Simple Model of Skin Formation Caused by Solvent Evaporation in Polymer Solutions

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(Received 30 May 2006; published 26 September 2006)

A simple model is proposed for the skin formation in the evaporation process of a polymer solution at a free surface. In this model the skin is regarded as a gel phase formed near the free surface, and the dynamics is described by a diffusion equation for the polymer concentration with moving boundaries. The equation is solved both analytically and numerically. It is shown that the skin phase appears when the evaporation rate is high or when the initial polymer concentration is high. An analytical expression is given for the criterion for the skin phase to be formed.

DOI: 10.1103/PhysRevLett.97.136103 PACS numbers: 68.03.Fg, 68.35.Fx, 82.70.Gg

Skin formation at free surfaces of polymer solutions, emulsions, or colloidal suspensions when the solvent evaporates is an interesting nonequilibrium phenomenon observed in our daily life. For example, a thin gel-like layer is often seen on a free surface of hot milk. The skin layer is also observed on a surface of drying paint, which often has wrinkles caused by the surface instability [1,2]. Front aggregation seen in the drying process of wet granular systems [3] is also a very similar phenomenon.

Controlling the skin formation is important in various technologies, such as painting, printing, and film making. In painting technology, the residual stress which appears when a thin film of the polymer solution is dried on a substrate is strongly affected by the process of skin formation. In ink jet printing, the shape of the final deposit left when solvent-rich ink is dried is strongly correlated with the phenomena of skin formation [4]. Although extensive hydrodynamic analyses have been done for the drying process of a droplet [5–10] or a film [11–14] on a substrate [15–17], not much work has been done which takes into account of the skin formation.

Skin is generally considered to be a gel phase formed by the solute (polymer, or colloidal particles) when the solute concentration near the surface becomes high. However, the exact nature of the skin phase is a matter of controversy: the question of whether it is a region of viscoelastic fluid, a layer of soft gels, or a film of glassy polymers has not been answered clearly. Whatever the nature of the skin phase is, the viscous fluid becomes elastic in the skin phase. Therefore when and how such skin phase is formed is an important question in controlling the drying process of droplet or thin liquid film.

In this Letter, we discuss the condition for the skin phase to be formed by using a simple model: we regard the skin as a gel through which a solvent can permeate, and discuss the time evolution of the thickness of the skin phase. Since our model is simple, an analytical expression is obtained for the criterion of the skin layer to appear.

We consider a layer of polymer solution with initial thickness h_0 placed on a flat substrate whose normal lies in z. When the solvent evaporates at the free surface, the volume fraction of polymers ϕ increases and the thickness h decreases in time t, while the total amount of polymers in the system is unchanged (we assume that the polymers do not evaporate). If the evaporation is rapid, ϕ near the free surface increases and forms a polymer rich region [Fig. 1(a)]. When ϕ reaches a certain value ϕ_g, the polymer solution becomes a gel and a skin phase is formed [Fig. 1(b)]. As the evaporation proceeds, the whole system finally becomes a gel [Fig. 1(c)]. The above process can be described by the following one-dimensional diffusion equation of $\phi = \phi(z, t)$ on $0 < z < h$:

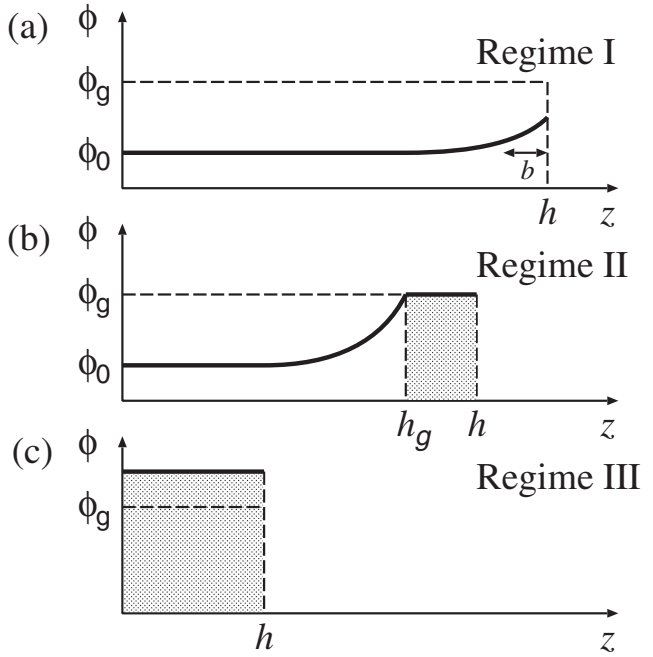

FIG. 1. Schematic pictures of profiles of ϕ in the three regimes: (a) In regime I, $\phi_0 < \phi_h < \phi_g$, a polymer rich region with a characteristic length b is formed near the free surface. (b) In regime II, $\phi_g \leq \phi_h$, a skin layer ($h_g < z < h$) is formed. (c) In regime III, the whole system forms a skin.

