chemically incompatible polymers A and B, and a good solvent, as illustrated in Fig.3.

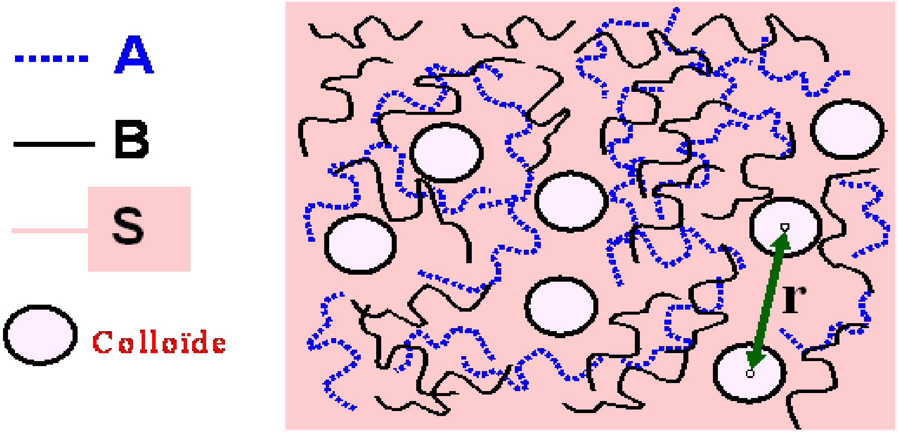
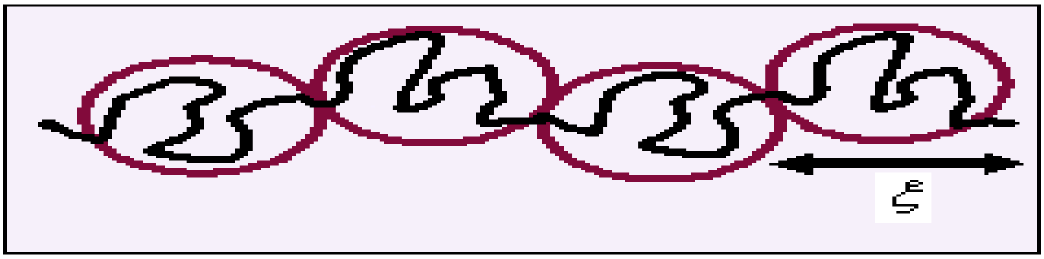


Fig.3: An assembly of colloidal particles, immersed in a ternary mixture of polymers A and B, of different chemical nature.

According to the blob model, each chain in the solution can be regarded as sequences of $Z(\phi)$ blobs of the same size $\xi(\phi)$,



This means that the ternary solution can be regarded as binary solution of blob of types A and B, with the simple substitutions: $l \to \xi(\phi), N \to Z(\phi)$.

Exploiting the results in [12], and using the above substitutions, we find for the relaxation time, τ',

$$\tau'^{-1} = \sigma \frac{1}{V} \frac{64}{27} \pi^2 N \phi^{5/4} d_0^2 (\xi_t^2 - \xi_{t^*}^2) \qquad (5)$$

Combining now expression (5) in the expression (2), we have:

$$\tau' = \tau \phi^{-5/4} \qquad (6)$$

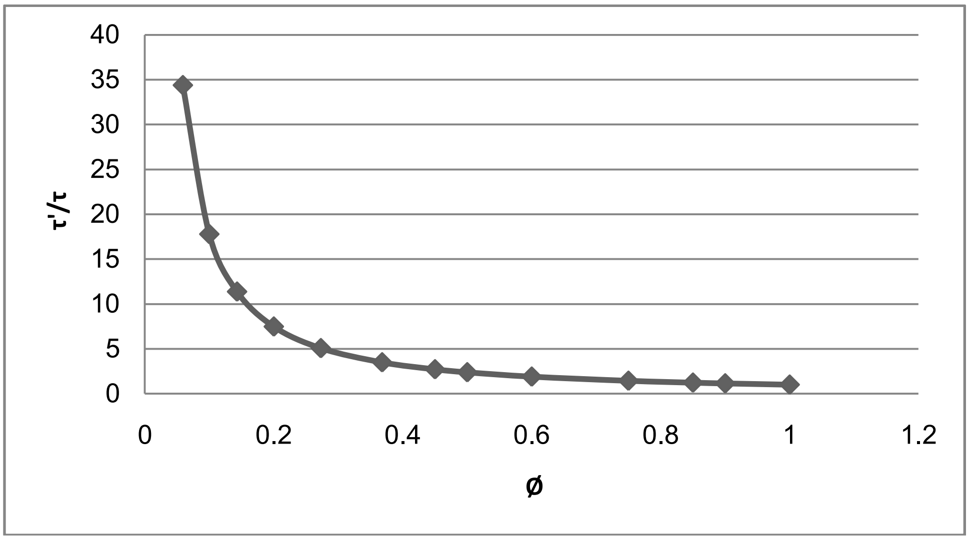


Fig.4: The variation of the ratio τ'/τ according to the concentration ϕ.

We note according this graph that the ratio τ'/τ takes very large values for small values of ϕ. When ϕ=1, τ'=τ. Thus, the relaxation time in the absence of solvent is less important than with solvent. Indeed, the interactions between the nanoparticles are more important because of the increased importance of the Casimir force [1,2 ,6,15] with the presence of the solvent. So, the fluctuations of the monomer concentration are increased, provided that the ternary polymer solution remains semi-dilute [7]. In the limit $\phi \to 1$, the results corresponding to the molten state are recovered.

If we take into account of the spatial fluctuations, the relaxation rate τ_q is not affected, in a qualitative way, by the presence of the solvent, we can write:

$$\tau'_q{}^{-1} = \sigma q^2 + \tau'^{-1} \qquad (7)$$

In this case also the relaxation rate is also more important in a ternary mixture than in a binary mixture.

Conclusion

In this work, we developed a dynamic study of the colloidal aggregation of nanoparticles immersed in a ternary mixture of polymers. In the order to understand the solvent effect on the relaxation rate, we compare the obtained results of the binary polymer mixtures and those of the ternary polymer solution. We found that the relaxation time in the absence of solvent is less important than with solvent. The difference comes from the fact that the solvent leads to the additional fluctuations of the monomer concentration, which absent in the molten state.

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