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Short Communication

Viscoelastic effect on nucleation in semidilute polymer solutions

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Abstract. — We study the growth of droplets consisting mostly of solvent in a metastable semidilute polymer solution. We introduce a modified Gibbs-Thomson relation at the interface which accounts for viscoelastic effects. The growth is much decelerated when the radius is shorter than a long viscoelastic length.

Not enough attention has yet been paid to nucleation phenomena in polymeric systems both theoretically and experimentally, whereas a great number of experiments on spinodal decomposition have been accumulated at present. Krishnamarthy and Bansil [1] performed the first nucleation experiment in a polymer solution near the critical point. They found a large asymmetry between the growth of polymer-rich droplets and that of polymer-poor droplets even not away from the critical point. There, $\Delta T \equiv T_c - T_{cx}$ and $\delta T \equiv T_{cx} - T$ were about 100 mK and 10 mK, respectively, where $T_c$ is the critical temperature and $T_{cx}$ is the temperature on the coexistence curve at a given polymer volume fraction $\phi$. They ascribed this asymmetry to strong concentration-dependence of the viscosity and the diffusion constant. The aim of this letter is then to examine nucleation in a more extreme case of semidilute solutions with poor solvent. We assume that the volume fraction $\phi$ considerably exceeds the overlapping volume fraction $\phi^*$ and entanglement effects are crucial. It is surprising that there seems to be no systematic experiment in such situations.

On the coexistence curve, $T = T_{cx}(\phi)$, a very dilute phase and a semidilute phase can coexist macroscopically with almost vanishing osmotic pressure $\pi_{cx} \cong 0$ [2]. If the temperature $T$ is slightly lowered and the deviation $\delta T = T_{cx} - T$ is increased with $\phi$ held fixed, we enter into a metastable region where droplets consisting mostly of solvent emerge. The so-called supersaturation $\Delta$ is defined by $\Delta = (\phi^{(1)}_{cx} - \phi)/(\phi^{(1)}_{cx} - \phi^{(2)}_{cx})$, where $\phi^{(1)}_{cx} (> \phi^*)$ and $\phi^{(2)}_{cx} (\cong 0)$ are the volume fractions on the coexistence curve at the temperature $T$. The osmotic pressure deviation $\pi - \pi_{cx}$ of the metastable solution is slightly negative and the critical radius is given by

$$R_c = 2\gamma/(\pi_{cx} - \pi) \cong 2\gamma/\left[\phi \left(\frac{\partial \pi}{\partial \phi}\right)_T \Delta \right]$$

(1)
where $\gamma$ is the surface tension. The scaling theory [2] shows that $\gamma \sim k_B T/\xi_b^2$ and $\phi(\partial \pi/\partial \phi)_T \sim k_B T/\xi_b^3$, where $\xi_b$ is the blob size inversely proportional to $\phi$ in poor solvent, so that we find $R_c \sim \xi_b/\Delta$. In terms of the interaction parameter $\chi$ [2] we have $\phi^{(1)} \equiv 3(\chi - \frac{1}{2})$ and $\Delta \equiv 3 |\partial \chi/\partial T| \delta T/\phi \approx \delta T/\Delta T$, which are valid at volume fractions considerably larger than $\phi^*$. The free energy to produce a critical droplet is then of order $(\pi_{cx} - \pi)R_c^3 \sim k_B T/\Delta^2$ as in usual low-molecular-weight fluids.

However, we expect anomalous viscoelastic effects on the droplet growth when the droplet radius $R$ is shorter than a characteristic length $\xi_{ve}$. This is because chain deformations around droplets should take place with a long rheological relaxation time $\tau$ and give rise to a large viscoelastic stress. Note that the usual Lifshitz-Slyozov theory [3] neglects such viscoelastic effects and predicts that the droplet radius $R$ obeys

$$ R \frac{\partial R}{\partial t} = 2Dd_0 \left( \frac{1}{R_c} - \frac{1}{R} \right) \quad (2) $$

where $D$ is the diffusion constant and $d_0$ is the capillary length. In polymer solutions $Dd_0$ is of order $k_B T/\eta_b$, where $\eta_b$ is the solvent viscosity. Then, if (2) were used in our case, small droplets would change on time scales even shorter than $\tau$. In fact, the rate $|\partial (\ln R)/\partial t|$ is of order $Dd_0/R^2$ for $R < R_c$ and exceeds $1/\tau$ with decreasing $R$.

