

Effects of elasticity on drying processes of polymer solutions

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Drying processes of polymer solutions on a solid substrate are studied, based on the two-fluid model for polymer solutions or gels. A simplified model which can describe a skin formation process is proposed to examine the diffusion process of polymers and the evaporation process of solvent. The authors show that when a skin (gel phase) is formed, the collective diffusion coefficient is greatly enhanced whereas the evaporation of solvent is considerably reduced. These two results originate from the bulk elasticity of polymer gels.

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Drying of polymer solutions or colloid dispersions is a nonequilibrium phenomenon that provides interesting problems such as coffee stain problems [1,2], pattern formation [3–5], skin formation (gelation near free surfaces of polymer solutions), and buckling instabilities [6–8]. In addition to these fundamental interests, it is a rather practical but important issue to know how to control the drying processes in various industrial applications, for example, manufacturing polymer films [10–12], inkjet printing [9], and so on. In order to establish a basis of these technologies, we must understand the underlying physics in the drying phenomena.

Extensive studies [13–19] have been devoted to understanding the drying processes of polymer solutions on a solid substrate. One of the main concerns in these studies is time evolution of the free surface at which the solvent evaporates accompanied by flow of the solution. The flow field is often solved via the lubrication approximation [20] on the assumption that the concentration of polymers is uniform or the variation of concentration is allowed only in the lateral direction. Not so much attention have been paid to the diffusion of polymers in the vertical direction (normal to the free surface). Bornside *et al.* [10] have taken into account the diffusion process in their model of spin coating and predicted numerically the formation of a solid “skin” at the free surface. De Gennes [12] have discussed the concentration profiles and the skin (crust) formation, and estimated the lifetime of the skin, theoretically. These studies show that the diffusion process plays an important role in the whole processes of the drying, especially, in the process of skin formation. However, they are not appropriate to describe the whole process of drying including the skin formation in a single model system.

Recently, we have proposed a simple model which describes the diffusion in the skin formation process and obtained a criterion for the skin to be formed [19]. This model gives an essence of the drying process in heuristic manner but includes some ad hoc assumptions. A crucial point in this model is that the collective diffusion coefficient in the skin is quite large so that the concentration of polymers is almost constant in that region. However, this assumption seems to contradict our intuition that the dynamics slows down when a skin is formed. Indeed, some experiments [6,7,21] imply that the evaporation rate of solvent greatly reduced after a skin forms.

In this paper we point out that these two things, namely, the increase of the diffusion coefficient and the decrease of

the evaporation rate are not inconsistent with each other but a result of an elastic effect due to the great increase of the bulk osmotic modulus in a skin. In the following, we construct a model from a unified point of view in which the elastic effect is taken into account and demonstrate that the collective diffusion coefficient greatly increases in a skin and the evaporation rate of solvent dramatically decreases as a result of the elastic effect.

Here we consider an isothermal system of a polymer solution extended on a solid substrate whose normal lies on the z axis (Fig. 1). In a drying process, we assume that only the solvent evaporates at the free surfaces $z=h(t)$ and the volume fraction ϕ of polymers near the free surface increases in time t . When ϕ at $z=h$ reaches a certain value, ϕ_g , a thin gellike layer, called a skin, is formed near the free surface.

The above dynamical processes can be described by the two-fluid model [22,23] for polymer solutions or gels with appropriate boundary conditions discussed later. One of the key concepts in the two-fluid model is the stress-diffusion coupling which is expressed as, in the absence of mean flow,

$$\frac{\partial \phi}{\partial t} = \nabla \cdot \left[\frac{\phi^2(1-\phi)^2}{\zeta} \left(\nabla \frac{\delta F_m}{\delta \phi} - \frac{\nabla \cdot \boldsymbol{\sigma}}{\phi} \right) \right], \quad (1)$$

where ζ is the friction coefficient between polymers and solvent and, in general, depends on ϕ . We, however, regard it as a constant throughout in this paper, for simplicity. F_m in Eq.

