Skin formation in drying a film of soft matter solutions: Application of solute based Lagrangian scheme*

Ling Luo(罗凌)[1,2], Fanlong Meng(孟凡龙)[3], Junying Zhang(张俊英)[1], and Masao Doi[2,†]

[1] School of Physics and Nuclear Energy Engineering Beihang University, Beijing 100191, China
[2] Center of Soft Matter Physics and its Applications Beihang University, Beijing 100191, China
[3] Cavendish Laboratory, University of Cambridge, Cambridge, CB3 0HE, United Kingdom

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When a film of soft matter solutions is being dried, a skin layer often forms at its surface, which is a gel-like elastic phase made of concentrated soft matter solutions. We study the dynamics of this process by using the solute based Lagrangian scheme which was proposed by us recently. In this scheme, the process of the gelation (i.e., the change from sol to gel) can be naturally incorporated in the diffusion equation. Effects of the elasticity of the skin phase, the evaporation rate of the solvents, and the initial concentration of the solutions are discussed. Moreover, the condition for the skin formation is provided.

Keywords: soft matter solution, skin formation, Onsager principle, solute based Lagrangian scheme

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1. Introduction

When soft matter solutions are dried, a skin layer is often observed at the surface of the solutions.[1–3] This phenomenon is commonly observed in our daily life, such as cooling of hot milk and drying paint; it also appears in many industrial applications, such as polymer film production, ink-jet printing, etc. It has been reported that when the skin layer is formed, the system often shows various instabilities,[4–9] including wrinkling, buckling and cavitation. Therefore understanding this process, especially when the skin layer forms and how it grows with time is an important issue.

Many theoretical studies have been done about the dynamics of the concentration profile of a solute (the non-volatile component) in drying solutions. The conventional approach is to solve the diffusion equation for solute concentration under moving boundary conditions due to the evaporation.[10–12] This approach is useful when the system remains in a liquid phase, but it becomes difficult when some part of the system turns into a gel phase, where the evolution equation takes a different form.[13,14] Recently, we have proposed a new scheme, called solute based Lagrangian scheme (Ref. [13]) to overcome the difficulty. This scheme utilizes the Lagrangian viewpoint of the solute motion, and describes the dynamics by tracing the average positions of the solutes. The scheme is suitable to deal with the moving boundaries and phase changes.

In this work, we will use this scheme to study the skin formation in a film of soft matter solutions placed on a substrate. We will numerically simulate the diffusion of the solutes, skin formation and its growth. We will also discuss how the elastic properties of the gel, the initial concentration of the solution, and the evaporation rate affect the skin formation.

This work is organized as follows. In Section 2, we will model the phenomenon of skin formation; in Section 3, we will describe the solute based Lagrangian scheme used in our calculation; in Section 4, we will numerically simulate the skin formation and its growth; and in Section 5, a brief conclusion is provided.

2. Simplified phenomenon

We consider a layer of soft matter solutions placed on a flat substrate whose normal direction lies in the x axis (Fig. 1).

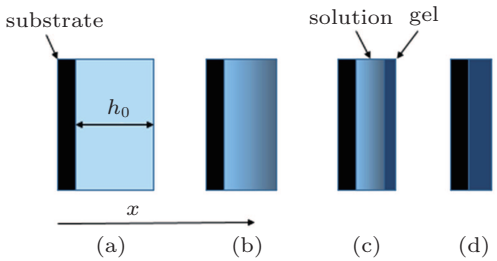


Fig. 1. (color online) Evolution of the state of a soft matter solution film during drying. (a) the initial state, (b) the state of a non-uniform solution, (c) the state where the solution and the gel coexist, and (d) the final state of a uniform gel.

We assume that the volume fraction of the solute is initially uniform, denoted by ϕ_0 and the thickness of the layer is h_0 (Fig. 1(a)). With the evaporation of the solvents, the thickness h decreases and the volume fraction ϕ near the free surface increases (Fig. 1(b)). When the local volume fraction of the solutes ϕ reaches a specific value ϕ_g (gelation point), this

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†Corresponding author. E-mail: masao.doi@buaa.edu.cn
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part is treated as a gel (Fig. 1(c)). The gel layer grows with time and eventually occupies the whole system (Fig. 1(d)).