We shall see that most important in our problem is the boundary condition at the interface between the two phases. We propose the following modified Gibbs-Thomson relation at the interface,

$$ \pi - \pi_{cx} - \sigma_n + \gamma \kappa = 0 \quad (3) $$

where $\pi = \phi \partial f/\partial \phi - f$ is the osmotic pressure of the solution, $f$ being the free energy density, $\pi_{cx}$ ($\equiv 0$) is its value on the coexistence curve, and $\kappa$ is the curvature at the interface. The $\sigma_n$ is the normal component of the network stress $\vec{\sigma}$ at the interface,

$$ \sigma_n = \vec{n} \cdot \vec{\sigma} \cdot \vec{n} \quad (4) $$
n being the normal unit vector. Notice that (3) is established for polymer gels [4] in which $\vec{\sigma}$ arises from permanent crosslinkages. (In Ref. [4], $\sigma_n$ is included into the definition of $\pi$ itself). In solutions, however, entanglements are transient and have life times of order $\tau$. We assume (3) in semidilute solutions even when the interface is moving on time scales longer than $\tau$. Therefore (3) is not an obvious relation. We will further comment on (3) around (16) to follow.

Recently use has been made of a two-fluid model for polymer and solvent to study dynamic coupling between stress and diffusion [5-8]. It describes dynamics of semidilute solutions and gels in a unified framework. For simplicity we assume that the polymer and solvent have the same specific volume and the total mass density $\rho$ is a constant. Let $v_p$ and $v_s$ be the velocities of polymer and solvent and $v = \phi v_p + (1 - \phi)v_s$ be the average velocity. Considering only slow disturbances and neglecting temperature inhomogeneities, we assume dynamic equations,

$$ \frac{\partial \phi}{\partial t} = -\nabla \cdot (\phi v_p) \quad (5) $$

$$ v_p - v = \zeta^{-1}(-\nabla \pi + \nabla \cdot \vec{\sigma}) \quad (6) $$

$$ \rho \frac{\partial v}{\partial t} = -\nabla (p_s + \pi) + \nabla \cdot \vec{\sigma} \quad (7) $$

where $\zeta$ is the friction constant of order $\eta_b \xi_b^{-2}$, $\eta_b$ being the solvent viscosity. The $p_s$ has the meaning of the solvent chemical potential multiplied by $\rho$ and here play the role of ensuring
the incompressibility condition \( \nabla \cdot v = 0 \). The total stress tensor in the solution is therefore equal to \((p_s + \pi)\delta_{ij} - \sigma_{ij}\).

In the linear regime the network stress \( \sigma_{ij} \) may be expressed in terms of \( \nabla v_p \) \cite{5, 8} as

\[
\sigma_{ij} = \eta \left( \frac{\partial}{\partial x_i} v_{pj} + \frac{\partial}{\partial x_j} v_{pi} - \frac{2}{3} \delta_{ij} \nabla \cdot v_p \right),
\]

where \( \eta \) is the viscosity of the solution due to entanglements much greater than \( \eta_s \). We shall find that the droplet radius \( R \) changes with rates much slower than \( 1/\tau \) even for small \( R \), so we will neglect the frequency-dependence of \( \eta \). Because \( \nabla \cdot \mathbf{a} = \eta (\nabla^2 v_p + \frac{1}{3} \nabla \nabla \cdot v_p) \) and \( \phi \nabla \cdot v_p = -\frac{\partial}{\partial t} \delta \phi \) for small deviations, we may linearize \( (5) \) in the form \cite{8},

\[
\frac{\partial}{\partial t} \delta \phi = D \nabla^2 \delta \phi + \xi_{ve}^2 \nabla^2 \frac{\partial}{\partial t} \delta \phi,
\]

where

\[
D = \zeta^{-1} \phi \left( \frac{\partial \pi}{\partial \phi} \right) ,
\]

\[
\xi_{ve}^2 = \frac{4}{3} \zeta^{-1} \eta
\]