$$\frac{\partial \phi}{\partial t} = \frac{\partial}{\partial z}\left[A(\phi)\frac{\partial \phi}{\partial z}\right], \tag{1}$$

where $A(\phi)$ is a cooperative diffusion coefficient which in general depends on ϕ [18].

The solvent evaporation rate decreases with the decrease of the solvent volume fraction at the surface. Here we assume that the amount of solvent evaporation at the surface is written as $J(1-\phi_h)$ [13], where J is a constant and ϕ_h is the polymer concentration at $z=h$: $\phi_h = \phi(h,t)$. Since polymers do not evaporate, the mass balance equation for the solvent and polymers in the layer can be expressed as

$$\frac{d}{dt}\int_0^{h(t)} dz(1-\phi) = -J(1-\phi_h), \tag{2}$$

$$\frac{d}{dt}\int_0^{h(t)} dz\phi = 0. \tag{3}$$

From Eqs. (2) and (3) we can derive the equation for the thickness h,

$$\frac{dh}{dt} = -J(1-\phi_h), \tag{4}$$

and the boundary condition at the free surface,

$$A(\phi)\frac{\partial \phi}{\partial z} = J\phi(1-\phi) \quad \text{at } z=h. \tag{5}$$

Here we have imposed the boundary condition at the substrate,

$$\frac{\partial \phi}{\partial z} = 0 \quad \text{at } z=0. \tag{6}$$

For the cooperative diffusion coefficient $A(\phi)$, we assume the following form:

$$A(\phi) = \begin{cases} D & (\phi < \phi_g), \\ D_g & (\phi \geq \phi_g), \end{cases} \tag{7}$$

where D and D_g are constants independent of ϕ and stand for the cooperative diffusion constants in solutions and in a gel phase.

For the concentration profile shown in Fig. 1(b) to be observed, D_g must be much larger than D. In the following, we shall conduct the analysis assuming that $D_g \gg D$. The physical reason for this assumption is that the osmotic modulus $\partial\Pi(\phi)/\partial\phi$ in a gel phase is much larger than that in the solution: $\partial\Pi(\phi)/\partial\phi$ in a gel phase has an extra contribution from the elastic modulus of polymer network [18–20].

Now we analyze the model equations (1) and (4) with Eq. (7) under the boundary conditions (5) and (6) and the initial condition $\phi(z,0) = \phi_0$. The time evolution of ϕ can be conveniently divided into two regimes: $\phi_h < \phi_g$ [Fig. 1(a)] and $\phi_h \geq \phi_g$ [Fig. 1(b)], called regime I and regime II, respectively.

In regime I, there is no gel phase. Evaporation of the solvent causes formation of a polymer rich region near the free surface with a characteristic size b [see Fig. 1(a)]. Introducing a new coordinate $\xi \equiv z - h(t)$, we rewrite Eq. (1) for $\phi = \phi(\xi, t)$ as

$$D\frac{\partial^2 \phi}{\partial \xi^2} + \dot{h}\frac{\partial \phi}{\partial \xi} - \frac{\partial \phi}{\partial t} = 0, \tag{8}$$

where $\dot{h} \equiv dh/dt$. If $h(t) \gg b(t)$, Eq. (8) may be solved on the semi-infinite region $-\infty < \xi < 0$ instead of the finite region $-h < \xi < 0$. The boundary conditions (5) and (6) now become

$$\frac{\partial \phi}{\partial \xi} = -\frac{\dot{h}}{D}\phi \quad \text{at } \xi = 0 \tag{9}$$

and

$$\frac{\partial \phi}{\partial \xi} = 0 \quad \text{at } \xi = -\infty. \tag{10}$$

