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Computer simulation of interface potentials: towards a first principle description of complex interfaces?

Luis G. MacDowell[1,a]

Departamento. de Química Física, Facultad de Ciencias Químicas, Universidad Complutense, Madrid 28040, Spain.

Abstract. We discuss the feasibility of a hierarchical protocol whereby the description and prediction of adsorbed fluids in confined systems at the mesoscopic scale is achieved by use of interface potentials that are obtained from raw molecular simulation data. Starting from a microscopic description of a fluid's interface on a flat substrate, we attempt to extract the minimum information that is required in order to predict the behavior of that fluid at larger length scales from coarse grained surface Hamiltonians. A critical assessment of this procedure hinges on controversial aspects of wetting behavior and more generally on the meaning of metastability and instability of thermodynamic systems.

1 Introduction

One outstanding challenge in current science and technology is the design, development and control of devices at the nanoscale. A relevant feature of most of these nanometric devices is the crucial influence of surface effects. Modern microprocessors are built on top of silicon wafers which are suitably prepared by means of lithographic and chemical processes [1]. A great number of molecular recognition mechanisms are based on the anchoring of selected polymers on metal surfaces [2]. Many advanced materials formed from polymers with different properties require careful minimization of the surface area in order to achieve compatibility [3]. The functionality of some molecular motors rests on the smooth variation of interfacial tensions of suitably prepared substrates [4].

One of the fields where surface effects are perhaps most relevant is that of "nanofluidics" [5]. There exists the hope that nanotechnology will allow for the development of microlaboratories where the chemical reactions will take place within small integrated labs the size of a chip [6]. This would allow to save a great amount of hazardous chemical products. It would allow to produce portable chemical analysis labs or to set superparallelized combinatorial chemistry reactors. In order to work, these devices will require a system of nano channels, tanks and crucibles which may be prepared by lithographic means or pattern guided self assembly [7].

Whereas filling a test tube or a flask is by no means a problem, filling a channel that is a few nanometers wide is another matter. The small amount of material that is required might either flood the channel, only fill the rims or fill it smoothly depending on the fluid–substrate properties [8].

It is clear that a proper control of condensates of different shape in small systems requires a detailed understanding of the fluid–substrate interactions, the stability of adsorbed films and the role of confinement. The complexity and intermediate length scale of these problems, make well known techniques such as density functional theory or computer simulations somewhat out of reach in terms of computational cost. A promising alternative is a coarse grained approach,

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[a] e-mail: `luis@ender.quim.ucm.es`

whereby information obtained for a flat film is used as input within an interface Hamiltonian that measures the free energy of the system, including the free energy cost of added inhomogeneities that result from confinement.

A key ingredient of this approach is the concept of interface potential, i.e., a measure of the free energy cost of forming a flat film of given thickness. Such a device is in principle a mean field construction, which shares some of the caveats of mean field bulk equations of state. i.e., the partition function is solved for states that are everywhere homogeneous, while the exact solution rules out such states if they don't correspond to an absolute minimum of the free energy.

In this work we will critically asses the possibility of meaningfully obtaining interface potentials that are a continuous function of the film thickness. i.e., the possibility of obtaining free energies of films that are metastable or even unstable in the thermodynamic limit. The hypothesis that is employed is that such *forbidden* films could be stabilized under appropriate constraints such as finite system size, constant adsorption or appropriate boundary conditions.

2 The interface potential

The microscopic description of an adsorbed layer on a complex substrate starts by writing down a density functional for the grand free energy, i.e., the Legendre transform of the Helmholtz free energy functional:

$$\Omega(T,\mu;[\rho]) = A(T;[\rho]) - \int \mathrm{d}\mathbf{r}\,(\mu - V_{\mathrm{ext}}(\mathbf{r}))\,\rho(\mathbf{r}) \tag{1}$$

where $\rho(\mathbf{r})$ is the density at position $\mathbf{r}$, μ is the fixed chemical potential and $V_{\mathrm{ext}}(\mathbf{r})$ is an external field that describes the influence of the substrate on the fluid properties.

This division of the different energy contributions is formally convenient, because it stresses the fact that $A[\rho]$, however complex, is at least independent on whichever detail of the external field. This is a significant observation because it allows to motivate the unknown functional density dependence of $A[\rho]$ using ideas borrowed from bulk liquid state theory. For this reason, $A[\rho]$ is sometimes known as the intrinsic free energy. The first microscopic density functional theory (DFT) due to van der Waals is only qualitatively accurate and appropriate for small density gradients. However, the last decades have witnessed an enormous improvement of free energy functionals for simple fluids [9].

