Stability of Evaporating Polymer Films

For:

Dr. Roger Bonnecaze

Surface Phenomena (ChE 385M)

Submitted by:

Ted Moore

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Motivation

This problem was selected because the writer observed a dependence on casting conditions of the stability of polymer films cast from a dilute solution of a volatile solvent; See Figure 1. Films were cast by dropping a dilute polymer solution onto glass slides and allowing it to spread, coating the slide. Polymer films were cast on slides contained in a large glass pan covered with Saran® wrap. The Saran® wrap was a barrier to prevent the slides from being exposed to the air currents of a hood, and all the particles these currents typically carry around. Holes that were just large enough for an eyedropper were poked in the Saran® wrap to facilitate dropping. Films cast in this manner almost always had waves in them. This problem was solved by placing the glass slides under a short cylindrical casting ring covered with Saran® wrap. This increased the partial pressure of the solvent in the small casting ring enclosure, thus decreasing the driving force and the evaporation rate. The same thing could have been accomplished with an inverted petri dish, which is of similar dimensions. However, a hole can't be made in the top to allow the solution to be dropped onto the slides. Indeed, initial experiments were done with petri dishes, but because the slides had to remain uncovered while the solution was dropped onto them, dust particles absorbed onto the films.
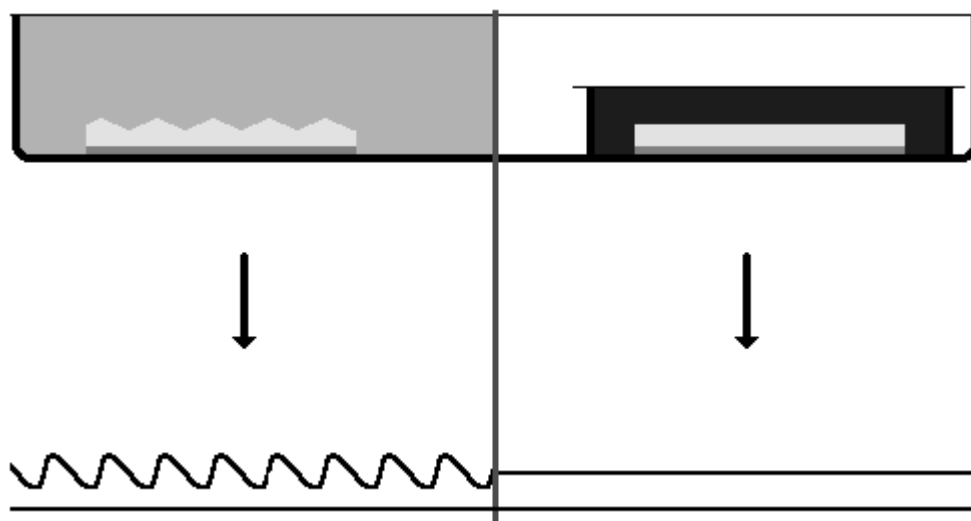

Figure 1: Sketch of Casting Conditions and the Resulting Polymer Films. The Darker Shade of Blue in the Right Case, Above the Film but Under an Intermediate Saran® Wrap Covered Casting Ring, Represents a Higher Dichloromethane Partial Pressure.

Hypothesis

Curvature causes differences in the local effective saturation pressure above a film which leads to position dependent evaporation rate since the mass transfer driving force, $P^{SAT}_{EFF}-P_{MeCl2}$ is a function of position. The local evaporation rate could either perpetuate or reduce this curvature. If the films evaporate quickly enough, as when left only covered in the large glass pan, the waves caused by the curvature could become "frozen" into the solventless polymer film. The thin film equation can be used to predict the curvature if a disturbance function is assumed; however, it