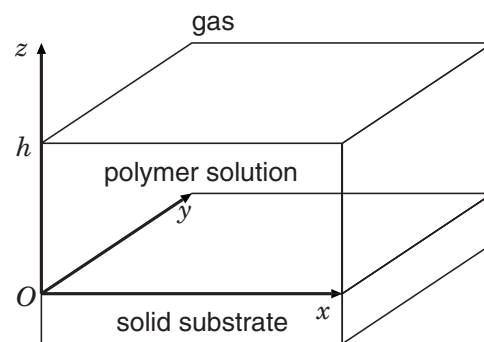


FIG. 1. Geometry and coordinates of our model system. A polymer solution is spread on a solid substrate and the solvent evaporates from the free surface at $z=h$. The system is homogeneous in x and y directions.

(1) is the mixing free energy of the polymer solution which is usually given by the functional form as

$$F_m = \int dr \left[\frac{C}{2} (\nabla \phi)^2 + f(\phi) \right] \quad (2)$$

with a constant C and the free energy density $f(\phi)$ of the Flory-Huggins type. In the limit of large polymerization index, $f(\phi)$ is given by

$$f(\phi) = \frac{k_B T}{v_1} [(1 - \phi) \ln(1 - \phi) + \chi \phi(1 - \phi)], \quad (3)$$

where T is the temperature, k_B the Boltzmann constant, v_1 the volume of a monomer, and χ the Flory-Huggins interaction parameter. Hereafter we neglect the gradient term in Eq. (2), provided that neither phase separation nor volume-phase transition occur. In a system of high volume fraction (ϕ), especially in a gel, the elastic free energy due to polymer networks enters the total free energy and affects the dynamics of ϕ , since fluctuations of ϕ inevitably involves deformation of the polymer networks. This gives rise to the elastic stress term in the dynamical equation of ϕ . The last term in Eq. (1) shows the dynamical coupling between the elastic stress and the diffusion, that is, the stress σ due to the polymer networks yields the diffusion flux of ϕ . It should be emphasized that the ‘‘diffusion’’ here expresses a collective motion of polymer networks and does not mean the self-diffusion of a single molecule.

Now we assume that all quantities are homogeneous in x and y directions. In this case, Eq. (1) can be recast into a one-dimensional diffusion equation given as

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z} \left[A(\phi) \frac{\partial \phi}{\partial z} \right], \quad (4)$$

with the collective diffusion coefficient

$$A(\phi) = \frac{\phi^2(1 - \phi)^2}{\zeta} \left[f''(\phi) + \frac{\kappa(\phi)}{\phi^2} \right], \quad (5)$$

where $f''(\phi) \equiv d^2 f(\phi)/d\phi^2$, $\kappa(\phi) \equiv -\phi \partial \sigma_{zz} / \partial \phi$ is the elastic contribution of the bulk osmotic modulus. Since in the gel phase ($\phi > \phi_g$) a permanent elasticity appears whereas in the solution ($\phi < \phi_g$) the elastic stress rapidly relaxes in the time scale of observation, we may use an approximate expression [24] for the bulk modulus as

$$\kappa(\phi) = K_g \theta(\phi - \phi_g), \quad (6)$$

where $K_g > 0$ is the bulk osmotic modulus in the gel which is quite large compared with that in the solution and $\theta(x) = 0$ (for $x < 0$) or 1 (otherwise) is the step function. Here we should note that the collective diffusion coefficient $A(\phi)$ is enhanced in the gel phase due to the elastic effect.

Next consider the evaporation process of the solvent. We assume that there is a fixed diffusion layer near the free surface in the gas phase so that the evaporation process is controlled by the diffusion of the solvent molecules in the diffusion layer. Furthermore, we assume a local equilibrium at the free surface, that is, the chemical potential of the solvent molecules is continuous: $\mu_s = \mu_v$ at $z = h$, where μ_s and

