

Piling-to-buckling transition in the drying process of polymer solution drop on substrate having a large contact angle

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We studied the drying process of polymer solution drops placed on a substrate having a large contact angle with the drop. The drying process takes place in three stages. First, the droplet evaporates keeping the contact line fixed. Second, the droplet shrinks uniformly with receding contact line. Finally the contact line is pinned again, and the droplet starts to be deformed. The shape of the final polymer deposit changes from concave dot, to flat dot, and then to concave dot again with the increase of the initial polymer concentration. This shape change is caused by the gradual transition from the solute piling mechanism proposed by Deegan *et al.* to the crust buckling mechanism proposed by de Gennes and Pauchard.

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I. INTRODUCTION

The drying process of a polymer solution drop on a substrate is an important problem in ink-jet printing which is considered to be the key technology in the next-generation production process of micro devices. An important problem there is how to control the shape of the solute deposit when the drop is dried up.

In the case of dilute solution, a commonly observed phenomena is the “coffee stain” [1]: the evaporation of solvent induces an outward flow, which brings the solute towards the perimeter of the droplet and creates a ring-like deposit after drying. The outward flow is a result of the combined action of the increased evaporation rate at the droplet edge and contact line pinning caused by solute deposition near the edge [2–4]. Detailed numerical study for the outward flow was done by Larson *et al.* [5], and an analysis has been done for the shape of the final deposit [6,8].

From the view point of application, it is preferable to have a uniform deposit rather than the ring-like deposit. One possibility to this end is to use a substrate which has a large contact angle with the droplet. De Gans *et al.* [9] showed that when a polymer solution is dried on a glass slide coated with hydrophobic materials, it leaves a small dot after the evaporation. They observed that the dots have small dimples in the center, the size of which can be changed by the solvent. They, however, did not conduct any quantitative study for the phenomena.

We conducted microscopic observation of the evaporation process of polymer solution on a substrate which has a large contact angle with the polymer solution. Here we report the experimental results for the deposit shape, especially the effect of polymer concentration, and discuss the mechanism of the polymer dot formation.

II. EXPERIMENTAL SECTION

The polymer solution is polystyrene (Sigma-Aldrich, USA; M_w 280000d) dissolved in anisole (Sigma-Aldrich, USA; T_b 152 ~ 155 °C). The substrate is a glass slide (Matunami, Japan) coated with hydrophobic conditioning materials (FS-1010, Fluoro Technology, Japan). The contact angle

of pure anisole on glass slides was 10 ± 5 deg, but becomes 75 ± 5 deg after coating. The volume of the droplet was ca. $0.5 \mu\text{l}$. They were placed on the coated glass by micro pipette and were dried in natural conditions. The total drying time was 20 ± 5 min. The side view of the droplets was taken by digital microscope (VHX-200, Keyence, Japan) and the time evolution of droplet, parameters such as the radius of the base circle, the height of the droplet, and the contact angle were obtained by image analysis.

The shape of the final deposit was measured by confocal microscope (Optelics C130, Lasertec, Japan) under a xenon lamp. A three-dimensional surface of the deposit was obtained by viewing the deposit from the top.

III. RESULTS AND DISCUSSION

A. Ring-like deposit and dot-like deposit

Figures 1 and 2 show the effect of the glass coating on the shape of the final deposit. On the uncoated glass, the polymer solution of initial volume fraction $\phi_i = 0.0370$ forms a ring-like deposit (Fig. 1). On the other hand, the polymer solution forms a small dot-like deposit on the coated glass (Fig. 2). Notice that the radius of the final deposit is much smaller for coated glass than for the uncoated glass even though the initial volume of the droplet is about the same. The evaporation process is also different. In the case of uncoated glass, the contact line becomes pinned soon after the droplet is placed on the glass and stays there until the end of evaporation. On the other hand, in the case of coated glass, the contact line is initially pinned and then starts to recede and then is pinned again. The dynamics of evaporation on the coated glass will be described in detail in the next section. In this paper, we used the coated (hydrophobic) glass for the substrate except for the experiment of Fig. 1.

B. Drying process

From the captured video image, we measured the time variation of droplet radius R (the radius of the base circle) and droplet height h .

In the uncoated (hydrophilic) substrate case, the initial radius R of the droplet of volume $0.5 \mu\text{l}$ is much larger than 1 mm (see Fig. 1).

