

Model of a Liquid Nanofilm on a Solid Substrate

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ABSTRACT

Van der Waals attractive forces drastically change the material properties of thin liquid layers when in contact with a solid. At this scale, the fluid is no longer homogeneous. Moreover, it has properties which analogous to those of solids. In particular, in equilibrium the stress tensor is no longer spherical. For such fluids, we use a long-wave approximation to derive the evolution of a liquid nanofilm on a substrate. We establish that the driving pressure in nanofilm should be associated with the mean value of the component of the pressure tensor tangential to the liquid interface (along the substrate). Finally, we derive the equation for nanofilm dynamics by using mass conservation formulation. This is not a conventional, conservative equation for the position of the free surface normally used in the theory of thick films where the density is homogeneous, but rather a conservative equation for the liquid mass. The equation turns out to be a nonlinear parabolic equation with a diffusion coefficient of a "good" sign.

Keywords: liquid nano film, intermolecular interactions, van der Waals concept.

1 INTRODUCTION

A mathematical treatment of the dynamics of liquid films on a solid substrate in general has to deal with the fact that film interface represents a free boundary whose configuration evolves both temporally and spatially. This configuration must be determined as a solution for governing equations. The most appropriate analytical method for dealing with the problem is to analyze long-scale phenomena only, in which the characteristic lateral length scale (along the substrate) is much larger than the average film thickness. Such a long-wave theory approach is widely and successfully used to model dynamics of relatively thick liquid films (see [1] for review). However, this approach cannot be scaled directly down to the nanoscale. That is because liquid in macro and micro films is normally treated as a viscous, incompressible fluid, and Navier-Stokes equations used as the governing equations fail at the nanoscale and have to be revised.

At this scale, interfacial transition layers (due to solid-liquid and liquid-gas interactions) completely overlap. The fluid is no longer homogeneous; its density varies in the direction normal to the solid interface. This nonhomogeneity can be taken into account by considering the physical concept where the liquid energy depends on the space derivatives of its density (Rayleigh [2], van der Waals [3]).

Volume energy dependent on density gradients also appears in the study of the kinetics of phase boundaries, moving contact lines and other phenomena (see [4], [5], [6] and [7] for a comprehensive review).

Rocard [8] introduced the anisotropic stress tensor in such liquids by using the methods of the kinetic theory of gases. The reversible dynamics of such liquids was derived from the Hamilton principle of stationary action in [9], [10], [11] (see also references in [6]).

These liquids (often called capillary fluids) have peculiar physical properties. In particular, in equilibrium the stress tensor is not spherical, and the fluids have properties analogous to those of solids. The boundary conditions for such fluids represent a correlation between boundary values of the density and its normal derivatives ([12], [13], [14], [15]). All these peculiarities provide main difficulties in the detailed mathematical treatment of specific physical problems.

We apply this concept to study the motion of liquid nanofilms on a substrate. The details can be found in [20].

2 STATIC PROBLEM

Consider a thin liquid film of thickness h occupying the domain Ω which is in equilibrium with a solid substrate. The boundary between the solid and liquid is denoted by S , the upper surface of the film is denoted by Σ . We will suppose that both S and Σ are flat. Gravity is ignored. The total energy of the system \mathcal{E}_T is

$$\mathcal{E}_T = \int_{\Omega} \left(W(\rho) + \lambda \frac{|\nabla \rho|^2}{2} \right) d\Omega + \int_S \mathcal{E}_S dS + \int_{\Sigma} \mathcal{E}_{\Sigma} d\Sigma \quad (1)$$

Here ρ is the liquid density which is supposed to be not uniform in space due to liquid-substrate and liquid-

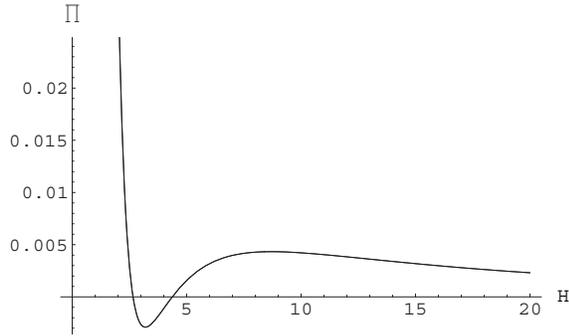


Figure 1: The normalized pressure vs normalized film thickness is shown for $M = 1$. This curve represents a typical van der Waals isotherm.