The \( \xi_{ve} \) is a long viscoelastic length of order

\[
\xi_{ve} \sim \xi_{b} (\eta/\eta_s)^{1/2} \gg \xi_{b}
\]

which can well exceed the critical radius \( R_c \sim \xi_{b}/\Delta \) for \( \Delta^2 \eta/\eta_s > 1 \).

We then set up boundary conditions other than \( (3) \). From conservation of polymer the interface velocity \( v_a \) and the polymer velocity \( v_p \) must coincide at the interface in the normal direction,

\[
v_a \ n = v_p \ n
\]

On the other hand, the average velocity \( v \) is continuous at the interface in the normal direction from conservation of polymer + solvent. In particular, we must have \( v = 0 \) around an isolated spherical droplet from \( \nabla \cdot v = 0 \). The stress balance at the interface yields

\[
p_s + \pi - \sigma_n + \gamma \kappa = p_s^0 + \pi_{cx},
\]

\[
\sigma \cdot n = \sigma_n n,
\]

where \( p_s^0 \) is the pressure inside the droplet and its deviation is equal to the chemical potential deviation multiplied by \( \rho \). The second relation \( (15) \) means that the shear stress on the interface vanishes, which is valid in the limit \( \eta >> \eta_s \). Note that \( (14) \) naturally leads to \( (3) \) if we further assume

\[
p_s = p_s^0
\]

at the interface. This is equivalent to assuming the continuity of the solvent chemical potential.

Usually the concentration field around a droplet is calculated using the quasi-static approximation, \( \nabla^2 \phi = 0 \), which is justified for small supersaturations \cite{3}. Our equations are complicated and such simplifying approximations are still more required to reach simple results. To this end we first treat an instructive example which allows analytic calculations. That
is, we consider growth of a spherical droplet with radius \( R \) very close to the critical radius \( R_c \). Then \( \delta R = R - R_c \) grows exponentially as

\[
\delta R = (\delta R)_0 \exp(\Gamma_c t) , \tag{17}
\]

and the other deviations also grow exponentially with the same \( \Gamma_c \). In this spherical case we have \( v = 0 \) and \( \sigma_{ij} = \sigma_n(\frac{3}{2} r^{-2} x_i x_j - \frac{1}{2} \delta_{ij}) \) with \( \sigma_n = (4 \eta/3)(\partial v_p/\partial r - v_p/r) \), where \( v_p \) is the radial component of \( v_p \). From (9) we find \( \delta \phi \propto \exp(-\kappa r)/r \) with

\[
\kappa^2 = \Gamma_c/(D + \xi_{ve}^2 \Gamma_c) \tag{18}
\]

The \( v_p \) is obtained from (5) in the form,

\[
v_p = (\Gamma_c/\kappa \phi)(1 + \frac{1}{\kappa r}) \delta \phi , \tag{19}
\]

and \( \sigma_n \) is calculated from \( \sigma_n = -(4 \eta/3)(\Gamma \delta \phi/\phi + 3 v_p/r) \). The boundary condition (13) yields \( \Gamma \delta R = v_p \) at \( r = R \), and (3) finally gives

\[
\Gamma_c = \Gamma_{c0}(1 + \kappa R_c) \left[ 1 + 3(1 + \kappa R_c) \frac{\xi_{ve}^2}{R_c^2} \right] , \tag{20}
\]

where \( \Gamma_{c0} = 2Dd_0/R_c^3 \) is the growth rate from the Lifshitz-Slyozov theory, \( d_0 = \gamma/\phi(\partial \pi/\partial \phi) \) being the capillary length of order \( \xi_b \). In our case \( d_0 \) is much shorter than \( R_c \) and \( \xi_{ve} \). Then we may confirm \( \kappa R_c \ll 1 \), irrespectively of the value of \( \xi_{ve}/R_c \), to have

\[
\Gamma_c \simeq \Gamma_{c0} / \left( 1 + 3 \frac{\xi_{ve}^2}{R_c^2} \right) \tag{21}
\]

The inequality \( \kappa R_c \ll 1 \) implies \( \delta \phi \propto 1/r \) or \( \nabla^2 \delta \phi \simeq 0 \), so the quasi-static approximation has been justified even in our case.

