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Effective Hamiltonian for a liquid–gas interface fluctuating around a corrugated cylindrical substrate in the presence of van der Waals interactions

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ABSTRACT

We investigate liquid layers adsorbed at spherical and corrugated cylindrical substrates. The effective Hamiltonians for the liquid–gas interfaces fluctuating in the presence of such curved substrates are derived via the mean-field density functional theory. Their structure is compared with the Helfrich Hamiltonian which is parametrized by the bending and Gaussian rigidity coefficients. For long-ranged interparticle interactions of van der Waals type these coefficients turn out to be non-universal functions of interfacial curvatures; their form varies from one interface to another. We discuss the implications of the structure of these functions on the effective Hamiltonian.

1. Introduction

The morphology of wetting layers adsorbed at planar substrates is nowadays rather well understood [1–4]. However, adsorption at non-planar substrates is rather ubiquitous in nature and one is led to study the behavior of inhomogeneous fluids in the presence of curved substrates, for example the adsorption at large colloidal particles [5–7] and fibers [8–11], capillary condensation in porous media, liquid bridge formations between spheres [12,13] and cylinders [14]. Though 60 years have passed since the landmark work of Tolman [15] on the surface tension of curved interfaces there are still many open problems related to adsorption at curved substrates.

Two basic approaches to the problem of the surface tension coefficient dependence on interfacial curvature have been developed [16]. The first is based on the analysis of the interface fluctuating around the planar configuration. The second approach focuses on the average shapes of the fluid interfaces curved around the non-planar substrates. In both cases the surface free-energy density is expanded in powers of curvature. The zeroth order term represents the surface tension coefficient of a planar interface, the coefficient in front of the linear term is related to the so-called Tolman length [15] while the second order terms contain the bending and Gaussian rigidity coefficients. These two coefficients for membranes parametrize the phenomenological Helfrich Hamiltonian [17]. One of the still open problems in this field is concerned with the status of this expansion and the existence of the bending and Gaussian rigidity coefficients. In particular one would like to know under what circumstances, if any, one might expect the non-analytic dependence of the surface free-energy density on the interfacial curvature.

In this paper we discuss these issues while investigating the fluctuating, cylindrically shaped liquid–gas interface. First (Section 3) we follow the standard approach and calculate the sum of bending and Gaussian rigidity coefficients for the spherical geometry. Then we investigate the cylindrical, fluctuating interface (Section 5) and obtain information separately

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on the bending and on the Gaussian rigidity coefficients. We discuss the structure of the ensuing coefficients from the point of view of their dependence on the interparticle interaction and the substrate geometries (Section 6). In Section 7 we summarize our results.

2. The model

In order to calculate the effective interface Hamiltonian for an interface separating a liquid-like layer adsorbed on the curved substrate from the gas phase we employ the density functional theory (DFT). The grand canonical density functional $\Omega([\rho(\mathbf{r})], T, \mu)$ depends parametrically on temperature T, chemical potential μ, interparticle potential $\tilde{w}(r)$ assumed to be spherically symmetric, and on the external potential $V(\mathbf{r})$ representing the effect of the substrate. The interparticle potential $\tilde{w}(r)$ is split into the short-ranged repulsive part $w_{hs}(r)$ and the long-ranged attractive part $w(r)$ which is of the van der Waals type

$$\tilde{w}(r) = w_{hs}(r) + w(r). \tag{1}$$

The mean-field version of the density functional takes the form [18,19]

$$\Omega([\rho(\mathbf{r})], T, \mu) = \int \mathrm{d}^3 r f_{hs}(\rho(\mathbf{r})) + \frac{1}{2}\int \mathrm{d}^3 r \int \mathrm{d}^3 r' w(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r})\rho(\mathbf{r}') + \int \mathrm{d}^3 r \left(V_{ext}(\mathbf{r}) - \mu\right)\rho(\mathbf{r}), \tag{2}$$