The grand free energy $\Omega(T,\mu;[\rho])$ may be viewed as a thermodynamic Landau potential. Therefore, the equilibrium density profile, $\overline{\rho}$ is obtained by functional minimization. The surface free energy consistent with the imposed fields, T, μ and V_{ext} is then given by:

$$\Omega_{eq}(T,\mu) = \Omega(T,\mu;[\overline{\rho}(\mathbf{r})]) \tag{2}$$

Thus in principle density functional theory for simple fluids could be employed to describe the problem of adsorption on whichever complex substrates, such as slit pores, wedges or reliefs of arbitrary shape. In practice, application of DFT to problems with inhomogeneities in more than one direction in space is numerically very involved and the attainment of self consistency is often more time consuming than performing first principle simulations for the same problem. However, for systems where the density profile is inhomogeneous in only one direction, say, z, and integrals of the irrelevant coordinates may be performed, DFT becomes an extremely useful tool, providing microscopic information at the level of the density profile as well as free energies.

As an extra bonus of the DFT formalism, the functional $\Omega(T,\mu;[\rho])$ provides a measure of the free energy of density profiles out of equilibrium, and is thus also very useful as a means of measuring fluctuations and assessing the stability of the equilibrium state. The most relevant non–equilibrium states that one may wish to consider are the minima of the free energy functional subject to the constraint of fixed arbitrary adsorption (i.e., minimization of a Helmholtz free energy functional under the influence of the external field) [10,11]. Note that,

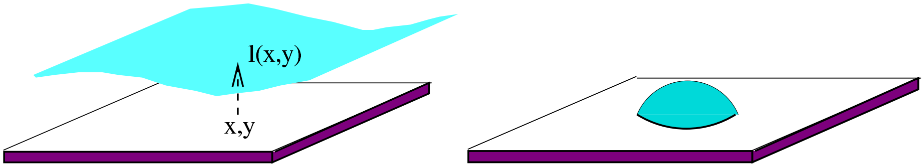

Fig. 1. Sketch of the interface potential construction. For each point $\mathbf{r}_{\|} = (x, y)$ on the plane, a film height $\ell(\mathbf{r}_{\|})$ is defined (left). Depending on the conditions and system size, either a film (left) or a drop (right) is most stable.

since μ in Eq. (1) can be interpreted as a Lagrange multiplier that fixes the overall content of the system, this actually amounts to a minimization of Ω for other chemical potentials.

The picture that emerges from this level of coarse–graining is that of a continuous free energy as a function of a subset of all possible density profiles consistent with a fixed adsorption. Obviously, this level of description is often much more detailed than is really necessary, as only the free energies are required to understand relevant macroscopic behavior such as phase transitions. Fortunately, further coarse graining is still possible, since these free energies are, by definition, a function of the adsorption, or of other convenient parameter able to describe the density profile. Often a *crossing* rather than an *integral* criterion is chosen to characterize the minimized density profile. For example, one can label the full microscopic state with a single parameter, the interface height, ℓ, such that $\rho(z = \ell) = \rho^*$, where ρ^* is a density lying somewhere between the bulk vapor and liquid densities.

Now, this approach allows us to define the system's free energy as a function of the interface height above a flat substrate. More conveniently, one writes the surface free energy as an excess over an infinitely thick adsorbed liquid layer:

$$g_\mu(\ell) = \frac{\Omega[\rho_\ell(z)] - \Omega_{\text{bulk}}}{\mathcal{A}} - (\gamma_{wl} + \gamma_{lv}) \tag{3}$$

where γ_{wl} and γ_{lv} are the surface free energies of the wall–liquid and liquid–vapor interfaces; Ω_{bulk} removes from $g_\mu(\ell)$ a bulk dependent contribution that is extensive in the system's volume and $\rho_\ell(z)$ denotes the density profile consistent with interfacial height ℓ. Note that the interface potential so defined is parametric in the chosen chemical potential, the most convenient choice being usually the coexistence chemical potential, μ_0. One can recover $g_\mu(\ell)$ from $g_{\mu_0}(\ell)$ easily, as they are simply related by a Legendre transform, $g_\mu(\ell) = g_{\mu_0}(\ell) - (\mu - \mu_0)\Delta\rho\ell$ where $\Delta\rho$ es the density difference between the adsorbed liquid layer and the vapor.[1]