Since $\dot{h}$ depends on the boundary value of ϕ, which is time dependent, as in Eq. (4), we cannot obtain any analytical solution of Eq. (8). However, if we regard $\dot{h}$ as a constant, which is a good approximation for $\phi_h \ll 1$, we can obtain an analytical expression of the solution. In particular, we have an expression for $\phi_h(t) = \phi(0,t)$ as

$$\phi_h(t) = \phi_0 - 2\alpha\phi_0\int_0^t dt'\left[\frac{\exp(-\alpha^2 t')}{\sqrt{\pi t'}} - \alpha\,\mathrm{erfc}(\alpha\sqrt{t'})\right], \tag{11}$$

with

$$\alpha \equiv \frac{\dot{h}}{2\sqrt{D}}, \tag{12}$$

where the error function $\mathrm{erfc}(x)$ is defined as

$$\mathrm{erfc}\,(x) = \frac{2}{\sqrt{\pi}}\int_x^\infty e^{-y^2} dy. \tag{13}$$

For $\alpha^2 t \ll 1$, $\phi_h(t)$ behaves as

$$\phi_h \simeq \phi_0 + \sqrt{\frac{4J^2}{\pi D}}\phi_0(1-\phi_0)t^{1/2}. \tag{14}$$

Here we have used an approximated value

$$\dot{h} = -J(1-\phi_0) \tag{15}$$

for the velocity of the boundary.

In regime II the problem is more complicated. However, in the limit of $D_g \to \infty$, we can solve the problem easily. In this limit, there may exist a point $z = h_g(t)$ such that $\phi(z,t) = \phi_g$ for $h_g < z \leq h$; that is, the skin is formed in this region [Fig. 1(b)]. Since, in this case,

$$\frac{d}{dt}\int_0^h dz\phi = \frac{d}{dt}\int_0^{h_g} dz\phi + (\dot{h} - \dot{h}_g)\phi_g \tag{16}$$

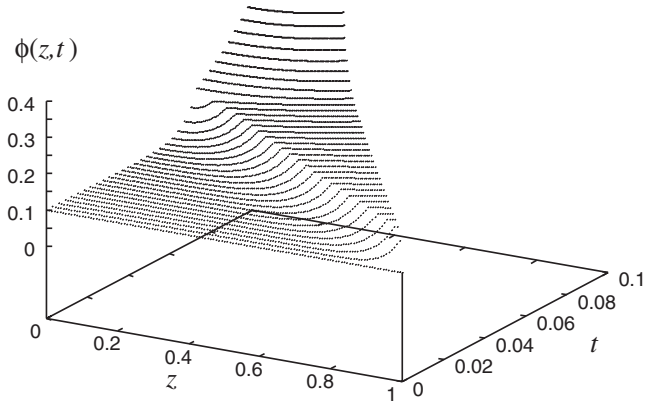

FIG. 2. Space-time plot of $\phi(z, t)$ obtained by the numerical simulation of Eqs. (1) and (4)–(6) for Pe = 10.

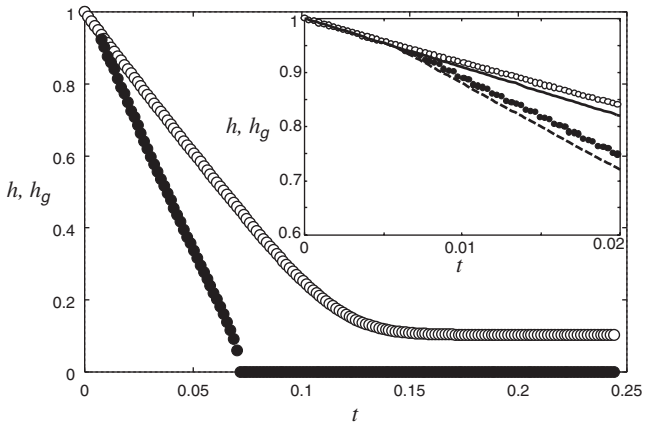

FIG. 3. Plots of $h(t)$ (open circles) and $h_g(t)$ (solid circles) as functions of t using the data obtained by the numerical simulation for Pe = 10. The inset shows the comparison with the analytical expressions Eq. (15) for $h(t)$ (solid line) and Eq. (19) for $h_g(t)$ (dashed line).