3. Solute based Lagrangian scheme

There are several approaches to obtaining a solute based Lagrangian scheme, and here we use the Onsager principle.[14–16]

The Onsager principle determines the time evolution of slow variables which describe the non-equilibrium state of the system. Here we choose the positions of the solutes $[X(x,t)]$ as the slow variable which denotes the average position of the solutes at time t that were located at x at time $t=0$. According to the Onsager principle, $\dot{X}(x,t)$, the time derivative of $X(x,t)$, is obtained by minimizing the following functional of $X(x,t)$ and $\dot{X}(x,t)$, called Rayleighian:

$$\mathcal{R}\left([X],[\dot{X}];t\right)=\dot{F}\left([X],[\dot{X}];t\right)+\Phi([X],[X];t), \tag{1}$$

where the first term on the right is the changing rate of the free energy of the system, and the second term is the energy dissipation of the system. According to the conservation law of the solutes, the local volume fraction of solutes located at X at time t will change from ϕ_0 to $\phi(X(x,t);t)$

$$\phi(X,t)=\frac{\phi_0}{X'}, \tag{2}$$

where $X'=\partial X/\partial x$. Before the soft matter solutions become a gel, the free energy of the system $F([X],t)$ can be written as

$$F([X],t)=\int_0^{h(t)}\mathrm{d}X f_{\mathrm{sol}}(X;t), \tag{3}$$

where $f_{\mathrm{sol}}(X;t)$ is the energy density of the solution per length, and the area of the solution is taken as "unit length^2". For dilute solutions, $f_{\mathrm{sol}}(X;t)$ can be written as

$$f_{\mathrm{sol}}(X;t)=\frac{k_{\mathrm{B}}T}{v_{\mathrm{c}}}\phi(X;t)\ln\phi(X;t), \tag{4}$$

where k_{B} is the Boltzmann constant, T is temperature, and v_{c} is the volume of one polymer molecule, or that of one colloidal particle for colloidal suspensions. Then the free energy of the system can be rewritten as

$$F([X],t)=\int_0^{h_0}\mathrm{d}x\frac{K_{\mathrm{B}}T}{v_{\mathrm{c}}}\phi_0\ln\phi. \tag{5}$$

The free energy changing rate can be calculated as

$$\dot{F}\left([X],[\dot{X}],t\right)=\int_0^{h_0}\mathrm{d}x\frac{K_{\mathrm{B}}T}{v_{\mathrm{c}}}\phi_0\left(-\frac{\dot{X}'}{X'}\right). \tag{6}$$

The energy dissipation in the present problem comes from the friction induced by the relative motion between solute and solvent, and therefore the energy dissipation function Φ is written as

$$\Phi\left([X],[\dot{X}],t\right)=\frac{1}{2}\int_0^h\mathrm{d}X\frac{\phi}{v_{\mathrm{c}}}\zeta\dot{X}^2$$

$$=\frac{1}{2}\int_0^{h_0}\mathrm{d}x\frac{\phi_0}{v_{\mathrm{c}}}\zeta\dot{X}^2, \tag{7}$$

where ϕ/v_{c} denotes the number density of the solute, and $\zeta=k_{\mathrm{B}}T/D_0$ is the friction constant between the solute molecules and solvents, where D_0 is the diffusion constant of the solute molecule.

Taking the functional variation of the Rayleighian $\mathcal{R}\left([X],[\dot{X}],t\right)$ with respect to $\dot{X}$,

$$\frac{\delta R}{\delta\dot{X}}=0, \tag{8}$$

we obtain the dynamical equation of the system as

$$\dot{X}=D_0\frac{X''}{X'^2}, \tag{9}$$

where $\dot{X}=\partial X/\partial t$ and $X''=\partial^2X/\partial x^2$.

