



Historical perspective

Calculation of nanodrop profile from fluid density distribution



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ARTICLE INFO

Available online 27 February 2016

Keywords:

Wetting
Drop profile equation
Contact angle
Microscopic approach
Density functional theory

ABSTRACT

Two approaches are examined, which can be used to determine the drop profile from the fluid density distributions (FDDs) obtained on the basis of microscopic theories. For simplicity, only two-dimensional (cylindrical, or axisymmetrical) distributions are examined and it is assumed that the fluid is either in contact with a smooth solid or separated from the smooth solid by a lubricating liquid film. The first approach is based on the sharp-kink interface approximation in which the density of the liquid inside and the density of the vapor outside the drop are constant with the exception of the surface layer of the drop where the density is different from the above ones. In this case, the drop profile was calculated by minimizing the total potential energy of the system. The second approach is based on a nonuniform FDD obtained either by the density functional theory or molecular dynamics simulations. To determine the drop profile from such an FDD, which does not contain sharp interfaces, three procedures can be used. In the first two procedures, P1 and P2, the one-dimensional FDDs along straight lines which are parallel to the surface of the solid are extracted from the two-dimensional FDD. Each of those one-dimensional FDDs has a vapor-liquid interface at which the fluid density changes from vapor-like to liquid-like values. Procedure P1 uses the locations of the equimolar dividing surfaces for the one-dimensional FDDs as points of the drop profile. Procedure P2 is based on the assumption that the fluid density is constant on the surface of the drop, that density being selected either arbitrarily or as a fluid density at the location of the equimolar dividing surface for one of the one-dimensional FDDs employed in procedure P1. In the third procedure, P3, which is suggested for the first time in this paper, the one-dimensional FDDs are taken along the straight lines passing through a selected point inside the drop (radial line). Then, the drop profile is calculated like in procedure P1. It is shown, that procedure P3 provides a drop profile which is more reasonable than the other ones. Relationship of the discussed procedures to those used in image analysis is briefly discussed.

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1. Introduction

The great success in the last decades in the experimental investigation of the liquid-vapor interfaces at nanoscale led to the increase in the interest to theoretical description of nanodroplets on smooth and rough surfaces. Traditionally, the main attention was given to

the calculation of the drop profile and the contact angle which the drop makes with the solid for various solid-liquid pairs. Because the macroscopic concept of surface tension is not clearly defined for nanodrops, the classical Young equation

$$\gamma_{lv} \cos \theta = \gamma_{vs} - \gamma_{ls} \quad (1)$$

where γ_{lv} , γ_{ls} , and γ_{vs} are the liquid-vapor, liquid-solid, and vapor-solid surface tensions, respectively, cannot be used to represent the

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contact angle θ . Therefore, microscopic approaches based on the interaction potentials between the molecules (fluids and solid) are most appropriate for the calculation of the drop profile which is needed to obtain the contact angle. Another specific feature of profile calculations for nanodrops is the comparable size of the nanodrop and of the range of strong fluid–solid interactions. For this reason, even though the gravity can be neglected for nanodrops, only the upper part of their profile can be approximated by a circle, whereas a considerable part of the profile has a much more complicated shape. In the present paper, a review of the procedures which can be used to calculate the drop profile is provided and a new procedure is suggested.

The first microscopic approach, which is denoted below as the sharp–kink interface approach, was suggested in Ref. [1] and modified later in Refs.[2]–[5]. The equation of the drop profile was obtained directly using the minimization of the total potential energy of the fluid–solid system due to the interactions between all the molecules belonging to the system. The assumptions used in the calculations are presented in Section 2.

The second approach uses various versions of the non-local density functional theory (DFT) [6]–[8] and provides the density distribution of the considered fluid from which the profile of the drop can be extracted. Note that the procedure of extraction of the drop profile from the fluid density distribution obtained by DFT is not unique and different procedures lead to different drop profiles and, as a consequence, to different values of the contact angles. The choice of the most appropriate one is a special problem which will be discussed below in Section 3. For simplicity, only drops with infinite length in one direction (cylindrical drops) will be considered.

The fluid density distribution (FDD) can be determined also by molecular dynamics simulations (see e.g. Refs. [9]–[14]). Because those FDDs are similar to the FDDs obtained by the DFT approach, the simulations methods themselves will not be examined separately in the present paper.

2. Sharp–kink interface approach

In this approach, the change of fluid density at the interfaces between a liquid drop and the surrounding vapor and solid is considered to occur discontinuously from a liquid like value to a vapor like value (sharp kink approximation [15]). The liquid density ρ_L in the drop is assumed to be uniform everywhere with the exception of the two monolayers at the liquid–solid and liquid–vapor interfaces where the liquid density is equal to ρ_{LS} and ρ_{LV} , respectively. The introduction of those monolayers accounts for the inhomogeneity of the fluid density at the liquid–solid and liquid–vapor interfaces.