and $\dot{h} = -J(1 - \phi_g)$, Eq. (3) requires

$$D\frac{\partial\phi}{\partial z} = J\phi_g(1 - \phi_g) \quad \text{at } z \uparrow h_g, \tag{17}$$

provided that ϕ is continuous at $z = h_g$. A solution of Eq. (1) can be obtained as

$$\phi = \phi_0 + (\phi_g - \phi_0)\exp\left[-\frac{\dot{h}_g}{D}(z - h_g)\right], \tag{18}$$

in $-\infty < z < h_g$. From Eqs. (17) and (18) we obtain the velocity of the interface between the liquid and the gel (skin) phases,

$$\dot{h}_g = -\frac{J\phi_g(1 - \phi_g)}{\phi_g - \phi_0}. \tag{19}$$

In particular, we have

$$\dot{h} - \dot{h}_g = J\frac{\phi_0(1 - \phi_g)}{\phi_g - \phi_0} > 0. \tag{20}$$

This means that once ϕ_h reaches ϕ_g, the thickness of the skin always grows with a constant rate.

Figures 2–4 show the results of numerical simulations of Eqs. (1) and (4)–(6). In the numerical simulations we choose h_0 and h_0^2/D as units of length and time, respectively, and we have dimensionless parameters Pe $\equiv h_0 J/D$, $G \equiv D_g/D$, ϕ_g, and ϕ_0 which control the system. The most important control parameter is Pe, which is given as the ratio of the time scale of diffusion to that of evaporation. This parameter is similar to that called the Péclet number in a sedimentation problem of colloids [21].

In Fig. 2 we show a space-time plot of $\phi(z, t)$ for Pe = 10, $G = 10$, $\phi_g = 0.2$, and $\phi_0 = 0.1$. As expected, a skin layer which is defined as the region where $\phi \geq \phi_g$ has an almost flat profile and grows in time after the time when ϕ_h reaches ϕ_g. The positions of the free surface h and the interface between liquid and gel (skin) phases h_g are plotted as functions of t in Fig. 3. In the inset of Fig. 3 we compare the numerical data with the analytical results given by Eqs. (15) and (19). The solid line and the dashed line in this figure show the analytical results for $h(t)$ and $h_g(t)$, respectively. We see that the numerical data are well fitted by the analytical expressions, although there is small discrepancy between the theory and the numerical data for $h_g(t)$. This discrepancy comes from the finiteness of G in the numerical simulations, whereas G is infinite in the theory.

Figure 4 shows a space-time plot of $\phi(z, t)$ for Pe = 1 (other parameters are same as before). In this figure the skin layer in regime II is obscure, since the characteristic length b in regime I is large and comparable with h. In this case we cannot observe a clear skin layer.

The above examples indicate that a clear skin phase is seen if the characteristic length b is much smaller than the film thickness $h(t)$ when the skin phase appears at the surface. In other words, if $\phi_h(t_D) < \phi_g$, we observe no skin phase, where $t_D \equiv h_0^2/D$ is the time for which the

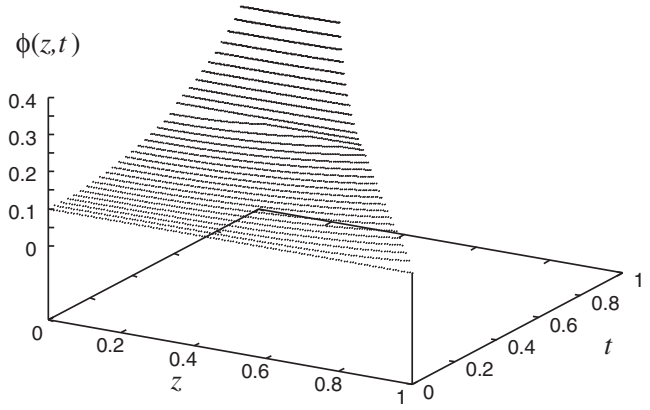

FIG. 4. Space-time plot of $\phi(z, t)$ obtained by the numerical simulation of Eqs. (1) and (4)–(6) or Pe = 1.