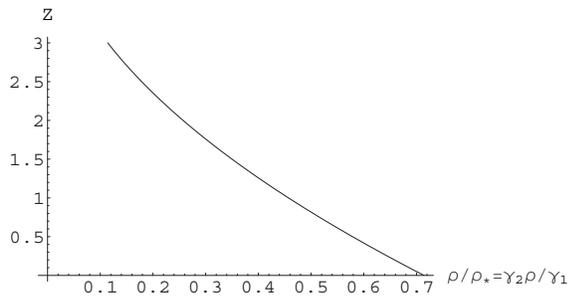


Figure 2: The normalized density profile is shown for the nanofilm of thickness $H = 3$.

liquid interactions. $W(\rho)$ is the bulk liquid energy related in general with the kinetic energy of thermal motion of liquid molecules and with the potential energy of interaction between the liquid molecules in uniform liquid of density ρ . The second term, depending on the density gradient $\nabla\rho$ is responsible for the capillary effects (the density nonhomogeneity) due to van der Waals attractive forces. Van der Waals forces are important when the film thickness is in the range of 10-100 nm ([5], [16], [17], [18]). Finally, the two last terms are the energies of the surfaces S and Σ .

A typical expression of \mathcal{E}_S is as follows [5] :

$$\mathcal{E}_S = -\gamma_1\rho_S + \frac{1}{2}\gamma_2\rho_S^2 \quad (2)$$

Here ρ_S is the liquid density at the surface S , $\gamma_1 > 0$ corresponds to the attraction between solid and liquid molecules, $\gamma_2 > 0$ is the repulsive component due to the attraction between liquid molecules, which are near the solid, and those in the bulk. For the energy \mathcal{E}_Σ we propose an analogous expression

$$\mathcal{E}_\Sigma = \frac{1}{2}\gamma_2\rho_\Sigma^2 \quad (3)$$

Here ρ_Σ is the liquid density on the upper boundary Σ . Parameter γ_1 is taken to be zero in the last formula because we neglect the interaction between liquid and gas/vapor at the film surface.

The parameters λ , γ_1 and γ_2 can be explicitly calculated in terms of molecular interaction potentials. An example of such a calculation was done in [19] for semi-infinite liquid in contact with a solid substrate for the Lennard-Jones potentials with hard-core repulsion.

For nanofilms, the volume energy W can be neglected in Eq. (1). On the contrary, we account for the capillary energy related to the distortion of the density profile due to van der Waals forces.

In static equilibrium, the total energy of the system is minimal. The solution of the minimization problem for the reduced energy functional

$$\mathcal{E}_T = \int_\Omega \lambda \frac{|\nabla\rho|^2}{2} d\Omega + \int_S \mathcal{E}_S dS + \int_\Sigma \mathcal{E}_\Sigma d\Sigma \quad (4)$$

looks as shown below ([12], [13], [14], [15])

$$\nabla(\Delta\rho) = 0, \quad \lambda \frac{\partial\rho}{\partial n}\Big|_S - \gamma_1 + \gamma_2\rho_S = 0, \quad \lambda \frac{\partial\rho}{\partial n}\Big|_\Sigma + \gamma_2\rho_\Sigma = 0 \quad (5)$$

Here Δ is the Laplacian operator, and ∇ is the operator gradient. We denoted here $\frac{\partial\rho}{\partial n}$ the normal derivative of the density, and \mathbf{n} is the external normal to the liquid volume.