3 Interface Hamiltonian

The interface potential of Eq. (3) is in principle suitable for the study of adsorbed liquid layers on flat substrates only. However, it is often used heuristically for the study of systems with additional inhomogeneities within the framework of a so called Interface Hamiltonian. In this approach, which can be formally justified in terms of a macroscopic model [12], one describes the film thickness above a point $\mathbf{r}_{\|}$ on a reference plane as $\ell(\mathbf{r}_{\|})$. For a flat film, one then assumes the free energy of an infinitesimal element $\mathrm{d}\mathbf{r}_{\|}$ centered on that point is just $g_\mu(\ell)\,\mathrm{d}\mathbf{r}_{\|}$, while for curved films, one adds an extra local term that accounts for the surface increment of the liquid–vapor interface (Fig.1):

$$H[\ell] = \int \mathrm{d}\mathbf{r}_{\|} \left(g_\mu(\ell) + \gamma_{lv}(\sqrt{1 + (\nabla\ell)^2} - 1) \right) \tag{4}$$

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[1] Strictly speaking this transformation is only exact when g_μ es expressed as a function of adsorption. The result used here assumes the vapor and liquid densities do not significantly change with chemical potential.

This kind of Hamiltonian is at the heart of most theoretical accounts of surface phenomena, including, the study of capillary waves [13], renormalization group analysis of wetting phenomena [14], the study of droplet profiles [15], the measure of line tensions [16], the structure of adsorbed films on patterned substrates [17], and the dynamics of dewetting [18].

Despite its theoretical importance, this model is actually a low curvature approximation, implicitly requiring the inhomogeneities along $\mathbf{r}_{\|}$ to be small compared to the interface width [19]. Indeed, already within the framework of an approximate microscopic functional one can only obtain Eq. (4) after several approximations. This can readily be seen by considering a square gradient approximation of the Cahn–Hilliard type:

$$\Omega([\rho(\mathbf{r}]) = \int \mathrm{d}\mathbf{r} \left(f(\rho) + \frac{1}{2} C (\nabla\rho)^2 \right) - \int \mathrm{d}\mathbf{r} \rho(\mathbf{r}) \left(\mu - V_{\mathrm{ext}}(\mathbf{r})\right) \tag{5}$$

This functional is clearly that leading to a Eq. (4) in the most natural way, because of the squared gradient approximation to the free energy. Whereas the task of relating $\Omega([\rho(\mathbf{r}])$ to $H[\ell]$ for other more accurate functional will be yet more difficult, at least we know that square gradient functionals are actually leading order approximation to more rigorous non–local expansions of the free energy based on the direct correlation function [20]. Separating the perpendicular and parallel contributions of the gradient, we readily obtain:

$$\Omega([\rho(\mathbf{r}]) = \int \mathrm{d}\mathbf{r}_{\|} \left\{ \int \mathrm{d}\mathbf{r}_{\perp} \left(f(\rho) + \frac{1}{2} C (\nabla_{\perp}\rho)^2 - \rho(\mu - V_{\mathrm{ext}}(\mathbf{r})) \right) + \frac{1}{2} \int \mathrm{d}\mathbf{r}_{\perp} C (\nabla_{\|}\rho)^2 \right\} \tag{6}$$

Assuming that at fixed $\mathbf{r}_{\|}$ the density profile along $\mathbf{r}_{\perp}$ is equal to that of a flat interface of height $\ell(\mathbf{r}_{\|})$, which we denote as $\rho_{\ell}(\mathbf{r})$, the first integral $\mathbf{r}_{\perp}$ will amount to the interfacial potential $g_{\mu}(\ell)$ within the square gradient approximation. However, transforming the second integral into a liquid–vapor surface tension clearly requires some additional approximations. e.g.: one can consider $\rho(\mathbf{r}) = \rho_{\ell}(z+\ell)$, which, after pluging into the above equation leads readily to the small gradient approximation of Eq. (4).

Unfortunately, attempts to improve the description above lead to added complications. This can be illustrated already for the simpler case of unbound interfaces (i.e., such that $\ell \to \infty$ and $g_{\mu_0}(\ell) = 0$) in the small curvature approximation. In this limit, Eq. (4) may be written in terms of the Fourier modes of ℓ, as $H = \frac{1}{2}\gamma_{lv} \sum \mathbf{q}^2 \ell_{\mathbf{q}}^2$ [13]. However, a careful analysis using microscopic density functional theory shows that a refined description requires the introduction of wave vector dependent surface tensions, $\gamma_{lv}(\mathbf{q})$, such that γ_{lv} can no longer factor out from the above sum [21]. Intriguingly, self consistent DFT approaches predict a monotonically decreasing wave vector dependence which cannot be accepted, as this would imply a diverging amplitude of short wavelength modes. Apparently, this spurious result stems from fundamental inconsistencies related to the attempt to describe the interfacial height from one particle distributions. A more refined description of the interface beyond the one particle distribution yields the expected monotonous increase for large wave vectors [22].