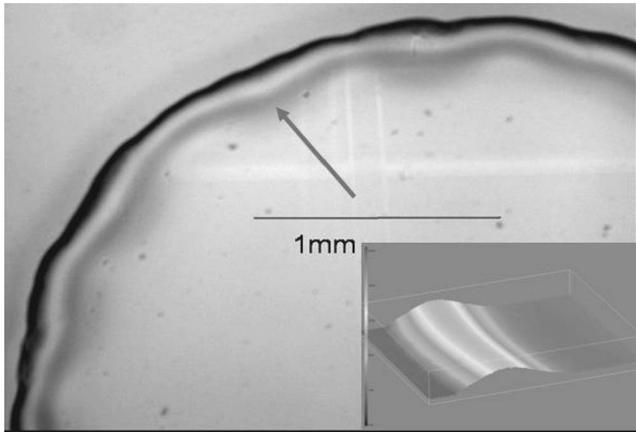


FIG. 1. The polymer deposit made on uncoated hydrophilic glass which has a low contact angle. The deposit is a thin polymer film with a ring-like bump. The initial volume fraction of polymer is $\phi_i=0.037$. The inset figure is the confocal microscope images which are close up to the edge of the deposit.

In the coated (hydrophobic) substrate case, the initial radius R of the droplet of volume $0.5 \mu\text{l}$ is about $800 \mu\text{m}$ (see Fig. 2). Since this is much smaller than the capillary length (which is $\approx 2 \text{ mm}$ [10]), the droplet takes a spherical shape in equilibrium. Assuming that the shape of the droplet is spherical in the early stage of drying, we calculated the contact angle θ_c and the droplet volume V by the following equation:

$$\theta_c = 2 \tan^{-1}(h/R), \tag{1}$$

$$V = \frac{\pi h(3R^2 + h^2)}{6}. \tag{2}$$

Figure 3 shows a typical time variation of the droplet volume. It is seen that the volume of the droplet decreases almost linearly in time. We fitted the curve by a straight line and determined the initial droplet volume V_i and the charac-

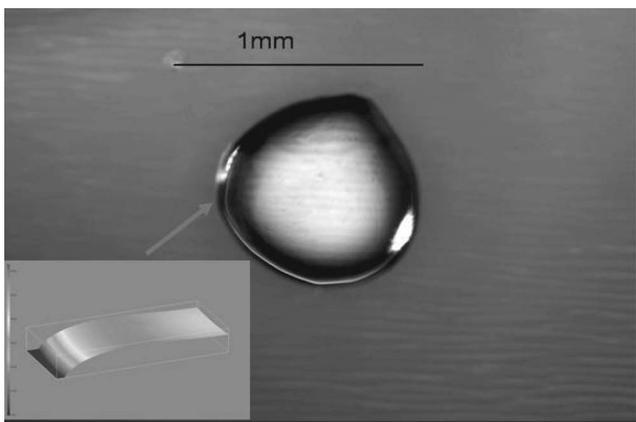


FIG. 2. The polymer deposit made on coated hydrophobic glass which has a large contact angle. The deposit is a cap with a shallow dimple. The initial volume fraction is $\phi_i=0.037$. The inset figure is the confocal microscope images which are close up to the edge of the deposit.

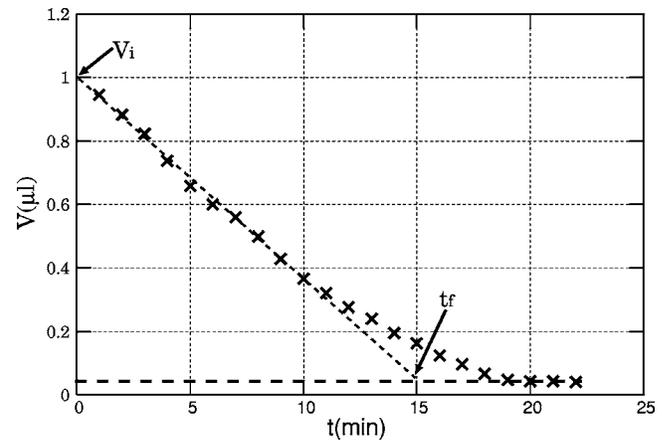


FIG. 3. The volume of a drying droplet is plotted against time. The initial part of the curve can be fitted by the straight line $V(t) = V_i(1 - t/t_f)$, which determines the parameter V_i and t_f . The slowing of the slope is due to the effect of crust formation.

teristic evaporation time t_f as it is shown in Fig. 3. (Notice that t_f is obtained by the linear extrapolation of the evaporation curve and is not the actual time needed to complete the evaporation.)

