Instabilities during the evaporation of a film: 
non glassy polymer + volatile solvent

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Abstract
We consider solutions where the surface tension of the solvent $\gamma_s$ is smaller than the surface tension of the polymer $\gamma_p$. In an evaporating film, a plume of solvent rich fluid, then induces a local depression in surface tension, and the surface forces tend to strengthen the plume. We give an estimate (at the level of scaling laws) for the minimum thickness $\varepsilon^*$ required to obtain this instability. We predict that a) $\varepsilon^*$ is a decreasing function of the solvent vapor pressure $p_v$ ($\varepsilon^* \sim p_v^{-1/2}$) b) $\varepsilon^*$ should be very small ($< 1$ micron) provided that the initial solution is rather dilute. c) the overall evaporation time for the film should be much longer than the growth time of the instability. The instability should lead to distortions of the free surface and may be optically observable. It should dominate over the classical Benard-Marangoni instability induced by cooling.

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Shortened version of the title: Film evaporation

1 Introduction
Spin casting of polymer films from solutions is an important practical process. The intrinsic state of these films after casting raises a number of questions - especially if they are thin [1]. In most cases, we are dealing with materials such as polystyrene, or polymethyl metacrylate, which are glassy in the final state: these glassy features complicate the process enormously.

In the present pages, we consider a simpler case: a) the dry polymer is assumed to remain fluid at room temperature (for instance, it could be a silicone oil) b) the polymer is assumed not to adsorb on the free surface of the solutions (this corresponds to $\gamma_p > \gamma_s$). We shall see that certain convective instabilities should occur during evaporation: one driven by concentration effects, and one driven by thermal effects (Benard Marangoni). We find that the concentration effects should usually be more important.

In section 2, we give a simple description of the classical evaporation process in a mixed film, associated with a diffusion flow of the solvent. Many more
precise discussions of this process exist in the literature [3], but the present crude picture is enough to estimate the concentration drop $\psi_d - \psi_u$ between the bottom plate ($\psi_d$) and the upper free surface ($\psi_u$). This drop is the essential control parameter for the onset of a convective instability (section 3).

This instability requires low viscosities: indeed the films are initially dilute and of low viscosity. We discuss the dilute limit in section 4.

Ultimately, we discuss another possible source of instability related to thermal effects: evaporation cools the outer surface. This leads to a classical Benard Marangoni instability [4]. We show in the appendix that, (when $\gamma_p > \gamma_s$), concentration effects should dominate over thermal effects.

All our discussion is restricted to the level of scaling laws. This is not unreasonable: even without instabilities, the concentration profiles in the evaporation problem are quite complex, and depend on many details: an exact hydrodynamic calculation of the thresholds in this situation would be purely numerical, and not very informative.

2 Steady evaporation profiles

The volume fraction of solvent $\psi(z)$ decreases when we move from the bottom plate ($z = 0$, $\psi = \psi_d$) to the free surface ($z = e(t)$, $\psi = \psi_u$). At the free surface, we assume instant equilibrium: the partial gas pressure of the solvent is equal to the equilibrium gas pressure $p_e(\psi_u)$, corresponding to $\psi_u$. In practice, we shall be concerned mainly with dilute solutions and replace (very roughly) $p_e(\psi_u)$ by the vapor pressure of pure solvent $p_v(T)$. Above the free surface, the solvent molecules diffuse in air, with a certain diffusion coefficient $D_a$. In practice, the air transport involves both diffusion and convection, dependent on various noise sources in the experimental room. As is often done, we assume that all this can be described as diffusion through a boundary layer of fixed thickness $\ell (\sim 1\text{mm})$. The number density of solvent molecules in the gas $\gamma_G(z)$ thus drops linearly from the value associated to $p_v$:

$$\gamma_G(z = e) = \frac{p_v}{kT}$$

(1)

to 0 at the upper end ($z = e + \ell$).

The diffusion current in the film (number of molecules per unit area and per second) is:

$$W = D_{\text{coop}} \frac{\psi_a - \psi_u}{a^2 e}$$

(2)

where $D_{\text{coop}}$ is the cooperative diffusion coefficient of the solution [5], and we ignore the $\psi$ dependence of $D_{\text{coop}}$. The same flux is found just above the free surface:

$$W = D_a \frac{\gamma_G(e) - \gamma_G(e + \ell)}{\ell} = D_a \frac{\gamma_G(e)}{\ell}$$

(3)

Our scaling estimate for the diffusion constant of solvent in air is $D_{\text{air}} \sim v_{\text{th}} / \lambda$, where $v_{\text{th}}$ is a thermal velocity for a solvent molecular, and $\lambda$ is a mean free path, inversely proportional to the air pressure $p_a$. This gives ultimately:
\[ D_{\text{air}} \approx \frac{v_{\text{th}} \ kT}{a^2 / p_a} \]  

where \( a \) is the size of a solvent molecule.