Further complications arise when one considers a bound interface. In this case, a formal treatment within the Cahn–Hillard approximation shows that the square gradient coefficient picks up a non–trivial ℓ dependence [23]. Not unexpectedly, the liquid–vapor interface feels the distortion of the density profile that results from interactions with the substrate. Yet a more refined treatment taking explicitly into account bulk fluid correlations leads to an interface Hamiltonian that is a non–local functional both of the interfacial height and the substrate geometry [24]. Fortunately, such added complications, which can very much affect the nature of critical fluctuations are less important in the presence of long range forces, where the upper critical dimensions for both critical and complete wetting are below the relevant three dimensional problem [25].[2]

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[2] Henderson argues convincingly in this issue [26] that the main difficulties highlighted above may be circumvected by generalization of the interface potential as a non–local functional together with a suitable choice of film thickness.

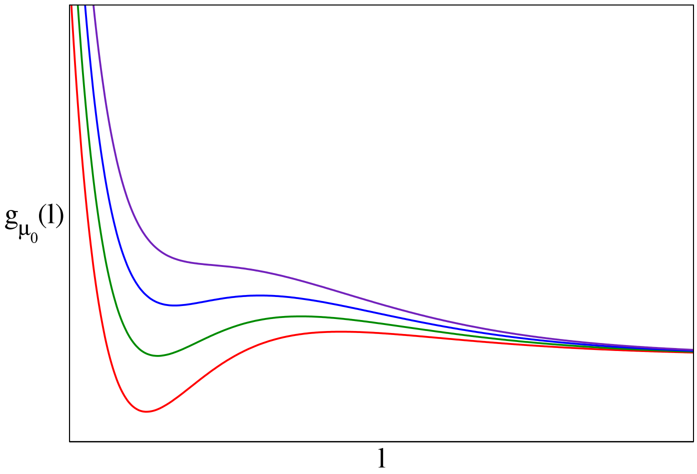

Fig. 2. Sketch of interface potentials for a system exhibiting first order wetting as measured at coexistence. Below the wetting transition (red), at the wetting transition (green), above wetting but below the prewetting critical point (blue) and above the prewetting critical point (indigo). Changing the chemical potential simply adds a linear term $-(\mu - \mu_0)(\rho_l - \rho_v)\ell$. Below the wetting transition (red) and supersaturation (i.e., adds a straight line with negative slope) $g_\mu(\ell)$ takes absolute minimum at infinite film thickness; while a thick film may be (meta)stabilized at undersaturation (i.e., adds a straight line with positive slope). Above the wetting transition (blue), an equilibrium between thin and thick films may be achieved at undersaturation.

4 Critique of the mean field scenario

Whereas the above discussion shows that the well known interface Hamiltonian of Eq. (4) is not exact, it can be considered as a reasonable approximation for problems where neither the substrate nor the liquid–vapor interface deviate strongly from planarity. Indeed, several predictions stemming from the model of Eq. (4) have been undoubtedly confirmed. For unbound interfaces, for example, the most salient features of the theory of capillary fluctuations, such as the increase of interfacial thickness with surface area, have been observed both experimentally and by means of computer simulations [27–29]. The influence of surface undulations on the shape of droplets as predicted by Eq. (4) has also been observed [15]. The dewetting patterns that are expected from dynamical theories based on Eq. (4) are also roughly accepted [30,31], etc.

