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A simple model of skin formation in solvent evaporation processes

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A simple model is proposed for the skin formation in the evaporation process of polymer solution at free surface. In this model the skin is regarded as a gel phase formed near the free surface, and the dynamics is described by diffusion equation for 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.

1 Model

We consider a layer of polymer solution with initial thickness $h_0$ placed on a flat substrate whose normal lies in $z$. When solvent evaporates at the free surface, the volume fraction of polymers $\phi$ 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, $\phi$ near the free surface increases and forms a polymer rich region. When $\phi$ reaches a certain value $\phi_g$, the polymer solution becomes a gel and a skin phase is formed. As the evaporation proceeds, the whole system finally becomes a gel.

The above process can be described by the following one-dimensional diffusion equation of $\phi = \phi(z,t)$ on $0 < z < h$,

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

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with the diffusion coefficient \( A(\phi) \) which is assumed to be

\[
A(\phi) = \begin{cases} 
D & (\phi < \phi_g), \\
D_g & (\phi \geq \phi_g),
\end{cases}
\tag{2}
\]

where \( D \) and \( D_g \) are constants independent of \( \phi \), and stands for the cooperative diffusion constants in solutions and in gel phase. Since the osmotic modulus in gel phase is much larger than that in solution due to an extra contribution of the elastic modulus of polymer network in gel phase, we can assume \( D \ll D_g \).

Assuming that the amount of solvent evaporation at the surface is written as \( J(1-\phi_h) \) with a constant \( J \) and \( \phi_h \equiv \phi(h,t) \), and imposing the boundary condition \( \partial \phi / \partial z = 0 \) at \( z = 0 \), we obtain the equation for the thickness \( h \) as

\[
\frac{dh}{dt} = -J(1-\phi_h)
\tag{3}
\]

and the boundary condition at the free surface,

\[
A(\phi) \frac{\partial \phi}{\partial z} = J\phi(1-\phi) \quad \text{at } z = h.
\tag{4}
\]

2 Conclusion

Analyzing the above model in the limit \( D_g/D \to \infty \), we obtain a criterion for the skin phase to be formed:

\[
Pe > \frac{\phi_g - \phi_0}{(1-\phi_g)\phi_g} - \frac{1-\phi_0}{\phi_0} \ln \frac{1-\phi_g}{1-\phi_0} - \ln \frac{\phi_g}{\phi_0},
\tag{5}
\]

where \( Pe \) is the Péclet number defined as \( Pe \equiv h_0J/D \) and \( \phi_0 \) is the initial concentration of polymers which is uniform. This result suggests that the skin formation can be controlled by \( Pe \) and \( \phi_0 \) for fixed \( \phi_g \) and that the smaller value of \( \phi_0 \) and the larger value of \( Pe \) lead to formation of the well-structured skins.

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.

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