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Dynamics of liquid nanofilms

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ABSTRACT

The van der Waals forces across a very thin liquid layer (nanofilm) in contact with a plane solid wall make the liquid nonhomogeneous. The dynamics of such flat liquid nanofilms is studied in isothermal case.

The Navier–Stokes equations are unable to describe fluid motions in very thin films. The notion of surface free energy of a sharp interface separating gas and liquid layer is disqualified. The concept of disjoining pressure replaces the model of surface energy. In the nanofilm a supplementary free energy must be considered as a functional of the density.

The equation of fluid motions along the nanofilm is obtained through the Hamilton variational principle by adding, to the conservative forces, the forces of viscosity in lubrication approximation. The evolution equation of the film thickness is deduced and takes into account the variation of the disjoining pressure along the layer.

1. Introduction

The theory of thin liquid layers of a microscopic thickness is well understood (for a circumstantial bibliography, we may refer to the review article by Oron et al. [1]), but the motions of very thin liquid films wetting solid substrates are always a object of many debates. In fact several problems appear: the liquid in very thin layers is no more incompressible and the equation of motion is no more Navier–Stokes'; the concept of superficial energy related to a singular surface between gas and liquid layer has no more sense.

Liquids in contact with solids are submitted to intermolecular forces inferring density gradients at the walls, making liquids strongly heterogeneous [2]. Often, the fluid inhomogeneity in liquid–vapor interfaces was taken into account by considering a volume energy depending on space density derivative [3]. However, the van der Waals square-gradient functional is unable to model repulsive force contributions and misses the dominant damped oscillatory packing structure of liquid interlayers near a substrate wall [4]. Furthermore, the decay lengths are correct only close to the liquid–vapor critical point where the damped oscillatory structure is subdominant [5]. Recently, in mean field theory, weighted density-functional has been used to explicitly demonstrate the dominance of this structural contribution in van der Waals thin films and to take into account long-wavelength capillary-wave fluctuations as in papers that renormalize the square-gradient functional to include capillary wave fluctuations [6]. In contrast, fluctuations strongly damp oscillatory structure and it is for this reason that van der Waals' original prediction of a density profile in *hyperbolic tangent* form is so close to simulations and experiments [7]. Consequently, depending of liquids and solids, a great number of different energy functionals may be proposed to model a liquid nanofilm in contact with a wall.

To compensate the disadvantage of a special functional density to represent a thin film of liquid, we consider the most general case of any non-local density free energy functional and deduce a corresponding *generalized chemical potential.* Then,

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we propose an equation of isothermal motions of flat nanofilms in contact with a plane solid wall. The classical chemical potential is obtained from the generalized chemical potential in the limit of homogeneous density. From the classical chemical potential it is possible to deduce the disjoining pressure value. The disjoining pressure exists only when the liquid is strongly nonhomogeneous [8,9]. The thin film is driven along the substrate by the disjoining pressure gradient depending on the layer thickness.

We must emphasis that the derivation of governing equations is different from other approaches we can found in the literature. For example, in Ref. [1], the equation of liquid film dynamics is derived in the case of incompressible liquids. The disjoining pressure is ad hoc added as a formal additional pressure contribution.

2. The disjoining pressure for horizontal liquid films

The following experiment explaining the disjoining pressure concept is carefully described in Ref. [9]. The liquid bulk of density ρ_b was submitted to the pressure p_b by means of a very small bubble of radius R attached to a solid wall (Fig. 1).

A thin film of thickness h separates a flat part of the bubble surface and the solid. The vapor bulk over the layer has a density ρ_{v_b} and a pressure p_{v_b}. The difference between the two bulk pressures is

$$\Pi(h) = \frac{2\sigma}{R},$$

where σ is the surface tension coefficient of the bubble; the curve $\Pi(h)$ obtained by changing the bubble radius is the so-called disjoining pressure isotherm.

Without repeating the main results of Ref. [9] related to thin liquid films, we enumerate only the properties we use to describe thin films in contact with a solid wall.

We consider the physical system at a given temperature θ and suppose that the film is thin enough such that the gravity is neglected across the interlayer. The hydrostatic pressure in a thin liquid interlayer included between a solid wall and a vapor bulk differs from the pressure in the contiguous liquid phase. The forces arising during the thinning of a film of uniform thickness h produce the pressure $\Pi(h)$ which is equal to the difference between the pressure p_{v_b} on the interfacial surface which is – following the expression given by Derjaguin – the pressure of the *vapor mother bulk* of density ρ_{v_b}, and the pressure p_b in the *liquid mother bulk* of density ρ_b from which the interlayer extends

$$\Pi(h) = p_{v_b} - p_b. \tag{1}$$

At equilibrium, this additional interlayer pressure $\Pi(h)$ is called the *disjoining pressure*.

The conditions of stability of a thin interlayer essentially depend on phases between which the film is sandwiched. In case of a single film in equilibrium with the vapor and a solid substrate, the stability condition is expressed as a form proposed in Refs. [10; 11, Chapter 4]:

$$\frac{\partial \Pi(h)}{\partial h} < 0.$$

Let us also notice an important property of a mixture of fluid and perfect gas: the total mixture pressure is the sum of the partial pressures of components and, at equilibrium, the partial pressure of the perfect gas is constant through the liquid–vapor–gas film where the perfect gas is dissolved in the liquid phase. Calculations and results are identical to those presented in the following sections: the disjoining pressure of the mixture is the same as for the fluid without the perfect gas when a thin liquid film separates liquid and vapor phases (see Appendix A).

3. Equation of motion of thin liquid films

In thin liquid films the density is strongly inhomogeneous. At temperature θ and for a given value μ_0 of the chemical potential, the free energy of a liquid film in contact with a solid is a functional of the density ρ [12]. The free energy is written in the form:

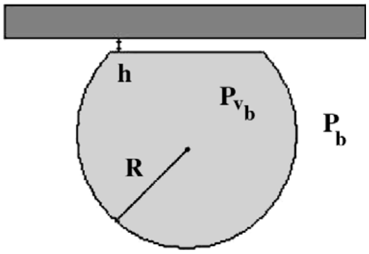

Fig. 1. The bubble method of determining the disjoining pressure isotherms of wetting films (From Ref. [9, p. 330]).