Despite this success, however, the local interface Hamiltonian is usually only employed as a qualitative approach, rather than a quantitative tool for the prediction of properties of specific fluid–substrate pairs. One reason is that experimental determination of the interface potential $V(\ell)$ of films adsorbed on solid substrates over the whole range of film thickness is quite a difficult matter (this does not include adsorbed layers of surfactants on water, or solvent mediated forces between solids, where a great amount of interesting experimental information has been collected [32]). Obviously, being $g(\ell)$ a free energy, it is rather the derivatives of $g(\ell)$ that are accessible, the most useful being adsorption and disjoining pressure. In adsorption experiments, one measures $\Gamma = \Gamma(\mu)$ and recovers the free energy exploiting $\mathrm{d}g = -\Gamma\,\mathrm{d}\mu$. Alternatively, experiments can be set up to measure the force per unit area or *disjoining pressure* that is required to stabilize a thin film. The interface potential can then be recovered by definition as $\mathrm{d}g(\ell) = -\Pi\,\mathrm{d}\ell$. Arguably the most transparent setup for the measurement of disjoining pressures is the captive bubble technique. Here one simply blows a bubble close to a substrate immersed in a liquid. Pushing the bubble against the solid surface stabilizes a thin film, and the disjoining pressure can be directly measured as the Laplace pressure difference across the bubble [33]. Usually, adsorption experiments are appropriate in the range of very thin adsorbed layers, while disjoining pressure measurements can be performed most easily for films of order $\approx 10\cdot$ nm, where the behavior is mainly governed by long range dispersive forces.

However, the major problem is not actually a matter of experimental limitations. Below the wetting temperature thin adsorbed layers are strictly stable only at undersaturation (Fig.2). For saturated systems, the stable state is one with an infinite film thickness. Systems with long range forces can in principle exhibit metastability, but only within a limited range of film thickness. Above a *spinodal point* corresponding to the change of curvature of the interface potential, the films become unstable and immediately break apart [15]. It follows that in principle experiments can only provide information of that region of the interface potential corresponding to thermodynamic equilibrium states, or, at most, when heterogeneous nucleation may be inhibited by the preparation of very pure substrates, also partially stable states [31].

This situation is even more dramatic for systems slightly above the wetting temperature, yet, below the prewetting critical point, T_{pwc}. There a first order surface phase transition leads from a thin, $\ell_{\rm thin}$, to a thick, $\ell_{\rm thick}$ film discontinuously as the undersaturated vapor approaches coexistence (Fig.2) [34–37]. Similar to the familiar bulk phase transitions, a system that is initially prepared with a film thickness lying between $\ell_{\rm thin}$ and $\ell_{\rm thick}$ phase separates forming coexisting thin and thick phases in amounts that are given by the lever rule.

The question then arises as to the significance of the interface potential (or its derivative, the disjoining pressure) in a large range of film thickness that are never actually experimentally accessible. A similar problem regarding the significance of the *van der Waals loop* in mean field isotherms of bulk phase transitions has been the subject of long standing discussions [38,39], with the pressure–volume isotherm playing exactly the same role as the disjoining pressure–film thickness isotherm.

It is widely believed that in the thermodynamic limit such loops are an artifact of mean field theory, i.e., an exact solution of the partition function would instead yield a *tie line* of constant disjoining pressure between the coexisting thin and thick films. Yet one cannot avoid the fact that film thickness corresponding to the extrapolation of the disjoining pressure isotherm within meta or unstable states form the basis of our understanding of wetting phenomena and are actually observed under many circumstances.

– An excess of adsorbed matter on a substrate below the wetting temperature forms a droplet. The droplet profile $\ell(y)$, with y a coordinate along the substrate, shows all possible values between the equilibrium thin film $\ell_{\rm thin}$ and the maximum droplet height, with values of ℓ running all the way across metastable and unstable film thickness (very much as the interface profile $\rho(z)$ perpendicular to a liquid–vapor interface exhibits densities lying in regions of the unstable portion of the mean field isotherm).
– At conditions between T_w and T_{pwc}, it is often found that the decay towards the thermodynamic equilibrium may be a very slow activated process, so that a degree of extrapolation within the metastable region of the interface potential is allowed experimentally during a limited time [40]. The relaxation of such metastable states is explained as a nucleation process, and the free energy of formation of such nuclei is described in terms of the disjoining pressure of the metastable state as predicted by mean field theory [41].
– Alternatively, the decay can proceed almost immediately after the preparation of the film, with a dewetting pattern exhibiting a preferred wavelength [31]. Such experimental findings are explained in terms of a dynamical Cahn–Hillard theory, with the preferred wavelength given in terms of the second derivative of the interface potential within the unstable region [18]. The precise frontier between nucleation and spinodal dewetting in films is expected to be fuzzy, as in bulk fluids [42], and not always depends simply on the curvature of the interface potential [30], but the two regimes are meaningful asymptotic limits which can be rationalized on the basis of the interface potential [31].