In this approach, the liquid density ρ_S on the substrate and ρ_Σ on the free surface are not yet defined. We propose a method to determine them as a function of the molecular interaction parameters and film thickness.

It is convenient to work with the dimensionless variable film thickness

$$H = \frac{h}{h_*}, \quad h_* = \frac{\lambda}{\gamma_2} \quad (6)$$

We also introduce the dimensionless mass per unit area

$$M = \frac{m\gamma_2^2}{\lambda\gamma_1}, \quad m = \int_0^h \rho dz \quad (7)$$

and express the dimensionless energy per unit area

$$E = \frac{\mathcal{E}_T\gamma_2}{\gamma_1^2} \quad (8)$$

as a function of H and M .

For a given mass M , in equilibrium the energy should be minimal. The critical points of the energy are defined by

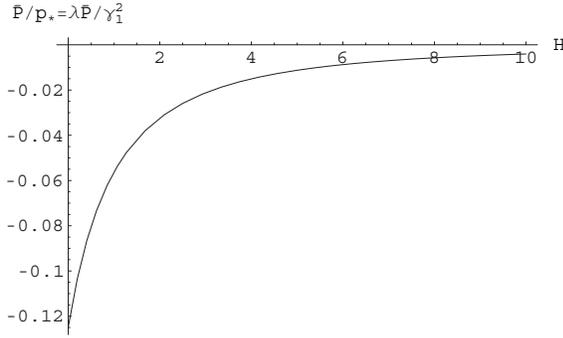


Figure 3: The mean pressure is a concave and monotonic function of the film thickness H .

$$\left. \frac{\partial E(H, M)}{\partial H} \right|_{M=const} = 0 \quad (9)$$

It corresponds to the normal pressure component equal to zero. This equation has two roots. One can prove that the first root corresponding to smaller H is stable (the second derivative of the energy is positive) and the second root is unstable (the second derivative of the energy is negative). It is clearly visible in Figure 1. The equilibrium density profile in the layer of thickness H corresponding to the stable root is shown in Figure 2.

3 DYNAMIC PROBLEM

We calculate the *mean pressure* in the nanofilm. It is shown in Figure 3. One can see that the mean pressure is negative.

We use now the approximation of “long waves” by employing that the vertical scale length (film thickness) is much smaller than the horizontal scale length (wavelength of perturbation of the film). This is reminiscent of the “shallow water” approximation used in the theory of gravity waves. In this limit we obtain the evolution equation in explicit form for dimensionless variable H

$$(M(H))_t - \left(\frac{\lambda \gamma_1^2}{3 \mu_* \gamma_2^2} H^2 M(H) (\Pi_d(H))_x \right)_x = 0, \quad (10)$$

where $M(H)$ is determined by

$$M = \frac{12H + 6H^2 + H^3}{3(8 + 6H + H^2)} \quad (11)$$

and the dimensionless driving pressure $\lambda p_d / \gamma_1^2$ (denoted as Π_d) can be calculated in explicit form

$$\Pi_d(H) = -\frac{2}{3} \frac{10 + 6H + H^2}{(8 + 6H + H^2)^2} \quad (12)$$

Equation (10) is parabolic with the diffusion coefficient of “good” sign because

$$\frac{d\Pi_d(H)}{dH} > 0 \quad (13)$$

For small H , the parabolic equation will look as follows

$$H_t - \left(\frac{\lambda \gamma_1^2}{32 \mu_* \gamma_2^2} H^3 H_x \right)_x = 0 \quad (14)$$

4 DISCUSSION

Let us calculate some characteristic parameters introduced and employed in this study. For estimation, we consider a liquid argon film on a pure silicon substrate. The masses of liquid and substrate molecules are $m_l = 59.78 \times 10^{-27} \text{ kg}$, and $m_s = 46.50 \times 10^{-27} \text{ kg}$, respectively. The density of the substrate is $\rho_{sol} = 2330 \text{ kg/m}^3$. The effective diameter of a liquid molecule is $\sigma_l = 0.34 \text{ nm}$. The effective diameter of a substrate molecule can be estimated as $\sigma_s = (M_s / (\rho_{sol} N_A))^{1/3} = 0.27 \text{ nm}$, where M_s is the molecular weight of the substrate, and N_A is the Avogadro number.