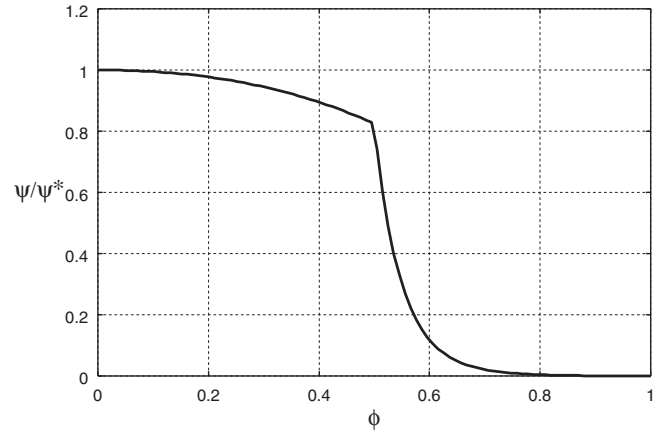


FIG. 2. Relative number density of solvent molecules ψ/ψ^* just above the free surface ($z=h+0$) is plotted as a function of the volume fraction of polymers ϕ just below the free surface ($z=h-0$) for $\chi=0$, $\hat{K}_g=10$, and $\phi_g=0.5$.

μ_v are the chemical potentials of the solvent molecules in the solution and gas phases, respectively. The chemical potential of the gas phase can be written as

$$\mu_v = k_B T \ln \frac{p}{p^*}, \quad (7)$$

where p is the partial pressure of solvent molecules in the gas phase and p^* the saturated vapor pressure of pure solvent. The chemical potential of the solvent in the solution or gel phase is related to the osmotic pressure Π via the relation $\mu_s = -v_1 \Pi$. Using Eqs. (3) and (6), we obtain [24]

$$\mu_s = k_B T [\ln(1 - \phi) + \phi + \chi \phi^2] - v_1 \kappa(\phi) \ln(\phi/\phi_g). \quad (8)$$

From Eqs. (7) and (8) and introducing a number density of the solvent molecules $\psi \equiv p v_1 / (k_B T)$, we obtain the local equilibrium condition ($\mu_v = \mu_s$) as a relation between ϕ and ψ at the interface ($z=h$),

$$\psi/\psi^* = (1 - \phi) \exp[\phi + \chi \phi^2 - \hat{\kappa}(\phi) \ln(\phi/\phi_g)], \quad (9)$$

where $\hat{\kappa}(\phi) \equiv v_1 \kappa(\phi) / (k_B T)$. In Eq. (9) ψ and ϕ should be evaluated at just above ($z=h+0$) and below ($z=h-0$) the interface, respectively. In Fig. 2 we plot ψ/ψ^* as a function of ϕ for $\chi=0$, $K_g=10$, and $\phi_g=0.5$. We find that the ψ/ψ^* is extensively reduced in $\phi > \phi_g$, which is consistent with a recent experiment [21]. This is due to the elastic effect in the gel phase. The above argument have been made by Leibler and Sekimoto [24] on the sorption of gases and liquids in glassy polymers.

Based on the above consideration, we now construct a model system of the drying process as follows. The total system with size L is composed of two regions. One is the liquid region ($0 < z < h$) where the polymer solutions or gels exist and the polymer volume fraction ϕ obeys Eq. (4). The other is the gas region ($h < z < L$) where the diffusion of vapor of the solution takes place in the air and the number density ψ of the solvent molecules follows the simple diffusion equation

$$\frac{\partial \psi}{\partial t} = D_a \frac{\partial^2 \psi}{\partial z^2} \quad (10)$$

with a diffusion constant D_a .

The boundary conditions for Eqs. (4) and (10) are given as follows. On the substrate ($z=0$) we impose no flux condition:

$$\frac{\partial \phi}{\partial z} = 0 \quad \text{at } z=0. \quad (11)$$

At $z=L$ the system is in contact with a kind of reservoir with a constant number density ψ_∞ of the solvent molecules

$$\psi = \psi_\infty \quad \text{at } z=L. \quad (12)$$

Hence there is a finite flux $\mathcal{J}_L \equiv -D_a(\partial\psi/\partial z)_{z=L}$ in the drying process.