The evolution equation in the gel phase can be obtained in the same way. Solutions and gels are different in the free energy density form. The free energy density of a solution can be expressed as a function of the volume fraction $\phi(X;t)$, but the free energy of a gel, in general, cannot be represented by $\phi(X;t)$ alone: we need another state variable, the strain tensor, to express the free energy density of a gel. This can be seen in our previous work.[13] However, in the present problem of the drying of a thin film, the strain can be represented by volume fraction, and the free energy density can be expressed by $\phi(X;t)$ alone. Here we assume that the energy density of a gel is written as

$$f_{\mathrm{gel}}=\frac{K_{\mathrm{B}}T}{v_{\mathrm{c}}}[\phi\ln\phi+\varepsilon\phi\left(\phi-\phi_{\mathrm{g}}\right)], \tag{10}$$

where the added term $\varepsilon\phi\left(\phi-\phi_{\mathrm{g}}\right)$ represents the extra interaction between solutes in the gel phase, and ε is the elastic parameter. The functional form of Eq. (10) was chosen to satisfy the following conditions. (i) The free energy density $f(\phi)$ must be continuous at $\phi=\phi_{\mathrm{g}}$ (see Ref. [13]); and (ii) the second derivative of free energy density $\partial^2f/\partial\phi^2$ in the gel phase must be larger than that in the sol phase due to the appearance of the shear modulus in the gel phase. Here ε represents the effect of the shear modulus. Repeating similar calculations to those for solutions, we can obtain the evolution equation of the gels as

$$\dot{X}=D_0\left(\frac{X''}{X'^2}+2\varepsilon\phi_0\frac{X''}{X'^3}\right). \tag{11}$$

Alternatively, it can be rewritten in the same form as the conventional diffusion equation

$$\frac{\partial\phi(X,t)}{\partial t}=\frac{\partial}{\partial X}\left[D(\phi)\left(\frac{\partial\phi(X,t)}{\partial X}\right)\right], \tag{12}$$

$$\frac{D(\phi)}{D_0}=1+2\varepsilon\phi. \tag{13}$$

Comparing Eqs. (9) and (12), we find that the effect of gelation only appears in the form of the diffusion constant. This is indeed the observation made in Ref. [11], where the same conclusion is obtained.

4. Results

In our numerical calculation, we take h_0, K_BT/v_c and ζ as the basic units of the system. Diffusion constant D_0=$K_BT/v_c\zeta$ then becomes 1. Similarly, the reduced time becomes $t_r = t/t_0$ with t_0 equal to h_0^2/D_0, and the reduced evaporation rate becomes $J_r = J/J_0$ with J_0 equal to D_0/h_0.

4.1. Validation of solute based Lagrangian scheme in simple solution

We first conduct a calculation to test the solutes based Lagrangian scheme, by comparing the numerical result of this method with that of the conventional one for a simple situation where there is no gelation. In this situation, the elastic parameter ε is zero, and the diffusion equation is written as

$$\frac{\partial\phi(X,t)}{\partial t} = D_0\frac{\partial^2\phi(X,t)}{\partial X^2}. \tag{14}$$

The boundary conditions are

$$\frac{\partial\phi}{\partial X} = 0, \quad X = 0, \tag{15}$$

$$D_0\frac{\partial\phi}{\partial X} + \phi\dot{h} = 0, \quad X = h, \tag{16}$$

$$\dot{h} = -J. \tag{17}$$

The results of these two methods are compared in Fig. 2. It is seen that both approaches give precisely the same results.

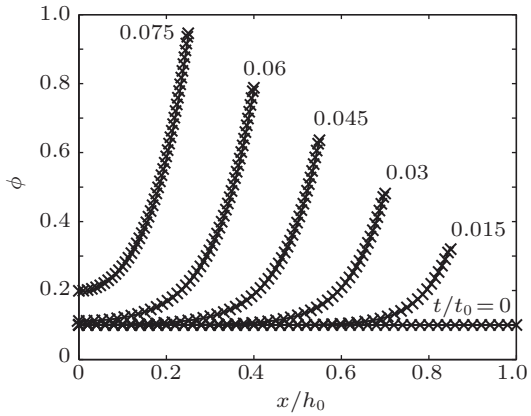


Fig. 2. Comparison between the solute based Lagrangian scheme (solid line) and the conventional method by solving the diffusion equation (cross line). The initial state $\phi_0 = 0.1$, and the evaporation speed $J/J_0 = 10$.