Combining eqs (1-4), we arrive at:

\[ \psi_d - \psi_u \sim \frac{e \ av_{\text{th}} \ p_v}{\ell \ D_{\text{coop}} / p_a} \]  

Typically, taking \( e = 1\mu \), \( \ell = 1\text{mm} \), \( av_{\text{th}} = 10^{-3}\text{cm}^2 / \text{sec} \), \( D_{\text{coop}} = 10^{-6}\text{cm}^2 / \text{sec} \), and \( p_v = 0.1 p_a \); we obtain \( \psi_d - \psi_u \sim 0.1 \). Eq. (5) is important, because it defines the driving force for the convective instability to be discussed in the next section.

### 3 Concentration

The principle is shown on fig.1. During the unperturbed evaporation process, we saw that there is a significant difference between the solvent fractions \( \psi_d \) and \( \psi_u \) (down and up) at the supporting surface and at the free surface. We now assume that a roll instability is superposed on the diffusion flux. We can visualise the system as a set of rolls of size \( e \), or as a set of plumes carrying extra solvent from down to up. The result is a slight difference in solvent concentration between point A \( (\psi_A) \) and point B \( (\psi_B) \). We estimate this difference by a balance between convection and diffusion:

\[ D_{\text{coop}} \frac{\psi_A - \psi_B}{e} \approx V (\psi_d - \psi_u) \]  

where \( V \) is the convective velocity. The difference \( \psi_A - \psi_B \) induces a gradient of surface tension:

\[ \nabla \gamma \approx \frac{\gamma_B - \gamma_A}{e} = \frac{-\gamma'_s}{e} (\psi_A - \psi_B) \]  

where \( \gamma'_s = d\gamma / d\psi \) is assumed negative: the polymer has a higher surface tension than the solvent.

Finally, we estimate \( V \) by a balance between surface forces and viscous stresses:

\[ \nabla \gamma \sim \frac{\eta V}{e} \]  

where \( \eta \) is the solution viscosity.

Combining eqs (6, 7, 8) one arrives at a minimal thickness:

\[ e^* \approx \frac{\eta D_{\text{coop}}}{|\gamma'_s| (\psi_d - \psi_u)} \]
For rough estimates, we can write in the semi dilute regime:

\[ D_{coop} = \frac{kT}{\eta_s \xi} \]  

(10)

where \( kT \) is the thermal energy, \( \eta_s \) the solvent viscosity, and \( \xi \) the mesh size in the solution. The result is:

\[ e^* \sim \frac{kT}{|\gamma'| \xi \eta_s (\psi_d - \psi_u)} \]  

(11)

We can now combine eq. (1) and eq. (3), arriving at:

\[ (e^*)^2 \sim \frac{kT \ell \eta}{|\gamma'| \xi \eta_s \alpha v_{th} p_v} D_{coop} p_a \]  

(12)

4  Discussion

a) Role of the solvent vapor pressure \( p_v \): we see on eq. (12) that high values of \( p_v \) lead to low values of \( e^* \). The instability (which occurs for \( e > e^* \)) is favored.

b) Role of the solution viscosity \( \eta \): if we were dealing with concentrated polymer films, \( \eta/\eta_s \) would be very high, and \( e^* \) would be prohibitively large. For instance, if we choose \( |\gamma'| = 10 mJ/m^2 \), \( \xi = 10nm \), \( \eta/\eta_s = 10^6 \), \( \ell = 1mm \), and \( D_{coop}/\alpha v_{th} = 10^{-3} \), we arrive at \( e^* \sim 0.2mm \). However, we must not forget that our films always start from a rather dilute state, with \( \eta/\eta_s \sim 1 \). The instability will grow during the early stages of evaporation. If we now switch to \( \eta/\eta_s \sim 1 \), we are led to \( e^* = 200 \) nanometers. Thus (even if there are large numerical prefactors in eq. (12)) we expect to find the instability in films around 1 micron.
c) To substantiate this prediction, we must show that the evaporation time $\tau_{ev}$ is longer than the growth time ($\tau_g$) of the instability. We estimate $\tau_{ev}$ as follows.

The rate of thinning is given by the flux $W$ of eq. (2):

$$\frac{de}{dt} = -a^3 W$$

(13)

Using also eq. (2), this gives an evaporation rate:

$$\frac{1}{\tau_{ev}} = \frac{1}{e} \frac{de}{dt} = \frac{D_{coop}}{e^2} (\psi_d - \psi_u)$$

(14)

Lest us now consider the growth time of the instability $\tau_g$. For simplicity, we shall focus our attention here on rather thin films, where inertial effects can be neglected. We can then rewrite a time dependent equation for the modulation $\psi_m \equiv \psi_A - \psi_B$ in the form:

$$\frac{\partial \psi_m}{\partial t} = -D_{coop} q^2 \psi_m + qV(\psi_d - \psi_u)$$

(15)

where $q$ is the horizontal wave vector of the modulation ($q \sim e^{-1}$). We also have, as in eq. (8):

$$\eta q V = q |\gamma'| \psi_m$$

(16)