Then a characteristic film thickness h_* may be estimated as

$$h_* = \frac{\lambda}{\gamma_2} = \frac{8\delta^2}{\sigma_l} = 2.19 \text{ nm} \quad (15)$$

A characteristic liquid density ρ_* is

$$\rho_* = \frac{\gamma_1}{\gamma_2} = \rho_{sol} \frac{m_l C_{ls}}{m_s C_{ul}} = 2996 \frac{C_{ls}}{C_{ul}} \text{ kg/m}^3 \quad (16)$$

A characteristic liquid pressure p_* is estimated as following

$$p_* = \frac{\gamma_1^2}{\lambda} = \frac{3\pi}{288} \frac{\sigma_l \rho_{sol}^2 C_{ls}^2}{\delta^4 m_s^2 C_{ul}} = 3158 \frac{C_{ls}^2}{C_{ul}} \text{ Pa} \quad (17)$$

The constant C_{ul} for the intermolecular potential can be estimated from the attractive part of the classic Lenard-Jones potential as follows: $C_{ul} = 4\epsilon \sigma_l^6$, where ϵ is a characteristic energy of the intermolecular interaction. For the argon $\epsilon = 1.65 \times 10^{-21} \text{ J}$, and one can get that $C_{ul} = 10^{-77} \text{ Jm}^6$.

Since the information about the argon-silicon intermolecular interaction is not available now, for rough estimation purposes we take here $C_{ls} = C_{ul}$. Then we can get the following values for the characteristic density and pressure: $\rho_* = 2996 \text{ kg/m}^3$, $p_* = 324 \text{ atm}$.

These characteristic values help to better read the plots presented in Figures. Namely, Figure 2 shows that in 7 nm thickness, the argon film liquid density changes from 2100 kg/m^3 at the substrate (higher than the liquid argon bulk density) to 360 kg/m^3 at the film free surface (lower than the liquid argon bulk density). For thicker

films, the liquid density at the substrate is gradually approaching its limit of 2996 kg/m^3 , which is even higher than the density of the substrate itself.

Figure 3 shows that the liquid in a nanofilm expresses a very strong tension along the substrate. For example, in 7 nm thickness film, the tension is about 7 atm . The tension increases when the film thickness decreases and approaches its upper limit at about 35 atm , when the film thickness tends to zero.

We have obtained evolution equation (10) for describing the free surface of a nanofilm. This equation is basically a nonlinear diffusion equation with a "good" sign of the diffusion coefficient. That means a nanofilm driven solely by capillary forces is unconditionally stable. It is found that the nanofilm is driven by the tension along the substrate (a negative pressure). It is proposed here that although the film is unconditionally stable, such a strong tension may cause the film to spontaneously breakup.

In the case of very thin films, an effective film diffusion coefficient is derived as

$$\kappa = \frac{\lambda \gamma_1^2}{32 \mu_* \gamma_2^2} \left(\frac{h}{h_*} \right)^3 \quad (18)$$

For given parameters of argon and silicon this coefficient is calculated as

$$\kappa = \frac{5 \times 10^{-12}}{\mu_*} \left(\frac{h}{h_*} \right)^3 \text{ m}^2/\text{s} \quad (19)$$

For example, for $\mu_* = 10^{-2} \text{ kg/(m} \cdot \text{s)}$ and $h = 7 \text{ nm}$ we get $\kappa = 1.35 \times 10^{-8} \text{ m}^2/\text{s}$.

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