must be modified to include the effects of the evaporating solvent. Differences in the local evaporation rate will lead to two effects: differences in the local surface concentration, and differences in the local surface temperature. Both cause differences in the local surface tension and thus will cause Marangoni flows. I hypothesize that temperature probably has a larger effect because of the large heat of vaporization of the solvent that we are using, so I have neglected concentration as a cause of Marangoni flows. Because the effective saturation pressure is higher at the top, the flux is higher at the peaks, denoted with subscript P. This means the temperature will be lower at the peaks. So the Marangoni flows will be from the troughs to the peaks, which will tend to perpetuate the disturbance. Note also that the temperature disturbance function and the height disturbance function are out of phase. Figure 2 summarizes some of the physics that is occurring in this problem.
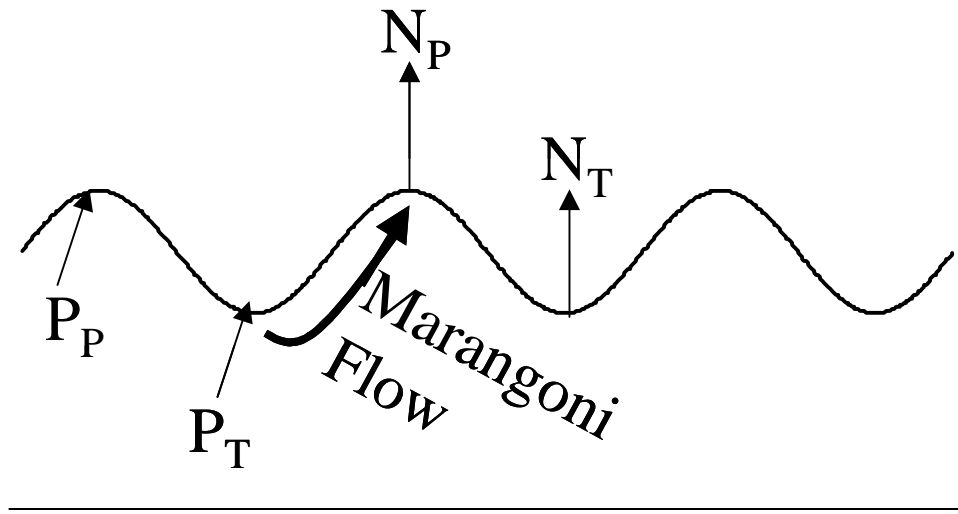

Figure 2: Summary of the Physics included in the Model

Model Equations

A modified thin film equation was used to model the system. In one dimension, this equation is:

$$\frac{dh}{dt} = \frac{1}{3\mu}\frac{d}{dx}\left(h^3\left(\rho g \frac{dh}{dx} - \gamma \frac{d^3 h}{dx^3}\right) - \frac{d\gamma}{dT}\frac{dT}{dx}\frac{3h^2}{2}\right) \qquad \text{Eq. 1}$$

This equation was developed in homework #4, problem #1. Here, $d\gamma/dx$ has been replaced by $\frac{d\gamma}{dT}\frac{dT}{dx}$.

The molar flux was assumed to be given by:

$$N(x,t) = k_M(P_{EFF}^{SAT} - P_{MeCl_2}) \qquad \text{Eq. 2}$$

where k_M is the mass transfer coefficient, which is equal to $D/\delta RT_{ATM}$. D is the binary diffusion coefficient of dichloromethane in air, and δ is the thickness of the boundary layer, which, assuming a stagnant boundary, is the distance between the film and the first layer of Saran® wrap. P^{SAT}_{EFF} is given by the Kelvin equation:

$$Ln\left(\frac{P^{SAT}_{EFF}}{P^{SAT}}\right) = \frac{v_M}{RT} \nabla \cdot \vec{n} \quad \text{Eq. 3}$$

where $(\nabla \cdot n) = -\nabla^2 h$ as proved in the class notes.

Combining Eq. 2 and a linearized Eq. 3, we obtain:

$$N(x,t) = k_M(P^{SAT} + P^{SAT}\frac{v_M\gamma}{RT} \nabla \cdot \vec{n} - P_{MeCl_2}) \quad \text{Eq. 4}$$

The molar flux is equal to the conductive heat flux at the surface divided by the heat of vaporization:

$$N(x,t) = k_M(P^{SAT} - P_{MeCl_2}) - k_M P^{SAT}\frac{v_M\gamma}{RT} \nabla^2 h = \frac{k_F}{\Delta H_V}\frac{dT}{dy} \quad \text{Eq. 5}$$

where k_F is the thermal conductivity of the fluid. In the solution, dT/dy is treated as a constant to make the mathematics more tractable. In addition, the heat flux has been limited to one dimension. Alternatively this is stated dT/dx $\ll$ dT/dy. Note that the left half of the mass transfer flux is the flux through an undisturbed surface. The heat flux can likewise be broken into undisturbed and perturbation heat fluxes, but the details are left in the appendix.