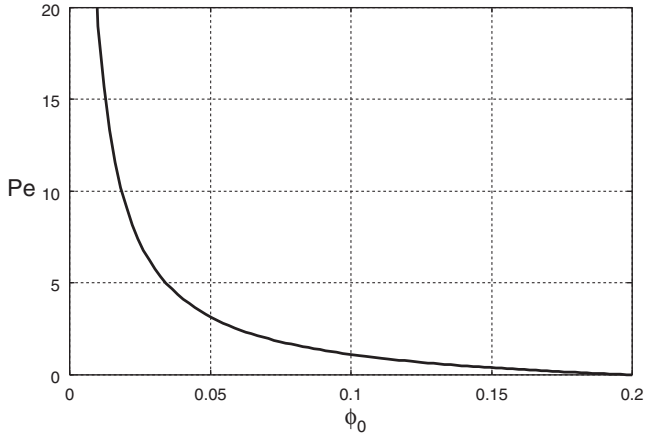

FIG. 5. Diagram of skin formation based on Eq. (21). For the parameters above the solid line, well-structured skin layers are formed.

diffusion takes place over the initial system size h_0. Using Eq. (14) we obtain a criterion for the well-structured skin phase to be observed:

$$\mathrm{Pe} > \frac{\phi_g - \phi_0}{(1-\phi_0)\phi_0}. \tag{21}$$

In Eq. (21) we have discarded the unimportant numerical factor $\sqrt{\pi/4}$ on the right-hand side. The region described by Eq. (21) in the parameter space (ϕ_0, Pe) for fixed $\phi_g = 0.2$ is shown in Fig. 5. This result suggests that the skin formation can be controlled by Pe and ϕ_0 for fixed ϕ_g and that the smaller value of ϕ_0 and the larger value of Pe lead to formation of the well-structured skins. This is consistent with the prediction of de Gennes [13] that the thin "crusts" phase, which corresponds to the skin phase in our analysis, appears for large evaporation rates.

In practical applications it is important to give a criterion of formation of the well-structured skin layer. The above results provide useful information in explaining the empirical fact that higher evaporation rates lead to more inhomogeneous deposits. In our analysis we have assumed $D_g/D \to \infty$. This assumption does not affect the criterion Eq. (21), since $\dot{h} - \dot{h}_g > 0$ even if D_g/D (>1) is finite. As mentioned before we emphasize that D_g is the cooperative diffusion coefficient including the elastic effect of polymer networks and is much larger than D. The assumption $D_g/D \gg 1$ is not only for theoretical convenience but also a practical requirement. Although our model is rather simple, we believe that it is valuable as a first step in constructing a more realistic model including hydrodynamic interactions and effects of the stress field in the skin in three-dimensional systems.

This work was partially supported by JSPS KAKENHI (No. 18540403).

[1] L. Pauchard and C. Allain, Europhys. Lett. **62**, 897 (2003).
[2] L. Pauchard and C. Allain, Phys. Rev. E **68**, 052801 (2003).
[3] Y. Yamazaki and T. Mizuguchi, J. Phys. Soc. Jpn. **69**, 2387 (2000).
[4] T. Kajiya, E. Nishitani, T. Yamaue, and M. Doi, Phys. Rev. E **73**, 011601 (2006).
[5] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Nature (London) **389**, 827 (1997).
[6] R. D. Deegan, Phys. Rev. E **61**, 475 (2000).
[7] R. D. Deegan, O. Bakajin, T. F. Dupont, G. Huber, S. R. Nagel, and T. A. Witten, Phys. Rev. E **62**, 756 (2000).
[8] H. Hu and R. G. Larson, J. Phys. Chem. B **106**, 1334 (2002).
[9] Y. O. Popov and T. A. Witten, Phys. Rev. E **68**, 036306 (2003).
[10] B.-J. de Gans and U. S. Schubert, Langmuir **20**, 7789 (2004).
[11] D. E. Bornside, C. W. Macosko, and L. E. Scriven, J. Appl. Phys. **66**, 5185 (1989).
[12] P. G. de Gennes, Eur. Phys. J. E **6**, 421 (2001).
[13] P. G. de Gennes, Eur. Phys. J. E **7**, 31 (2002).
[14] M. Tsige and G. S. Grest, Macromolecules **37**, 4333 (2004).
[15] H. Hu and R. G. Larson, Langmuir **21**, 3963 (2005).
[16] H. Hu and R. G. Larson, Langmuir **21**, 3972 (2005).
[17] K. Ozawa, E. Nishitani, and M. Doi, Jpn. J. Appl. Phys. **44**, 4229 (2005).
[18] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, 1979).
[19] F. Brochard and P. G. de Gennes, Macromolecules **10**, 1157 (1977).
[20] M. Doi and A. Onuki, J. Phys. II (France) **2**, 1631 (1992).
[21] W. B. Russel, D. A. Saville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge, New York, 1989).