where the first term on the rhs represents the free energy of the fluid interacting via short-ranged repulsive potential $w_{hs}(r)$ evaluated in the local density approximation. In the following analysis the long-ranged attractive part of the potential $w(r)$ is modeled by

$$w(r) = -\frac{A}{(\kappa^2 + r^2)^3} \tag{3}$$

which decays $\sim r^{-6}$ at large distances (we neglect the retardation effect). The parameter κ corresponds to the hard core radius of the fluid particles and the amplitude $A > 0$ characterizes the strength of the attraction. The external potential $V_{ext}(\mathbf{r})$ acting on the fluid particle located at position $\mathbf{r}$ comes from its interactions with all substrate particles. This interaction can be again split into the short- and long-ranged parts. The long-ranged part is again modeled by the potential $w_s(r) = -A_s/(\kappa_s^2 + r^2)^3$, i.e.

$$V_{ext}(\mathbf{r}) = \int_{\mathcal{V}_s} \mathrm{d}\mathbf{r}' \, \rho_s \, w_s(|\mathbf{r}-\mathbf{r}'|), \tag{4}$$

where $\mathcal{V}_s$ denotes the region occupied by the homogeneous substrate with density ρ_s. The effect of the short-ranged repulsive part of the substrate–fluid interaction is to prevent the fluid particles from penetrating the region $\mathcal{V}_s$; it is taken into account by the appropriate specification of the different regions' integration present in the density functional, Eq. (2).

The thermodynamic state of the fluid is taken to be slightly off the bulk coexistence line in the regime of the stable bulk gas phase, and far away from the critical point. This implies that the bulk correlation length is comparable with the size of fluid particle characterized by κ. In such circumstances the position of the liquid–gas interface is represented by function $z = f(\mathbf{R})$, $\mathbf{R} = (x, y)$, and the nonuniform density profile $\rho(\mathbf{r})$ can be described by the so-called sharp-kink approximation

$$\rho_{shk}(\mathbf{R}, z) = \rho_l \, \Theta(f(\mathbf{R}) - z) + \rho_g \, \Theta(z - f(\mathbf{R})), \tag{5}$$

where $\Theta(z)$ is the Heaviside function while ρ_l and ρ_g denote the densities of the coexisting bulk liquid and gas phases, respectively. Thus by invoking the sharp-kink approximation we disregard any effects that the van der Waals tails in the density profiles for long-ranged forces might introduce to the system under investigation. For a finite system the density functional $\Omega([\rho(\mathbf{r})], T, \mu)$, Eq. (2), evaluated at $\rho(\mathbf{r}) = \rho_{shk}(\mathbf{R}, z)$ can be represented as the sum of bulk, surface, line, etc. contributions [19]. We discuss two shapes of substrates which induce the corresponding shapes of interfaces: a spherical substrate of radius R_s, and an axially symmetric substrate represented by a corrugated cylinder of infinite length. In each case the gas phase is present away from the substrate while a liquid-like layer is adsorbed on the substrate. Our analysis is concentrated on surface and interfacial contributions to $\Omega([\rho(\mathbf{r})], T, \mu)$.

3. Spherical interface

The system under consideration in this section consists of the spherical substrate of radius R_s on which a uniform liquid layer of constant thickness ℓ is adsorbed. The remaining part of the system is filled with the gas phase of volume V_g while the volume of the liquid layer is denoted by V_l. The density functional, Eq. (2), evaluated for this geometry and for the spherically symmetric density profile in the sharp-kink approximation – after taking into account contributions due to the finite size of the system – equals (the upper index (s) refers to the spherical case and the lower index s refers to the surface properties)

$$\Omega^{(s)} = (V_g + V_l)\,\omega_b(\rho_g) + \Omega_s^{(s)}, \tag{6}$$

where $\omega_b(\rho)$ is the grand canonical potential density of a fluid system with the uniform density ρ

$$\omega_b(\rho) = f_{hs}(\rho) + \frac{1}{2}\rho^2 \int \mathrm{d}\mathbf{r}\, w(|\mathbf{r}|) - \mu\rho. \tag{7}$$