Finally, the height was assumed to be a base height plus a perturbation:

$$h(x,t) = h_0 + \eta(x,t) = h_0 + \eta_0 exp(st + ikx) \quad \text{Eq. 6}$$

was assumed. The perturbation has the form of a decaying traveling wave.

Model Solution

Detailed solutions can be found in the appendix. However, important results are presented below.

Before the equations could be solved, the relationship between the temperature disturbance and the height disturbance needs to be determined. As determined in the hypothesis section, the temperature and height disturbance functions will be out of phase. So the temperature as a function of position is:

$$T(x,t) = T_{S0} + T_0 exp(st + i(kx + \pi)) \quad \text{Eq. 7}$$

Note that this means a Marangoni flow will be induced that will drive solvent from the troughs to the peaks which will tend to amplify the disturbance. By solving Eq. 5 with equations 6 and 7, we can determine the relationship of the temperature amplitude to the disturbance amplitude:

$$\frac{T_0}{\eta_0} = \frac{k_M P^{SAT} v_M \gamma k^2}{RT} \frac{\Delta H_V h_0}{k_F} + \frac{T_B - T_{SO}}{h_0} \qquad \text{Eq. 8}$$

One can see that increasing the heat of vaporization, ΔH_V, or the mass transfer coefficient, k_M, will tend to increase the ratio of the amplitudes, while decreasing the thermal conductivity, k_F, of the fluid will tend to minimize it. These agree with physical intuition. Here T_{SO} is the temperature of an unperturbed surface. It can easily be related to the flux through an unperturbed surface.

After linearizing and solving Eq. 1 for s using Eq. 6 and 7 for h and T, respectively, we obtain:

$$s = \frac{1}{3\mu}\left(-\rho g h_0^3 k^2 - \gamma h_0^3 k^4 + \frac{3\gamma_0 h_0^2 k^2}{2T_0}\frac{T_0}{\eta_0}\right) \quad \text{Eq. 7}$$

Substituting Eq. 8 for $\frac{T_0}{\eta_0}$:

$$s = \frac{h_0^3 k^2}{3\mu}\left(-\rho g - \gamma k^2(1 - \frac{3\gamma_0}{2T_0}\frac{k_M P^{SAT} v_M}{RT}\frac{\Delta H_V}{k_F}) + \frac{3\gamma_0}{2T_0}k^2 \frac{\Delta H_V k_M}{h_0 k_F}(P_{EFF}^{SAT} - P_{MeCl_2})\right) \qquad \text{Eq. 8}$$

We can compare this to the s that we calculate for a nonevaporating surface:

$$s = \frac{h_0^3 k^2}{3\mu}(-\rho g - \gamma k^2) \quad \text{Eq. 9}$$

Eq. 9 is always negative, whereas the two terms that account for the evaporating solvent in Eq. 8 are both positive, so the evaporating solvent tends to destabilize the film.

Finally, we can derive λ_{MAX}, the fastest growing wavelength, by first taking the derivative of s with respect to k and then recognizing that $\lambda_{MAX} = 2\pi/k_{MAX}$:

$$\lambda_{MAX} = \left\{ \frac{16\pi^2\gamma(1 - \frac{3\gamma_0}{2T_0}\frac{k_M P^{SAT} v_M}{RT}\frac{\Delta H_V}{k_F})}{-2\rho g + \frac{3\gamma_0}{T_0}\frac{\Delta H_V k_M (P^{SAT} - P_{MeCl_2})}{k_F h_0}} \right\}^{\frac{1}{2}} \qquad \text{Eq. 10}$$

In Eq. 10, it is possible for the right hand side to be the square root of a negative number. The physical meaning of this is that the stability coefficient is negative at that point, and so all disturbances will decay. Only when s is positive will λ_{MAX} be a real number and thus have physical meaning.