4.2. Skin formation

Figure 3 shows the results of the numerical solution for Eq. (11) for varying the elastic parameter ε. Here the volume fraction ϕ_g is taken to be 0.2, and the dynamics is switched from the sol equation (15) to the gel equation (12) when ϕ exceeds 0.2. It is seen that for small ε the change from that of a pure solution is not so obvious, but for large ε the change is obvious: the concentration in the gel phase becomes almost a constant, and the slope of the curve is discontinuous at the sol/gel interface. Such volume fraction profiles were proposed in Ref. [11], but have not been confirmed. From Fig. 3, one can tell that gelation quickens the diffusion of solute apart from the evaporation surface.

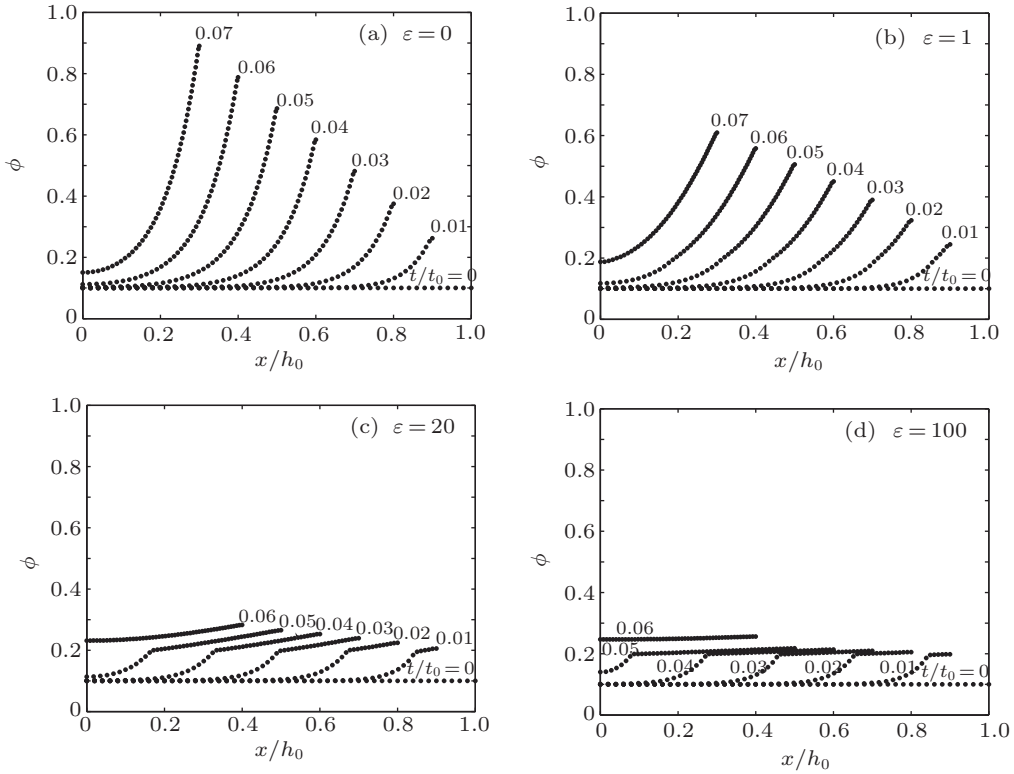


Fig. 3. Volume fraction profile for different elastic constant ε. (a) $\varepsilon = 0$, (b) $\varepsilon = 1$, (c) $\varepsilon = 20$, and (d) $\varepsilon = 100$. The other parameters are $\phi_0 = 0.1$, $J_r = 10$, $\phi_g = 0.2$.

To discuss when a clear skin phase appears, we fix ε at 100, and solve the evolution equation by changing the evaporation rate and the initial volume fraction. The results are shown in Fig. 4. It can be known that the skin forms when both initial volume fraction and evaporation are large. In Figs. 4(b) and 4(c), a clear skin phase forms, but in Fig. 4(a) it does not. In Fig. 4(b) a clear skin phase forms, but in Fig. 4(d) it does not. When the initial concentration is high, the solution can become a gel early, which provides a positive feedback to the growth of the gel layer, due to a quicker diffusion of the solute towards the substrate surface. When the evaporation rate is large, the solution at the surface becomes a gel quicker, and there is a clear interface between the solution and the gel. Once the gel layer forms, it will grow quickly due to a promoted diffusion of the solutes.