Since the initial droplet volume was not controlled very precisely, we normalized R , V , and t by the initial radius R_i , the initial volume V_i , and the evaporation time t_f in the following analysis.

Figures 4 and 5 show the variation of the droplet radius R/R_i and the contact angle θ_c plotted against t/t_f for various initial polymer concentrations, respectively. It is seen that the evaporation process has three distinct stages.

In the first stage, the droplet radius remains constant, i.e., the contact line is pinned. This first pinning is considered to be the same as the usual pinning of the fluid droplet on the substrate caused by the irregularities or defects of the substrate [10,11]. In fact, the initial behavior of the polymer solution is the same as that of the pure solvent. In the first stage, while the droplet radius remains constant, the contact

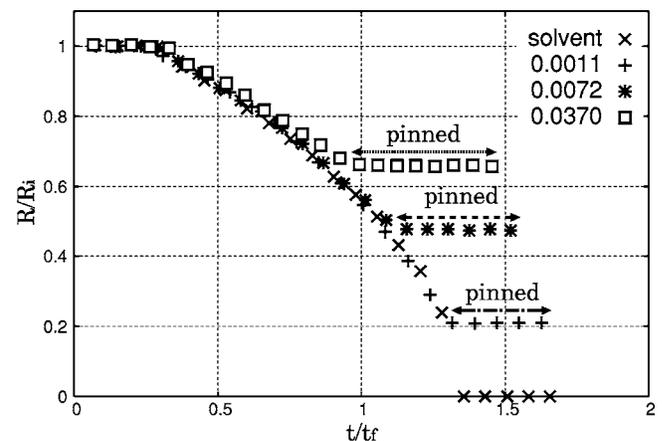


FIG. 4. The radius of droplet R normalized by the initial radius R_i is plotted against the normalized time t/t_f for various polymer concentration. The number in the figure is the initial volume fraction.

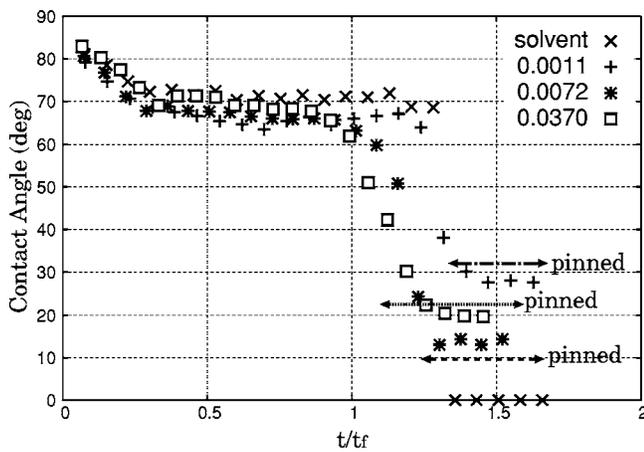


FIG. 5. The contact angle of the droplet is plotted against the normalized time t/t_f for various polymer concentrations. The number in the figure is the initial volume fraction.

angle keeps decreasing. When the contact angle reaches the receding angle θ_R , the contact angle starts to move.

In the second stage, the droplet recedes with constant velocity, keeping its contact angle constant. In the second stage, the shape of the droplet is unchanged (i.e., the droplet shrinks uniformly). As it is seen in Fig. 5, the receding angle θ_R is almost independent of the polymer concentration in the concentration region studied here.

In the third stage, the contact line becomes pinned again. This second pinning is considered to be the self-pinning: the polymer concentration near the edge becomes so high that the solution at the edge loses mobility. Figures 6 and 7 show the droplet radius R_{pin} and the time t_{pin} at which the second pinning occurs as a function of the initial polymer concentration. In the case of dilute solution ($\phi_i \leq 0.01$), the second pinning occurs at a rather late stage of evaporation, i.e., when the droplet shrinks very little: As ϕ_i increases, the second pinning occurs earlier. When ϕ_i exceeds 0.3, the pinning radius becomes equal to the initial droplet radius. In this case the first two stages of the above processes are skipped. The figures indicate that the second pinning is due to the solute deposition near the edge, that is, the self-pinning.

