Numerical investigation of thin film of polar liquid with added surfactant

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Abstract. The thin film of polar liquid with an added surfactant is investigated numerically in this paper. The evolution equations for film thickness and surface concentrations were solved using the semi-implicit Crank-Nikolson scheme. A few profiles on the liquid film developing from an ellipse-shaped drop were received. It was confirmed that the developing film divides into two coexisting films with predictable thickness. It was discovered that this peculiarity of the polar liquid is valid only in little range of vapor pressure, which corresponds to the disjoining pressure. It was found that the surfactant desorbed on the gas-liquid interface does not effect to the thickness of the film while the surfactant desorbed on the substrate does effect. It was also found that the stable thickness of the film grows with absolute value of the vapor pressure in stated little range.

1. Introduction

Thin films could be used in production of electronic devices, in biochemical investigations, and in various technological applications like coatings and paintings. One of ways to produce the technological thin film is to evaporate a liquid film with dissolved matter. Here, the behavior of the liquid solvent should be considered because the evaporating liquid can produce some patterns of the dissolved matters which is not always desired.

There are many experimental and theoretical papers dedicated to investigations of thin films [1; 2]. Only few theoretical papers consider the disjoining pressure [3] because properties connected to the disjoining pressure have their effect only in case of thin films with thickness around 100 Å.

Polar liquids have a specialty to “find” some special stable thickness compared to distance of dipole interaction. It corresponds to its disjoining pressure which consists not only of van der Waals interaction but also of electric interaction between interfaces. Disjoining pressure is an additional pressure in the thin film which was described by Deryagin [4]. It consists of van der Waals interaction, electrostatic interaction in polar liquids, capillary osmosis determined by a surfactant desorbed on substrate, and term of shape.

It was showed [5; 6] that little evaporating drops of water change their shape and decrease in thickness until they "found" some stable value of thickness, so that liquid layer divides into two parts: “thin” and “thick”. After that, the film saves this thickness, and volume of the evaporating liquid reduces in account of area of “thicker” part. The goal of this paper is to find some way to control thickness of thin film of the polar liquid.
2. Numerical simulation

The thin layer of polar liquid is investigated which is put on a solid substrate and bordered from above with a free-deformable gas-liquid interface. A surfactant is added to the liquid which can be desorbed on both interfaces. The disjoining pressure is considered in the mechanics of the thin film. Evolution equations received in paper [7] were used for simulation of the system: a lubrication equation for the liquid film, and two diffusion equations considering adsorption-desorption processes for surface concentration on both interfaces:

\[ \partial_t H - \partial_x \left[ H^2 \left( \frac{H}{3} + \frac{\beta_0}{2} \right) \partial_x (P + \Phi) \right] - \frac{Ma}{2} \partial_x \left[ (H^2 + \beta_0 H) \partial_x \Gamma_A \right] = 0, \]  

(1)

\[ \partial_t \Gamma_A + \partial_x \left( U \Gamma_A \right) = \frac{\partial^2 \Gamma_A}{P_{\epsilon A}} - K_A \left( 1 - \Gamma_A \right) + K_A \Gamma_A = 0, \]  

(2)

\[ \partial_t \Gamma_S + \partial_x \left( U \Gamma_S \right) - \frac{\partial^2 \Gamma_S}{P_{\epsilon S}} - K_S \left( 1 - \frac{\Gamma_S}{\gamma} \right) + K_S \Gamma_S = 0, \]  

(3)

with the velocity equation

\[ U = \left( \frac{Z^2}{2} - H(Z + \beta_0) \right) \partial_x (P + \Phi) - (Z + \beta_0) Ma \partial_x \Gamma_A, \]  

(4)

and the added pressure

\[ P + \Phi = -Ca \partial^2_x H - \frac{1}{H^3} + e^{-\gamma/H} + W_1 + W_0 \ln(\gamma - \Gamma_S), \]  

(5)

The following dimensionless governing parameters are used in the evolution equations:

- Marangoni number \( Ma = \frac{\alpha \Gamma_A}{\sigma_0}, \)
- adsorption parameters \( K_{1,3} = \frac{k_{1,3}}{\epsilon U_0} \) with subscript 1 for gas-liquid interface and 3 for solid-liquid interface,
- desorption parameters \( K_{2,4} = \frac{k_{2,4} h_0}{\epsilon U_0} \) with subscript 2 for gas-liquid interface and 4 for solid-liquid interface,
- capillary number \( Ca = \frac{\epsilon^3 \sigma_0}{\mu U_0}, \)
- Peclet numbers \( P_{\epsilon A,S} = \frac{h_0 U_0}{\epsilon D_{\epsilon A,S}}, \)
- parameter of slipping along the substrate \( \beta_0 = \frac{\beta}{h_0}, \)
- evaporation parameter \( \Omega = \nu \sigma_0 \mu \left( \frac{6\pi}{A S^{1/3}} \right)^{2/3} \)
- vapor pressure \( S = \frac{\rho v_S}{S^{1/3}} \)
where subscripts \(A\) and \(S\) mean the liquid-gas and liquid-solid interface correspondingly, \(\mu\) is the liquid viscosity, \(D_i\) is the surface diffusion, \(\rho\) and \(\phi_v\) are the pressure and chemical potential of the vapor, and \(v\) is the latent heat of vaporization.

The semi-implicit Crank-Nicolson scheme was used for linearizing of the equations. The equations were discretized by finite difference method.