The way one can reconcile the double tangent construct, which rules out the metastable and unstable portions of the interface potential, with the mean field description of widely different

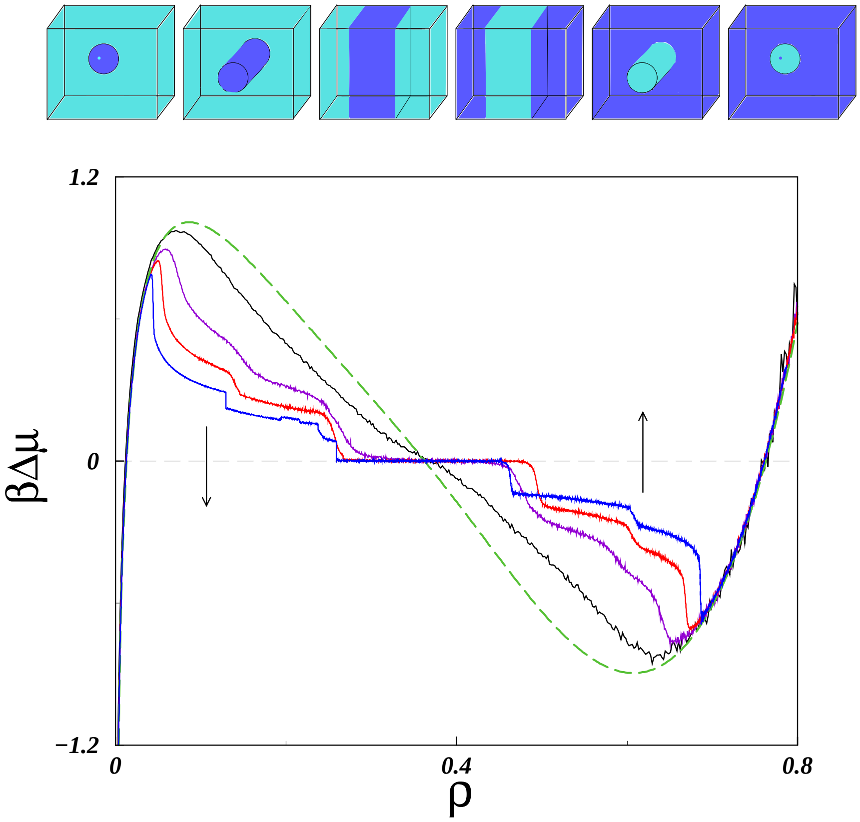

Fig. 3. (bottom) chemical potential versus density isotherms of a Lennard–Jones fluid well below the critical point as obtained from computer simulations. Results (full lines) are shown for different system sizes with lateral dimensions ranging from 9 to 21 molecular diameters in lateral side, with the arrows pointing in the direction of increasing system size. The dashed line is the prediction of an accurate mean field equation of state that reproduces exactly the first five virial coefficients. The chemical potential is measured as an excess over the coexistence chemical potential. Note that this results correspond to an isotherm obtained as a measure of chemical potential under the constraint of fixed density. Removing the constraint would produce monotonous isotherms with positive slope. Results adapted from Ref.[44]. (top) Illustration of the domains that are formed along the different regions of the isotherm for large systems.

phenomena in terms of extrapolated portions of such potential is as follows: The thermodynamic limit is actually an idealization. It corresponds to the solution of the partition function in the limit where one can ignore constraints or boundary conditions. In practice, it is a convenient mathematical device which one usually requires for solving the partition function. Actually, systems do have boundaries. Such boundaries perturb the solutions, leading to states that would seem to be forbidden in the thermodynamic limit. The practical question to answer then could be phrased as follows: could one use the extrapolation of the interface potential inside the meta/unstable region as obtained from mean field theories in order to describe the solution of problems where boundaries or constraints have an important role [43] ?

5 Solving the exact partition function with system size constraints

The above discussion establishes a link between the concept of mean field interface potentials and the solution of problems with specific boundary conditions or constraints. For example,