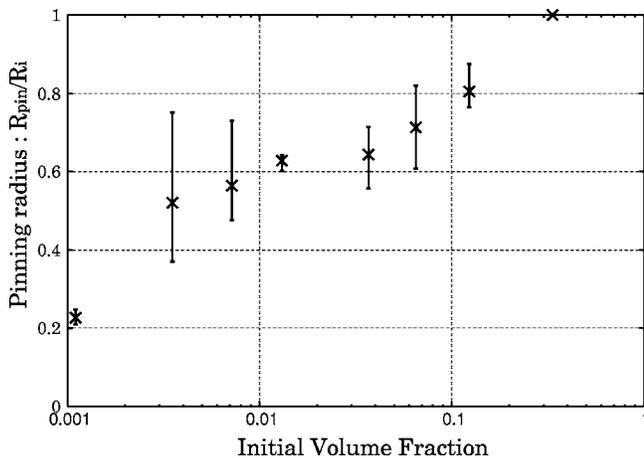


FIG. 6. The normalized pinning radius R_{pin}/R_i is plotted against the initial polymer volume fraction ϕ_i .

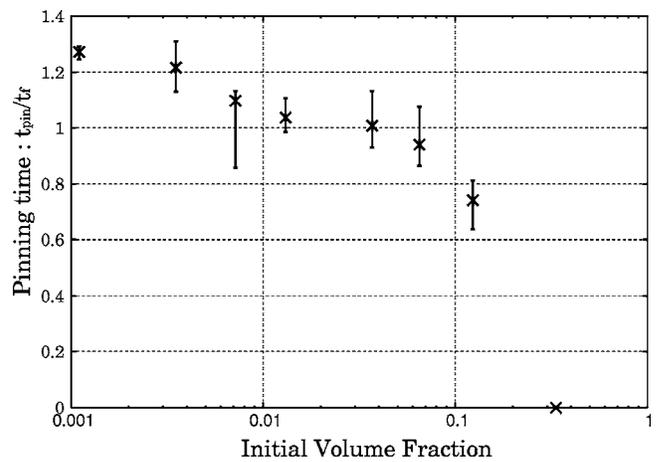


FIG. 7. The normalized pinning time t_{pin}/t_f is plotted against the initial polymer volume fraction ϕ_i .

C. Shape of the final deposit

Figure 8 shows the final shape of the polymer deposit. To show the shape change clearly, we have normalized the horizontal axis and the vertical axis by the deposit radius R_s and the deposit height H_s at the center.

The final form of the deposit varies considerably depending on the initial polymer concentration ϕ_i . When ϕ_i is very low (e.g., $\phi_i=0.0035$), the edge is much higher than the center and a distinct dimple can be seen. As the initial concentration ϕ_i increases, the height at the edge becomes smaller and, in the case of $\phi_i=0.0653$, the deposit becomes almost flat. With further increase of ϕ_i , a dimple appears again, and its size becomes larger as ϕ_i increases. The reason is discussed in the following.

1. Dilute solution

In the dilute solution ($\phi_i \leq 0.01$), a pronounced dimple is formed. We consider that the mechanism of the dimple formation in this regime is essentially the same as that of the

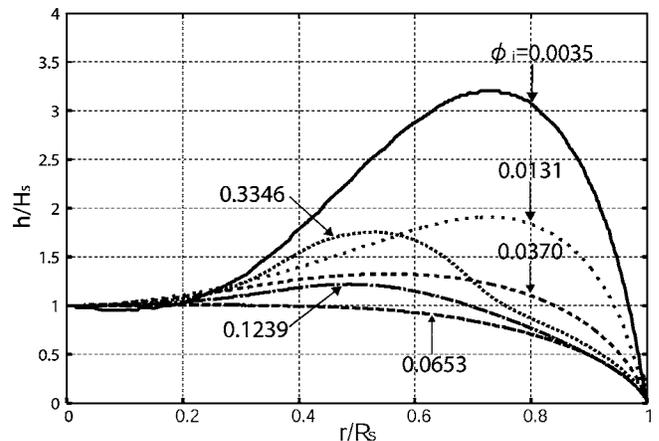


FIG. 8. The cross section of the polymer dot obtained after evaporation is shown for various initial volume fractions ϕ_i . For the sake of comparison, the radius is normalized by the dot radius R_s , and vertical components are divided by the height in the center H_s .