Results

Since the motivation for this experiment was the observation that waves were "frozen" into polymer films from which solvent had completely evaporated, I wanted see if this phenomena is

explained by the above theory. Table 1 shows parameters and their sources that were used in Eq. 10 to find λ_{MAX}, which should be the observed wavelength since it is the fastest growing.

Table 1: Values Used for the Prediction of λ_{MAX}

Parameter	Value	Source	Parameter	Value	Source
γ, 25ºC	27.2mN/m	CRC, p. 6-155	T_C	207ºC	See Note
ρ, 25ºC	1.317g/cm^3	Himmelblau CD	ΔH_V, 25ºC	28.82kJ/mol	CRC p. 6-117
G	9.81m/s^2		k_M, 25ºC	4.25×10^{-7} mol/Pa/m^2/s	Calculated
γ_0	30.92mN/m	See Note	k_F, 25ºC	147mW/m/K	Perry's, 3-253
P^{SAT}, 25ºC	58.119kPa	Himmelblau CD			

Note: g_0 and T_C were calculated by assuming the slope of the surface tension of CH_2Br_2 was the same as the slope for CH_2Cl_2 since only one temperature data point was given for CH_2Cl_2. Data was taken from the CRC Handbook, p. 6.155.

Where k_M is given by $D/R/T_{ATM}/\delta$ as stated above. δ, the boundary layer thickness, was assumed to be 1cm, the approximate distance between the evaporating polymer film and the Saran® wrap. D was found to be 0.105cm^2/s by the equation of Fuller, Schettler, and Giddings, as given in Perry's. Here, the surface tension was assumed to be that of pure solvent, since we don't know the surface tension of our solvent-polymer mixture as a function of concentration. This is probably not a good assumption, but it is the best we can do in the absence of data, and it shouldn't affect the order of magnitude of our calculations.

Figure 3 shows the effect of changing the partial pressure of dichloromethane above the film on the observed wavelength, with the mass transfer coefficient as a parameter. You can see that the equation predicts that the disturbance wavelength blows up near the saturation pressure of 58kPa. This is because the mass transfer rate goes to zero because the driving force goes to zero. Unfortunately, Eq. 8 predicts stability at all partial pressures for the mass transfer coefficient that I predicted. It is, however, quite possible that the mass transfer coefficient that I predicted was too low. The model for the mass transfer coefficient that I used assumes a totally quiescent fluid above the evaporating films. Since no special precautions were taken to insure this, it is quite likely that there was some velocity above the films, especially in the case where the films were evaporating just into the large covered pan. Any velocities at all could drastically increase the mass transfer coefficient.
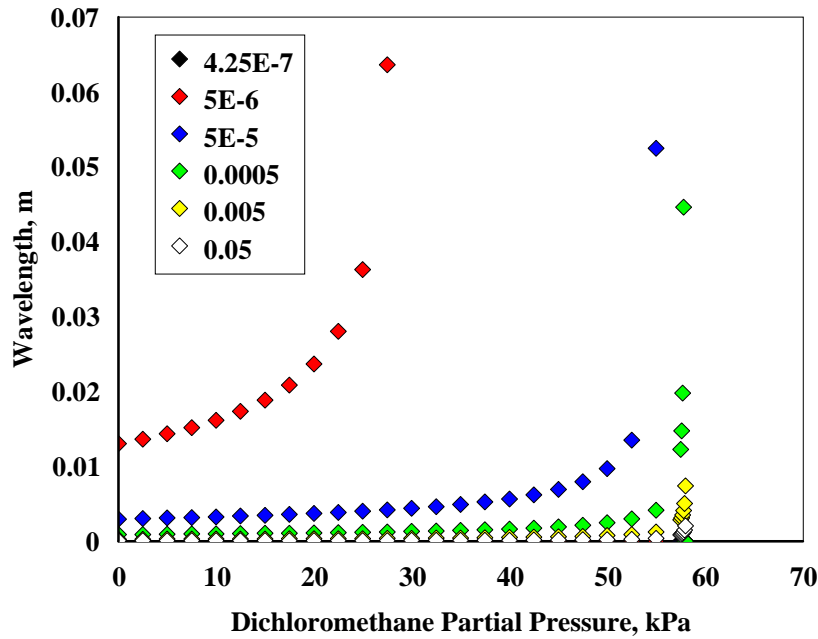
Figure 3: Effect of Dichloromethane Partial Pressure and Mass Transfer Coefficient on Observed Disturbance Wavelength. Values in the Legend represent k_M, mol/Pa/m^2/s.