At threshold, the two terms in eq. (15) balance each other. We now consider situations definitively above threshold, where the convection term in (15) is dominant. Using eq. (16), this leads to:

$$\frac{1}{\tau_g} \approx \frac{|\gamma'|}{\eta e} (\psi_d - \psi_u)$$

(17)

Comparing eqs (17) and (14) we find:

$$\frac{\tau_{ev}}{\tau_g} \approx \frac{|\gamma'| e}{\eta D_{coop}} \approx \frac{|\gamma'| e \xi}{kT}$$

(18)

Taking a dilute system, with $|\gamma'| = 10 mJ/m^2$, $e = 1 \text{micron}$, $\xi = 10 \text{nm}$, we find $\tau_{ev}/\tau_g \approx 2.10^4$. Thus, the instability should grow easily before complete evaporation - during a time interval $\tau_g < < \tau_{ev}$, where the viscosity is low and $e^*$ is small.

Another estimate for $\tau_g$, can be written down, when inertia is dominant (and eq. (16) is modified). But the conclusion remains the same for most practical film thicknesses.

d) There are a number of details which are not included in our discussion: for instance, the dependence of the surface tension $\gamma(\psi)$ on solvent concentration in the dilute limit ($\psi \to 1$) has not been considered. In fact, we
know that when the polymer surface tension is higher than the solvent surface tension, there is a depletion layer of thickness $\xi$ near the free surface, and the surface tension has the following scaling form [3]:

$$\gamma(\psi) - \gamma(1) \simeq \frac{kT}{\xi^2} \simeq \frac{kT}{a^2} (1 - \psi)^{3/2}$$

Thus, the parameter $|\gamma'|$ of eq. (19) is really $\psi$ dependent:

$$|\gamma'| \sim \frac{kT}{a^2} (1 - \psi_u)^{1/2}$$

But, for reasonable values of $\psi_u$ (e.g. $\psi_u = 0.9$) this brings in only minor corrections on $e^* -$proportional to $(1-\psi_u)^{1/4}$.

5 Conclusions

All our discussion ignored numerical coefficients, and we know how they can be important (e.g. for the onset of thermal convection in the Rayleigh problem). But some conclusions do emerge:

1) The convective instability due to concentration gradients in the film should show up for non glassy polymer films (of thickness $e > e^*$).

2) It takes place early: when the film is still dilute.

3) It will induce a certain surface roughness. To compute the amplitude of the surface undulations resulting from the rolls is a delicate task and will not be attempted here.

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6 Appendix

We now ignore all concentrations effects, and focus on fig. 3. Here, we have a thermal plume, terminating at point A, and we estimate the temperature difference by a balance of heat fluxes:

$$D_t \frac{T_A - T_B}{e} = V(T_d - T_u)$$

$D_t$ is the thermal diffusion coefficient of the liquid. The difference $T_d - T_u$ is due to evaporation and cooling at the upper surface. The vertical solvent flux towards the air is:

$$J_s \simeq D_{coop} \frac{\psi_d - \psi_u}{e}$$

This corresponds to an outward energy flux:
Figure 2:

\[ J_E = U_v J_s \]  \hspace{1cm} \text{(A3)}

where \( U_v \) is the heat of evaporation (per unit volume of liquid).

Balancing \( J_E \) against a vertical heat flux (from the support to the outer surface), we obtain:

\[ C_p D_t \frac{T_d - T_u}{e} \approx J_E \]  \hspace{1cm} \text{(A4)}

Here, \( C_p \) is the specific heat per unit volume (assumed constant), and \( D_t \) a thermal diffusion coefficient in the liquid.

Finally, we have a stress balance similar to eq. (8), giving:

\[ \eta V \approx \gamma'_T(T_A - T_B) \]  \hspace{1cm} \text{(A5)}

where:

\[ \gamma'_T \equiv \frac{d\gamma}{dT} < 0 \]  \hspace{1cm} \text{(A6)}

Combining eqs (A2-A5), we arrive at a threshold thickness:

\[ e^{**} = \frac{\eta}{\gamma'_T} \left( \frac{D_t}{D_{coop}} \right)^2 \frac{C_p}{U_v} \frac{1}{\psi_d - \psi_u} \]  \hspace{1cm} \text{(A7)}

We can now compare the two processes, however:

\[ \frac{e^{**}}{e^*} = \frac{\gamma'_s C_p}{\gamma'_T U_v} \left( \frac{D_t}{D_{coop}} \right)^2 \]  \hspace{1cm} \text{(A8)}

The factors \( \gamma'_s C_p / \gamma'_T U_v \) combine to give a constant of order unity, and the major features are related to the diffusion coefficients. Typical values are \( D_{coop} = 10^{-6} \text{cm}^2/\text{sec} \), \( D_t = 10^{-3} \text{cm}^2/\text{sec} \), and we thus expect \( e^{**} >> e^* \): for films with \( \gamma_p > \gamma_s \), thermal processes should be dominated by concentration processes.
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