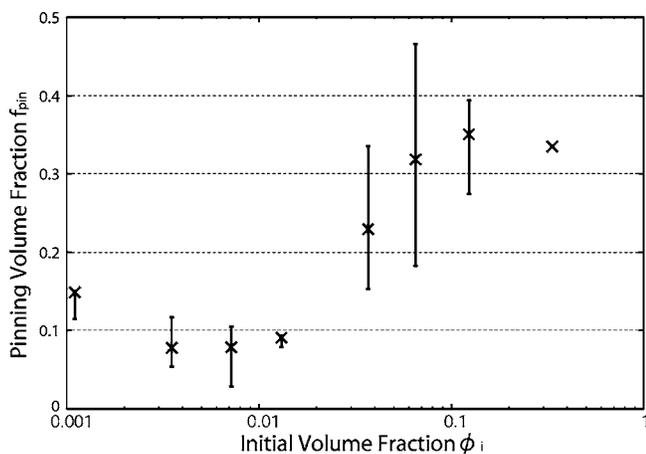


FIG. 9. The average volume fraction ϕ_{pin} at the moment of self-pinning is plotted against the initial volume fraction ϕ_i .

coffee stain [1], i.e., the piling of the solute near the droplet edge due to the outward capillary flow.

In the intermediate concentration ($0.01 \leq \phi_i \leq 0.1$), the dimple becomes less pronounced as ϕ_i increases. This is because the solution viscosity η increases rapidly. (see Chap. 8 in [7]) As the viscosity increases, the outward flow becomes suppressed and the piling of polymer becomes weaker, giving a less pronounced dimple [8].

2. Concentrated solution

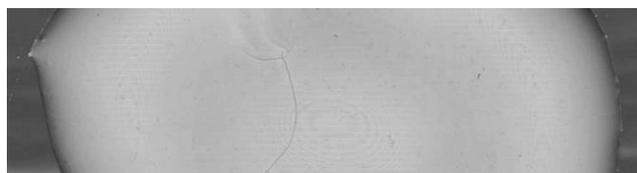
In the concentrated solution ($\phi_i > 0.1$), the dimple appears again and becomes larger as ϕ_i increases. The mechanism of the dimple formation in this regime is considered to be different from that in the dilute solution for the following reasons.

(1) The concentration ϕ_{pin} at which the pinning occurs in this regime is much higher than that in the dilute solution. Figure 9 shows the average polymer concentration ϕ_{pin} when the second pinning takes place ($\phi_{pin} = \phi_i V_i / V_{pin}$). It is seen that ϕ_{pin} has a plateau in the dilute region, increases, as the initial polymer concentration increases and saturates in the concentrated region. This suggests that the dimple formation in the concentrated solution has a mechanism different from that in the dilute solution.

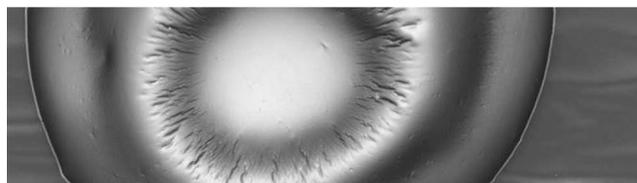
(2) The outlook of the dot surface obtained from the concentrated solution is different from that obtained from the dilute solution. Figure 10 shows the image of the dot formed from the dilute solution ($\phi_i = 0.0072$) and that from the concentrated solution ($\phi_i = 0.3346$). In the case of the dilute solution, the dot surface is smooth, while in the case of the concentrated solution, the surface is rough and crimps and stretching in the radial directions are seen in the dimple.

(3) In the evaporation process of the concentrated solution, we often observed that the area near the center of the droplet starts to move and caves in. This takes place in a short time, typically several seconds. When this happens, it looks as if the surface of the droplet is covered by a soft film.

These observations indicate that the dimple in the concentrated solution is created by the buckling of the “crust” proposed by de Gennes [12]. As the solvent evaporates, the



(a)



(b)

FIG. 10. Images of the surface of the polymer dot. (a) Polymer dot obtained from the polymer solution of initial polymer volume fraction $\phi_i = 0.0072$. (b) Polymer dot obtained from that of $\phi_i = 0.3346$.

polymer concentration near the surface of the droplet increases rapidly, and the solution forms a soft elastic phase (the crust phase) near the surface. As the solvent keeps evaporating, the volume of the droplet keeps decreasing, and the pressure inside the droplet keeps decreasing. When the internal pressure becomes less than a certain critical value, the droplet cannot keep the spherical shape and buckles in to form the dimple.

The buckling phenomena has been observed by Pauchard *et al.* [13–15] for concentrated polymer solutions. They reported various shapes of buckling other than that reported here. Depending on the contact angle and the humidity, a “Mexican hat” (a dimple is formed around the center, leaving a top in the center) and other patterns have been observed.

Two reasons can be conceived for the buckling at the center position in our experiment.