More generally, we can check the validity of the quasi-static approximation self-consistently. Namely, we are allowed to set \( \partial \phi/\partial t = 0 \) and \( \partial v_p/\partial t = 0 \) in (5) and (7) around a slowly evolving droplet. Then \( \delta \phi \propto 1/r, \quad v_p \simeq (\partial/\partial t)R^2/r^2, \) and

\[
\sigma_n \simeq 2\eta \frac{\partial}{\partial r} v_p \simeq -4 \eta R^{-1} \frac{\partial}{\partial t} R \tag{22}
\]

at \( r = R \). The semidilute region near the interface is now being uniaxially deformed in the normal direction. Here the deformation rate is much slower than \( 1/r \) and the frequency-dependence of \( \eta \) is negligible, so that the surrounding semi-dilute region behaves as a very viscous fluid. The large size of \( \eta \) can make \( \sigma_n \) important in the present problem. Substitution of (18) into the boundary condition (3) leads to

\[
\frac{\partial}{\partial t} R = 2Dd_0 \left( \frac{1}{R_c} - \frac{1}{R} \right) / \left( R + 3 \xi_{ve}^2 / R \right) \tag{23}
\]

This is the main result in this letter, which reproduces (21) for \( R \simeq R_c \). The Lifshitz-Slyozov theory holds for \( R > 1 \xi_{ve} \), while small droplets with \( R \ll \xi_{ve} \) obey

\[
\frac{\partial}{\partial t} R \simeq \frac{\gamma}{2 \eta} \left( \frac{R}{R_c} - 1 \right) \tag{24}
\]
Therefore, $\delta R = R - R_c$ changes exponentially as (17) even if $\delta R$ is not small. The growth rate is given by

$$\Gamma = \gamma / 2\eta R_c,$$

which is of order $\xi_b / R_c \tau$ and is slower than $1 / \tau$ as expected.

Finally let us consider a slightly deformed sphere, whose radius depends on the polar coordinates $\theta$ and $\psi$ as $r = R + \sum_j \zeta_j Y_j(\theta, \psi) \exp(\omega_j t)$, where $Y_j$ are the spherical harmonic functions. We notice that the anisotropic part $\delta v$ of the polymer velocity is generally expressed as $\delta v = \nabla K + Q r$ from (15), where $K$ and $Q$ are some scalar functions. Again setting $\partial \phi / \partial t = 0$ and $\partial v / \partial t = 0$ in (5) and (7) we may calculate $K$ and $Q$ to arrive at

$$\omega_j = -\frac{(j - 1)}{(2j^2 + 1)} \left[ (2j^2 + 3j + 1) \left( \frac{\gamma}{2\eta R} \right) + \frac{(4j^2 + 9j + 2)}{(j + 2)R} \frac{\partial}{\partial t} R \right]$$

We can show $\omega_j < 0$ for any $j$ and $R$ using (23), so the spherical shape is stable with respect to deformations. Namely, the Mullins-Sekerka (dendritic) instability [9] becomes nonexistent in our case. This is because growth of surface protuberances is much suppressed by the normal stress $\sigma_n$ in (3).

In summary, we have shown the crucial role of the normal stress $\sigma_n$ in the modified Gibbs-Thomson relation (3) in the droplet growth. It is then of interest how droplets deform in shear flow. Our theory should be generalized to polymer blends [8] and to spinodal decomposition processes. The topics in this letter, though special, seems to constitute the simplest starting point to study a broad range of viscoelastic effects on phase separation.

References