Boundary conditions at the interface and equation of motion of $h=h(t)$ can be derived from the conservation laws of polymers and solvent which are expressed as

$$\frac{d}{dt} \int_0^h dz \phi(z,t) = 0, \quad (13)$$

$$\frac{d}{dt} \int_0^L dz \psi(z,t) = -\mathcal{J}_L. \quad (14)$$

From these equations and the incompressibility condition $\phi + v_1\psi = 1$ in $0 < z < h$, we obtain

$$\dot{h} = -\frac{A(\phi)}{\phi} \frac{\partial \phi}{\partial z} \quad \text{at } z=h-0, \quad (15)$$

$$= \frac{v_1 D_a}{1 - v_1 \psi} \frac{\partial \psi}{\partial z} \quad \text{at } z=h+0. \quad (16)$$

In addition to these conditions we must impose the local equilibrium condition Eq. (9) so that we have a closed set of equations.

In a particular case that the diffusion process of ψ can be regarded as a steady state, Eq. (10) is readily solved. Then we obtain from Eq. (16)

$$\dot{h} \approx \frac{v_1 D_a}{L} [\psi_\infty - \psi(h+0, t)]. \quad (17)$$

Here we have assumed that $v_1\psi \ll 1$ and $h \ll L$. Since ψ in Eq. (17) is given by Eq. (9), the evaporation rate defined as $|\dot{h}|$ is given as a function of ϕ at the interface. In this case $|\dot{h}|$ as a function of ϕ shows the same behavior as ψ/ψ^* in Fig. 2. This means that the evaporation rate is extensively reduced by gelation or the skin formation near the free surface. We should emphasize that the decrease of the evaporation rate originates from the elastic effect on the bulk osmotic modulus.

Equations (4)–(6), (9), and (17), with the boundary conditions (11), (12), and (15), and (15) form a closed set of equations. We solve these equations numerically, in the units of length $h_0 \equiv h(0)$ and time h_0^2/D with $D \equiv k_B T / (\zeta v_1)$, for given dimensionless parameters $\hat{J}_0 \equiv v_1 \psi^* D_a h_0 / (DL)$, \hat{K}_g

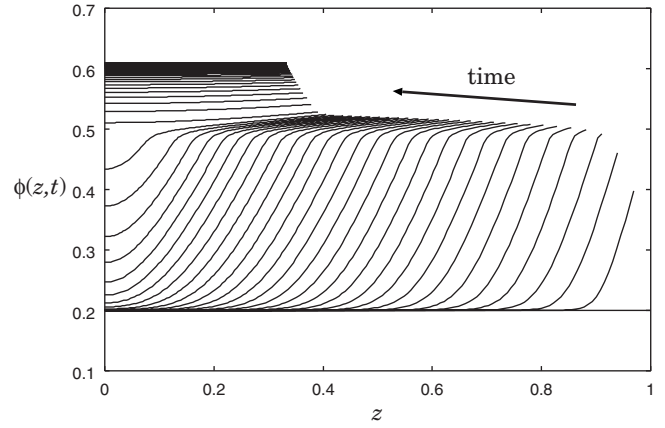


FIG. 3. Time evolution of the profile $\phi(z,t)$ obtained by the numerical simulation for $\hat{J}_0=1$, $\hat{K}_g=10$, $\chi=0$, $\phi_g=0.5$, and $\psi_\infty/\psi^* = 0.1$. Plots of $\phi(z,t)$ at constant time interval are shown simultaneously. The left upper curves correspond to the later profiles.

$\equiv v_1 K_g / (k_B T)$, and ψ_∞/ψ^* . Note that in these units the rate equation of h is given as

$$\dot{h} = \hat{J}_0 \left(\frac{\psi_\infty}{\psi^*} - \frac{\psi}{\psi^*} \right). \quad (18)$$

The following numerical calculations have been done on a regular one-dimensional lattice via coordinate transformation $z \rightarrow \hat{z} \equiv z/h(t)$. Instead of the step function $\theta(x)$ in Eq. (6) we have used $[1 + \tanh(x/\epsilon)]/2$ with $\epsilon = 10^{-2}$ to avoid a numerical instability.