(1) As the solvent evaporates, the polymers move to the edge of droplet, so the concentration near the contact line is higher than that at the center position. Therefore the crust at the center is thinner than that near the contact line, so the buckling occurs at the center.

(2) According to the work of Hu and Larson [5], the evaporation rate near the contact line is much faster than that of the center position, so the crust of the contact line is thicker than that of center position.

As a result, buckling occurs near the center position.

They did not observe the receding process of the contact line since their initial polymer concentrations were high (ϕ_i being ca. 0.4)

D. Dot formation in slow evaporation

We have shown that there are two mechanisms for the dimple formation, the outward flow and the buckling of the crust. Both mechanisms are driven by evaporation of solvent. If the evaporation is slowed down, both effects become weaker, and the dimple formation is expected to be suppressed by restraining these processes. To test this idea, we conducted an evaporation experiment in a closed box. The

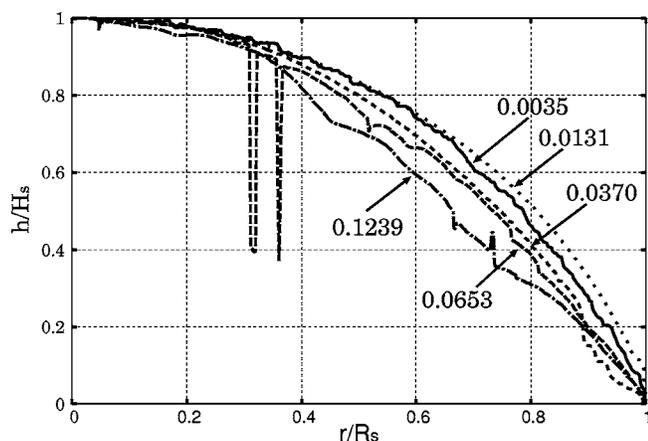


FIG. 11. The shape of the polymer dot obtained at high humidity. Numbers in the figure show the initial polymer volume fraction ϕ_i .

box gives higher humidity of solvent and reduces the evaporation speed by about one quarter. The reduction of the evaporation speed gives the following effect.

(1) The concentration gradient created by the outward flow is moderated by the diffusion process. If the evaporation takes place very slowly, the piling of the polymer near the edge does not occur and the self-pinning at the edge is delayed.

(2) The crust layer becomes thicker for slow evaporation since the thickness of the diffusion layer increases with the decrease of the diffusion current [12]. This suppresses the buckling of the crust layer.

The shape of the polymer dot obtained in this way is shown in Fig. 11. It is seen that the dimple disappears for all droplets the dot takes a cap shape independent of the initial polymer concentration.

IV. CONCLUSION

In this study, we observed the evaporation process of a droplet of polymer solution placed on a substrate which has a large contact angle for the droplet.

In our experiment, the evaporation process consists of three stages. (1) In the initial stage, the contact line is fixed

and the contact angle decreases as the volume of the droplet decreases by evaporation. (2) The contact line starts to move when the contact angle reaches the receding angle. The droplet shrinks uniformly, keeping the contact angle constant. (3) The contact angle is pinned due to the accumulation of polymer near the edge and the droplet starts to be deformed.

The shape of the polymer deposit left on the substrate is determined by the process taking place in the third stage. Two processes take place here: the piling of solute by the outward capillary flow and the buckling of the crust layer. The former process is important in dilute solutions and the latter is important in concentrated solutions.

We conjecture that the above scenario is generally true in the evaporation of polymer solutions. For the substrate having low contact angle for the droplet, the first two stages have not been reported, but we consider that this is because the pinning takes place so quickly. As it was shown by Deegan *et al.* [2,5], the evaporation rate $J(r)$ at the distance r from the center is written as $J(r) \propto [1 - (r/R)^2]^{-\lambda}$ with $\lambda = (\pi - 2\theta_c)/(2\pi - 2\theta_c)$. Therefore, for small contact angle, the evaporation at the edge is much faster than at the center, causing a strong outward flow. Therefore, the piling of the solute takes place more quickly for a droplet of small contact angle than for a droplet of large contact angle. Furthermore, the solidification process takes place much earlier for small contact angle than for large contact angle. Therefore, the self-pinning of the droplet of small contact angle is expected to take place at a time much earlier than that of the droplet of large contact angle.

We thus consider that the drying process of drops on substrate can be consistently explained by the three stages explained above. By modeling these processes quantitatively, it will be possible to predict the droplet shape of polymer solutions for given polymer concentration, droplet volume, and humidity.

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