It is natural to assume that the vapor around the drop has the constant density ρ_V which is much smaller than ρ_L . For this reason, the contribution of liquid–vapor interactions to the total potential energy of the system can be neglected. The solid substrate is considered homogeneous with a density ρ_S . The values of ρ_L , ρ_{LV} , ρ_{LS} , and ρ_V which should be selected before calculating the drop profile, define the fluid density distribution in the system.

The potential $\phi_{LL}(r)$ of interaction between the liquid molecules is selected in the form of the London–van der Waals potential with a hard core repulsion

$$\phi_{LL}(r) = \begin{cases} -\epsilon_{LL} \left(\frac{\sigma_{LL}}{r}\right)^6, & r \geq \sigma_{LL}, \\ \infty, & r < \sigma_{LL} \end{cases} \quad (2)$$

where r is the distance between the centers of the interacting molecules, $\sigma_{LL} > 0$ and $\epsilon_{LL} > 0$ are the size of the repulsive core (hard core diameter) and the energy parameter, respectively. In the calculations, the cutoff diameter $\eta > \sigma_{LL}$ was used ($\phi_{LL}(r) = 0$ for all $r > \eta$).

The interaction potential between a molecule of liquid and a molecule of solid is selected as the sum of long–range ($\phi_{LS}^l(r)$) and short–range ($\phi_{LS}^s(r)$) interactions. The former potential is selected in the form

$$\phi_{LS}^l(r) = \begin{cases} \epsilon_{LS} \left[k_\phi \left(\frac{\sigma_{LS}}{r}\right)^{12} - \left(\frac{\sigma_{LS}}{r}\right)^6 \right], & r \geq \sigma_{LS}, \\ \infty, & r < \sigma_{LS}, \end{cases} \quad (3)$$

where $k_\phi = 0$ or 1, σ_{LS} and $\epsilon_{LS} > 0$ are, respectively, the size of the repulsive core and the energy parameter of the liquid–solid interactions. For $k_\phi = 0$ one recovers the London van der Waals potential and for $k_\phi = 1$ the Lennard–Jones (LJ) potential. In real systems σ_{LL} and σ_{LS} are of the order of several angstroms [16].

The potential energy $\Phi_{LS}^l(h)$ of a liquid molecule interacting with a semi–infinite solid, possessing a planar surface, through the long–range interactions can be written as

$$\Phi_{LS}^l(h) = \frac{\pi}{6} \epsilon_{LS} \rho_S \sigma_{LS}^3 \left[\frac{2}{15} k_\phi \left(\frac{\sigma_{LS}}{h + \sigma_{LS}}\right)^9 - \left(\frac{\sigma_{LS}}{h + \sigma_{LS}}\right)^3 \right], \quad h \geq 0, \quad (4)$$

where $h + \sigma_{LS}$ is the distance measured from the center of a molecule of liquid to the center of the first layer of solid atoms ($h = 0$ corresponds to the center of the layer of liquid molecules on the solid surface).

The short–range potential $\phi_{LS}^s(r)$ which accounts, for example, for the acid–base interactions is assumed to be effective only for the molecules in the first liquid layer near the solid surface. As a result, the potential energy $\Phi_{LS}^s(h)$ is given by

$$\Phi_{LS}^s(h) = \begin{cases} -\epsilon_{LS}^s, & h = 0, \\ 0, & h > 0 \end{cases} \quad (5)$$

where ϵ_{LS}^s is the energy parameter for the short–range interaction.

Combining the potentials Eqs. (4) and 5, one obtains the total potential $\Phi_{LS}(h)$ of a molecule of liquid interacting with the solid

$$\Phi_{LS}(h) = \begin{cases} \Phi_{LS}^l(0) + \Phi_{LS}^s(0), & h = 0, \\ \Phi_{LS}^l(h), & h > 0. \end{cases} \quad (6)$$

The interaction between the molecules of vapor and solid is supposed to have only a long–range component. For low–density vapors, only the molecules of a monolayer adsorbed on the solid surface ($h = 0$) are taken into account. As a consequence, the potential $\Phi_{VS}(h)$ of that interaction can be written in the form

$$\Phi_{VS}(h) = \begin{cases} \Phi_{VS}^l(0), & h = 0, \\ 0, & h > 0 \end{cases} \quad (7)$$

where the potential $\Phi_{VS}^l(h)$ has the same form as $\Phi_{LS}^l(h)$ given by Eq. (4), where ϵ_{LS} and σ_{LS} have to be replaced by ϵ_{VS} and σ_{VS} , respectively.

Neglecting the vapor–vapor and vapor–liquid potential energies in the calculation of the total potential energy U_{total} of the system and taking into account only the interaction of the adsorbed vapor molecules with the solid, U_{total} can be written in the form

$$U_{total} = U_{LL} + U_{LS} + U_{VS} \quad (8)$$

where U_{LL} and U_{LS} are the potential energies due to the interactions of the molecules of liquid between themselves and with those

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