Low dichloromethane partial pressures would occur in the large covered pan above the evaporating film without extra covered casting ring . Figure 4 shows the effect of mass transfer coefficient on the expected observed wavelength for a dichloromethane partial pressure of zero. As you can see from Figure 3, this infinite dilution observed wavelength approximates the observed wavelengths at most partial pressures of dichloromethane for all but the lowest mass transfer coefficients. Also, it is apparent that there is a critical mass transfer coefficient of about 2.5×10^{-6} mol/Pa/m^2/s below which all films are stable. The wavelength that I observed in my experiments for the case where the solvent was evaporating into the covered pan, without the extra covered casting ring, was about one to three mm. This corresponds to a mass transfer coefficient of $\sim 1 \times 10^{-4}$ mol/Pa/m^2/s.
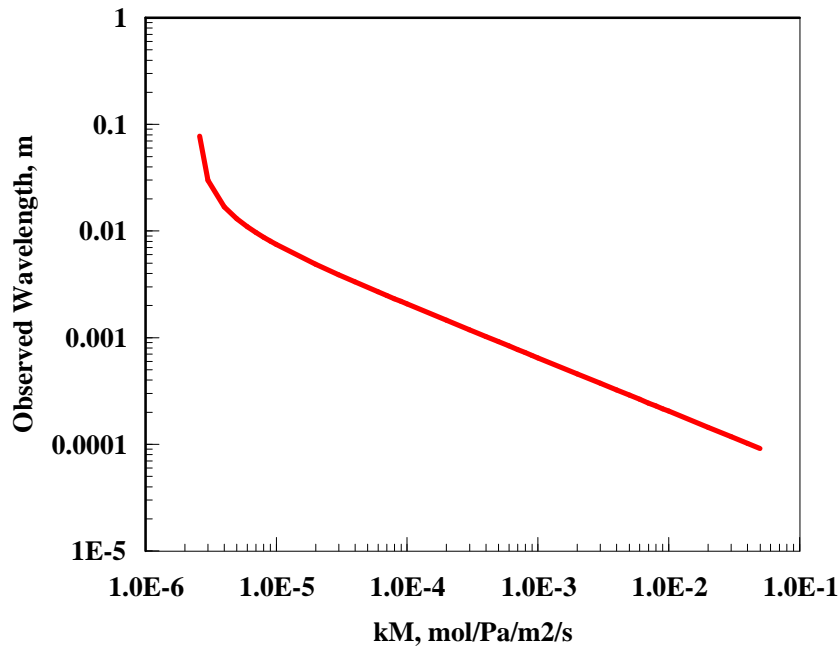
Figure 4: Effect of Mass Transfer Coefficient on the Expected Observed Wavelength for a Dichloromethane Partial Pressure of Zero.

Conclusions

Equations were developed for the stability coefficient and fastest growing wavelength for an evaporating film. These equations incorporate the effect of temperature driven Marangoni flows. They predict instability at high evaporation rates, as expected. They also predict that increasing heats of vaporization or decreasing thermal conductivities will make the film less stable, in agreement with intuition. A small amount of polymer in these films does not evaporate, leaving a snapshot of the disturbance at the time the solvent is finished evaporating. Unfortunately, these equations do not accurately predict experimentally observed wavelengths, but this could be due to inaccurate calculations of the mass transfer coefficient. If the calculated mass transfer coefficient is off by one order of magnitude, instability is predicted at low partial pressures of dichloromethane, which would be present if the solvent was evaporating into the large covered pan but not if the solvent was evaporating into the smaller covered casting ring. If the mass transfer coefficient is off by two orders of magnitude, then the equations for the observed wavelength accurately predict the experimentally observed wavelengths.