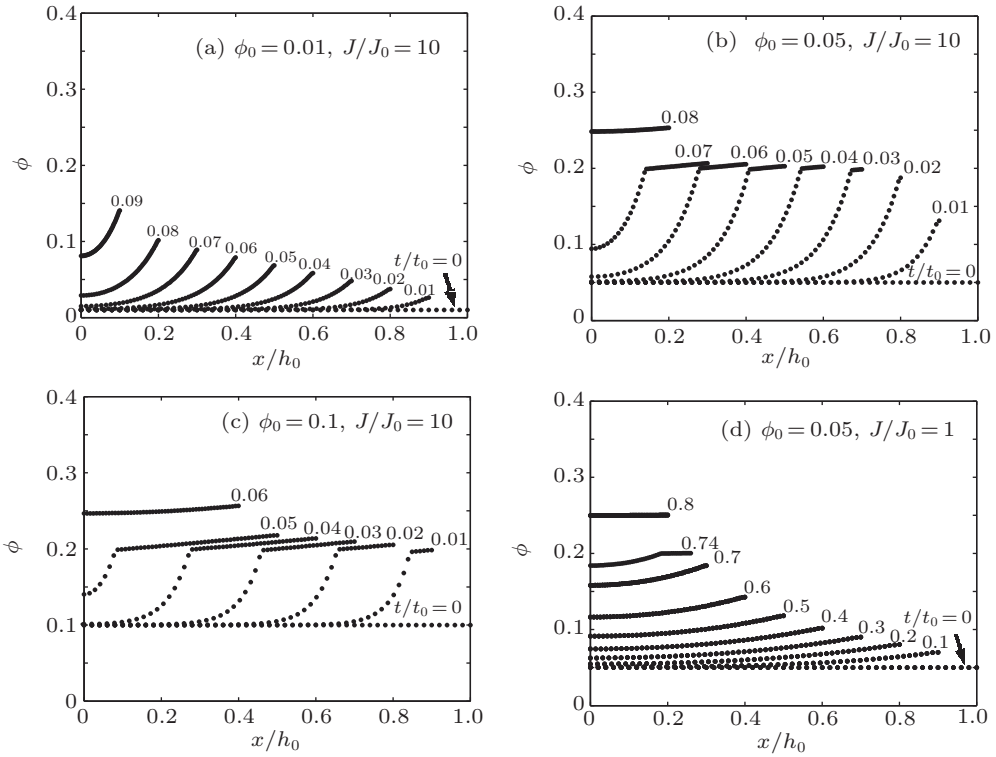


Fig. 4. Evolution of the volume fraction profile for various initial volume fraction ϕ_0 and evaporation rate J/J_0. The other parameters are $\varepsilon = 100$ and $\phi_g = 0.2$. Comparison between panels (a) and (b) indicates that the initial volume fraction ϕ_0 affects the skin formation, while a comparison between panels (b) and (d) indicates that *e* vaporation speed J/J_0 is also important in the skin formation.

To define when the skin layer is formed, we introduce a parameter

$$G = \frac{(\phi(0,t_g) - \phi_0)}{(\phi_g - \phi_0)}, \tag{18}$$

where t_g is the time at which the gelation starts at the surface of the solution, and $\phi(0,t_g)$ is the volume fraction at the bottom of the solution when this happens. The parameter G stands for the comparison between the surface and the bottom when the gelation starts. If G is small, the skin phase is distinctively different from the solution phase, and we regard such a case as the case that a skin phase is formed. In Fig. 5, we have plotted G as a function of evaporation rate and the initial volume fraction. The figure clearly shows that the skin phase appears when both the initial volume fraction and the evaporation rate are large. This is in agreement with the observation of Ref. [11]. Figure 5 also includes the Peclet number line which was proposed in Ref. [11] to represent the condition for the appearance of the skin phase. The line is in agreement with the contour of G at $G = 0.3$, and therefore is consistent with the criterion we propose in this paper.