3. Results and discussion

First we proved that the drop of polar liquid with initial shape of ellipse takes a form showed in paper [5] and finds some stable thickness. This simulation has been made for clear liquid without surfactant: \(\Gamma_A = \Gamma_S = 0\). Another parameters used: \(Ca = 0.001, Ma = 1, \chi = 1.085, \varepsilon = 0.001, \beta = 0.001, Pe_A = 5, Pe_S = 100, \Omega = 1, W_0 = 0.03, W_1 = -0.02, K_1 = 1, K_2 = 0.9, K_3 = 0, K_4 = 0, \gamma = 1\); dimensionless time interval \(dt = 0.01\). Here, only parameters of evaporation and vapor pressure can influence. Results of the simulations at various values of vapor pressure \(S\) are showed in figure 1. One can see that the velocity of drop evaporation depend on the vapor pressure: the higher absolute value of the vapor pressure is, the quicker the drop evaporates.

**Figure 1.** Evolution of drop of a polar liquid at various values of the vapor pressure and in various moment of simulation: (a) \(S = -0.022\), solid lines at moment \(0.3 \times 10^4, 12 \times 10^4, 20 \times 10^4\) of dimensionless time; (b) \(S = -0.023\), solid lines at moment \(0.3 \times 10^4, 1 \times 10^4, 1.5 \times 10^4\) of dimensionless time. The dashed line shows initial form of the drop.

Figure 2 shows that the vapor pressure also determines the higher stable thickness. We can conclude that the stable thicknesses can be predicted from the disjoining pressure equated with the vapor pressure because the evaporating drop comes to balance when the disjoining pressure becomes equal to the vapor pressure.

Earlier investigations showed that diffusivity of the surfactant on the liquid-gas interface can influence on stability of the film, so the faster the surfactant diffuses along the interface the more stable the interface is. Meanwhile, the solutal Marangoni instability arises only with anti-surfactant [7; 8] which increases surface tension. So, for goal of this paper, we simulated high-diffusive surfactants which decrease the surface tension but is present only on the gas-liquid interface. Simulation showed that the presence on the surfactant only on the gas-liquid interface does not effect to evolution of the film. After that, we simulated the liquid drop with the similar surfactant but desorbed also on the solid-liquid interface. As it was marked in [4], one of addends of the disjoining pressure is capillary osmosis determined by the surfactant concentrated on substrate below the liquid film. This idea was realized in equation (5). Result of the simulation is shown in figure 3.
Figure 2. Comparison of liquid drop evolution at various vapor pressure: (a) after $0.8 \times 10^4$ of dimensionless time; (b) after $1 \times 10^4$ of dimensionless time. 1 means the layer at $S = -0.022$, and 2 means the layer at $S = -0.023$.

Figure 3. Simulation result for the drops with the surfactant desorbed on both interfaces ($\Gamma_S = 0.15$). The solid line is for vapor pressure $S = -0.027$, the dashed line is for $S = -0.028$.

Comparing figure 3 with figure 1 we can see that the values of stable thickness, both for “thick” and “thin” parts, do not change after addition of the surfactant on the substrate, but the vapor pressure does: the same values of thickness were received at another vapor pressure.

Figure 4. A chemical potential of a polar liquid in dependence on the film thickness. The plots (a) and (b) are received from equation (5) and reproduced in various scales. The dashed line is for $\Gamma_S = 0.15$ and the solid line is for $\Gamma_S = 0$. Plot (b) is for $\Gamma_S = 0.15$. 
The possibility to predict the film thickness is valid only for polar liquids because their disjoining pressure is non-monotonically connected with the film thickness as it is shown in figure 4. It can be also understood from figure 4 that the surfactant desorbed on the substrate doesn’t change dependence of disjoining pressure on the thickness but only reduces the values of the disjoining pressure. One can find that there is a little range of vapor pressure values where the two stable thicknesses can exist simultaneously: for example, from -0.028 to -0.025 in dimensionless units at concentration of the surfactant on the substrate $\Gamma_S = 0.15$. It is the range where three values of thickness coexist at one value on the disjoining pressure, two stable thicknesses and one unstable between them (“three-point range”). If the vapor pressure is outside of the range, the drop will have only one stable thickness, around 2.2 of dimensionless units, which corresponds to 1.1 nm [6].

In order to find how the surface concentration on the substrate effects to the three-point range, we calculated the ranges at various values of the concentration. Results of the calculation are present in table 1.

| Surface concentration at the substrate, $\Gamma_S$, dimensionless units | Min disjoining pressure $dg/dH$ | Max disjoining pressure $dg/dH$ |
|--------------------------------------------------|-----------------|-----------------|
| 0.04                                             | -0.02472        | -0.02142        |
| 0.05                                             | -0.02503        | -0.02173        |
| 0.06                                             | -0.02535        | -0.02205        |
| 0.07                                             | -0.02567        | -0.02237        |
| 0.08                                             | -0.02599        | -0.02269        |

Further, we have to find how the higher stable thickness depends on the vapor pressure in stated range. Plot of this dependence is showed in figure 5. We can see from the figure 5 that the higher stable thickness grows while the vapor pressure reduces in its absolute value.

4. Conclusion
The thin film of polar liquid in presence of surfactant was simulated. It was confirmed that in little range (“three point range”) of the vapor pressure the film divides into two parts with stable thicknesses. It was found that the stable thickness can be predicted from the disjoining pressure equation. The “three-point” ranges of the vapor pressure were calculated for various values of surface concentration on the substrate. It was found that the higher stable thickness grows while the vapor pressure reduces.

It can be concluded that the experimentalist could control the thickness of the film of polar liquid by change of vapor pressure in special experimental setup, or by putting some low-dissolving surfactant on the substrate under the liquid.

![Figure 5. Dependence of higher stable thickness on the vapor pressure, the values are received for $\Gamma_S = 0.05.$]
References

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