In Fig. 3 we show a time evolution of the profile $\phi(z,t)$ for $\hat{J}_0=1$, $\hat{K}_g=10$, $\chi=0$, $\phi_g=0.5$, and $\psi_\infty/\psi^*=0.1$. The initial condition $\phi(z,0) = \phi_0$ with $\phi_0=0.2$ has been used. In the initial time regime in which $\phi(h,t) < \phi_g$, a polymer-rich region is formed near the free surface but no skin layer is observed (regime I). After $\phi(h,t)$ reaches ϕ_g , a skin layer [$h_g \leq z < h$ such that $\phi_g \leq \phi(z,t)$] is formed (regime II). In the final time regime the skin layer extends in the whole liquid region (regime III). The above behavior is qualitatively similar to that obtained with our previous models [19].

Next we plot $h(t)$ (thick solid line), $h_g(t)$ (thin solid line), and $\phi(h,t)$ (dashed line) as functions of t in Fig. 4. The thickness of skin layer $h-h_g$ grows linearly in the beginning of regime II since $\phi(h,t)$ stays near ϕ_g in that regime. After the skin layer fills the region $0 < z < h$ (regime III), $\phi(h,t)$ grows again and then the slope of $h(t)$, that is, the evaporation rate extremely decreases. When $\psi(h+0,t)$ reaches ψ_∞ , the whole system equilibrates and the drying ceases. This result implies that the time when the evaporation rate is significantly lowered is not the time when the skin begins to form but the time when the whole liquid region becomes gel (skin). This point should be explored by experiments.

The above results are obtained for a one-dimensional system such as a uniform layer of polymer solution on a flat substrate. For two- or three-dimensional systems the results should be modified depending on the geometry (e.g., a spherical drop) of the system, which can be seen as follows. The deformations which cause the stress σ in Eq. (1) include

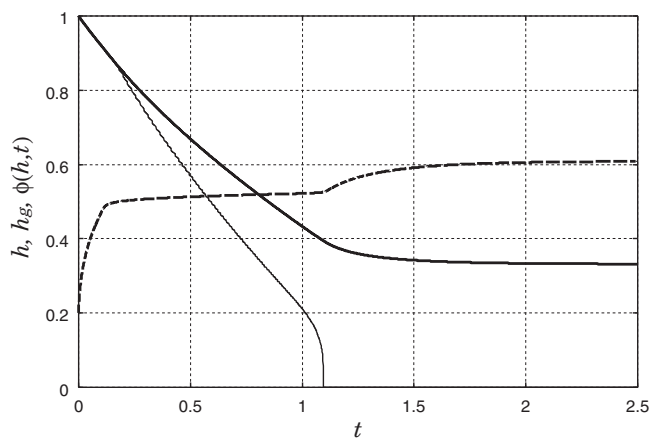


FIG. 4. Plots of $h(t)$ (solid thick line), $h_g(t)$ (solid thin line), and $\phi(h,t)$ (dashed line) as functions of t using the data obtained by the numerical simulation for $\hat{J}_0=1$, $\hat{K}_g=10$, $\chi=0$, $\phi_g=0.5$, and $\psi_\infty/\psi^*=0.1$.

not only the bulk mode (changing volume) but also the shear mode, in general. The former deformation mode is directly connected to the volume fraction ϕ , whereas the latter does not change ϕ . However, the stress-diffusion coupling allows the shear deformation to induce a diffusion flux. This means

that Eq. (1) cannot be reduced to a simple form of Eq. (4) in two- or three-dimensional systems. Hence, we cannot exclude the possibility that the shear deformation causes reduction of the diffusion flux which modifies the above numerical results. In order to examine such effects we must introduce a new variable describing deformation of polymer networks and an appropriate constitutive relation between the deformation and the stress. However, this subject is beyond the scope of this paper, and we will discuss this problem in detail elsewhere.

In this paper we have constructed a model of drying process in polymer solutions based on the two-fluid model in which the elastic effect due to polymer networks is taken into consideration. We have pointed out that the increase of the bulk osmotic modulus due to the gelation causes both the increase of the collective diffusion coefficient and the decrease of the evaporation rate of solvents. We believe that this result provides a fundamental knowledge to the related technologies and might be useful for practical applications.

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