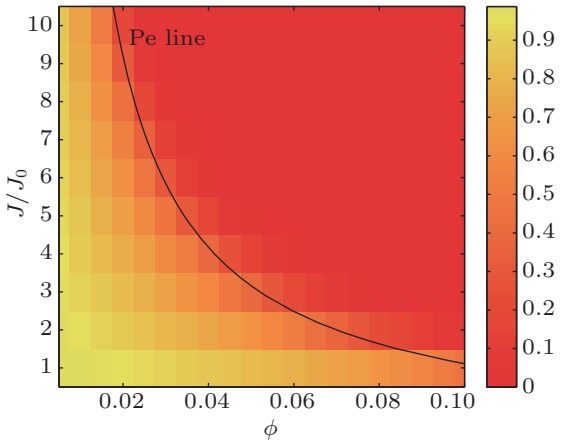


Fig. 5. (color online) Gelation number $G = (\phi(0,t_g) - \phi_0)/(\phi_g - \phi_0)$ and Pe line $\mathrm{Pe} > (\phi_g - \phi_0)/(1 - \phi_0)\phi_0$.

4.3. Growth of skin phase

At the beginning of the drying process, the volume fraction of the solutes at the free surface increases, due to evaporation. When ϕ reaches a critical value ϕ_g, the soft matter solution becomes a gel. As the evaporation goes on, the thickness of the gel becomes larger.

Figure 6(a) shows an example of how skin grows. It is seen that after the free surface becomes a gel, the skin grows with time. However, the skin starts to shrink when the whole solution becomes a gel.

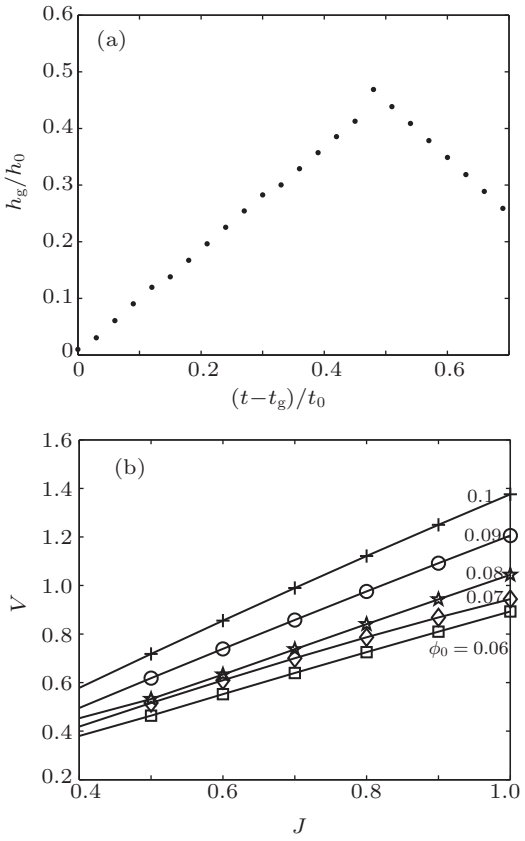


Fig. 6. Growth of the skin layer. Parameters are $J/J_0 = 10$, $\phi_0 = 0.1$, ϕ_0, $\varepsilon = 100$.

Figure 6(b) shows the growth rate of the gel as a function of the evaporation rate. It is seen that the growth rate is in proportion to evaporation rate J. This can be understood as follows. Consider the situation at a large evaporation rate. In this case, when the gel forms, the volume fraction at the bottom remains at ϕ_0, while the volume fraction at the surface remains at ϕ_g. Then the conservation of solute and solvent indicate that $J\Delta t + \Delta h_g$ is equal to $\Delta h_g \phi_g/\phi_0$. Hence the growth rate of the gel phase, $\Delta h_g/\Delta t$, is obtained as $J\left(\phi_g/\phi_0 - 1\right)$. This expression is compared with that obtained by numerical calculation in Fig. 6(b). The agreement is good.

5. Conclusion

We have proposed a new model which describes the drying behavior of a thin film of soft matter solutions placed on a flat substrate. We have conducted extensive numerical calculations to study the dynamics of the skin phase formation, especially how the dynamics depend on the elastic parameter, the evaporation rate and the initial volume fraction. We have discussed the growth rate of the skin layer, which is shown to be linear with the evaporation rate.

The realistic case can be more complex than our simple model. Evaporation rate can change with time due to the evaporation, rather than keeping as a constant. Moreover, heat transfer can influence the diffusion process, while we neglect its effects for simplicity in this work. In spite of these, we believe that this work can provide a basic tool in handling the film formation process of drying soft matter solutions on a flat substrate.

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