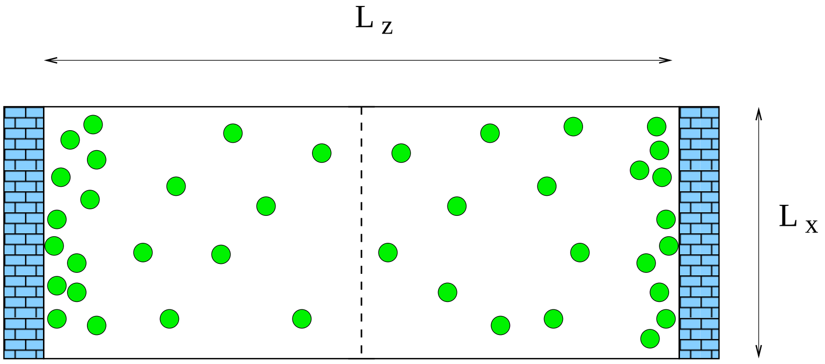

Fig. 4. Sketch of the simulation setup for the measurement of interfacial free energies, $\tilde{g}(\ell)$. The substrate is placed perpendicular to the z axis, and the adsorption on a wall is measured by counting the number of molecules in the half box closest to that wall.

the constraint of fixed adsorption on a substrate below wetting will result in the formation of a droplet exhibiting film thickness that are *forbidden* for flat films in the thermodynamic limit. Due to Laplace pressure effects, such a droplet coexists with a supersaturated vapor exhibiting densities which are *forbidden* from the bulk equation of state in the thermodynamic limit.

This point can be illustrated by the simulation of bulk isotherms of finite size systems under periodic boundary conditions. Fig.3 shows chemical potential versus density isotherms obtained well below the critical point for different system sizes. Several remarks can be made:

- The isotherms are clearly not flat between the coexistence points, but gradually flatten as system size increases. Eventually, for large system sizes that can actually not be simulated in affordable computer time, the isotherms would become completely flat as is expected in the thermodynamic limit.
- A smooth prolongation (positive slope) of the vapor and liquid branches inside the coexistence region is also clearly visible. It can be shown that such *apparently metastable* states are actually absolutely stable for the finite sized systems. i.e., under the *constraint* of fixed density, they are stable against phase separation [45–47] The size of this region shrinks gradually as the system size increases.
- The smooth prolongation of the isotherms inside the coexistence region end at a point where the isotherms change slope. As the system size becomes larger, the change of slope gradually becomes discontinuous. In the thermodynamic limit it will become the well known discontinuity that signals a first order phase transition. However, for small systems the isotherms are smooth, exhibit no discontinuity and closely approach the behavior of a mean field *van der Waals loop*.
- The discontinuities in the isotherms, of which there can be as much as six, correspond to transitions between different states, including a homogeneous phase and phase separated domains of different shape. Only those states with a truly flat interface yield a zero slope isotherm. As the system size diminishes, the zero slope region altogether vanishes.

Whereas the results described above refer to a bulk phase transition, the first half of the isotherm (with vapor as the majority phase) resembles the result that is expected for a slit pore exhibiting complete drying; while likewise, the second half of the isotherm (with liquid as the majority phase) resembles what is expected for a slit pore exhibiting complete wetting. Actually simulating the slit pore with walls in the incomplete wetting regime produces indeed very similar results as those shown in Fig.3 [48].

This analogy notwithstanding, the relevant observation here is the fact that the system size provides a constraint on the partition function which in fact allows to approach closely the expected mean field result. Hence, a similar procedure could be envisaged for the calculation of interface potentials by means of computer simulations.

Our strategy follows closely ideas that are borrowed from the study of bulk phase transitions [49,50].

The simulation setup consists of a cuboidal box of dimensions $L_x = L_y$ and $L_z > L_x$. A substrate is placed at both sides of the simulation box parallel to the x–y plane (Fig.4). Performing a grand canonical simulation, one fixes temperature, volume and chemical potential. In this way, a film consistent with the imposed thermodynamic conditions builds on the substrate. However, because of the finite system size of the simulation box, fluctuations away from the equilibrium state may be observed (and enhanced in a controlled manner when necessary [51, 52]). This fact is exploited in our procedure in order to measure free energy differences. During the simulation, one simply monitors the probability $P_{1/2}(N)$ of observing N molecules inside the half of the simulation box closest to the studied substrate [53,54]. Accordingly, one can define the instantaneous adsorption akin to that substrate as:

$$\Gamma = (N - \frac{1}{2}\rho_v L_x L_y L_z)/L_x L_y \tag{7}$$

A surface free energy or *effective interface potential* of a film with adsorption Γ, or likewise, film thickness $\ell = \Gamma/(\rho_l - \rho_v)$, can then be estimated up to additive constants as:

$$\tilde{g}_\mu(\Gamma) = -\frac{k_B T}{L_x L_y} \ln P_{1/2}(\Gamma) \tag{8}$$

Fig.5 shows a set of $\tilde{g}_\mu(\Gamma)$ obtained for an adsorbed polymer film at coexistence as the Hamaker constant is gradually increased. The features of this effective interface potentials are clearly reminiscent of those expected from a mean field interface potential in the presence of long range forces. For small Hamaker constants $\tilde{g}_\mu(\Gamma)$ shows a deep minimum consistent with a state of incomplete wetting, together with a maximum at intermediate film thickness. Increasing the Hamaker constant one reaches a point where the minimum has the same height as the infinitely thick film, as in a first order phase transition. Above this point, a metastable minimum at thin film thickness can survive up to a prewetting critical point. Equilibrium film thickness at other conditions, and particularly, the prewetting phase transition may be studied by searching the minimum/minima that result after Legendre transformation, i.e., $\tilde{g}_{\mu'}(\Gamma) = \tilde{g}_\mu(\Gamma) + \Gamma(\mu' - \mu)$.

Whereas the strategy described above has a clear potential for the study of wetting transitions [28,53–55], its relation to a conjectured mean field interface potential for use with interface Hamiltonians is certainly a matter of concern. Indeed, a system in the thermodynamic limit would not exhibit stable films beyond the equilibrium film thickness $\ell_0(\mu)$, and would rather form droplets or prewetting films there. The effective interface potential as defined above would still provide a meaningful estimate of the droplets free energy, but would become meaningless as a measure of the free energy of an adsorbed film.

However, one must consider that the simulations are performed in finite sized systems, which could have a similar stabilizing role as that discussed for bulk systems. Forming a droplet has an energy cost due to the formation of the liquid–vapor and the solid–liquid interfaces, plus extra terms that are linear on the droplet perimeter. For systems that are small enough, it could result that the formation of a thick film with no lateral inhomogeneities has a smaller energy cost.

This may be illustrated already without invoking explicitly the system size by considering the classical theory of heterogeneous nucleation. In its simplest version, where one simply accounts for surface tension contributions, the size of the critical nucleus is merely dictated by Laplace's and Young's equations. Since the size parameters, radius and contact angle, are uncoupled a solution always exists. On the contrary, if one explicitly takes into account the role of line tension, τ, the resulting modified young equation becomes coupled to the Laplace equation, with τ entering as a parameter. A consequence of this coupling which was unnoticed for many years is that for positive τ, and sufficiently small droplet radii, the extremal condition has then no solutions [56]. For an open system, this is not a dramatic effect, it simply implies that the nucleation barrier is actually larger than expected otherwise. However, for closed systems, the implication is that there exists a range of conditions where a droplet can simply not be stabilized.

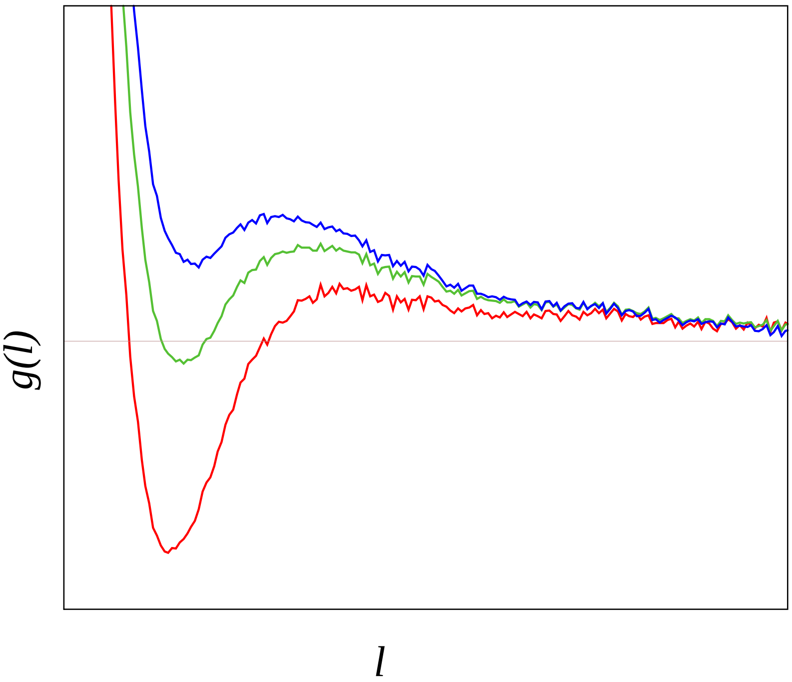

Fig. 5. Effective interface potentials, $g(\ell)$ obtained for a polymer adsorbed on a brush by means of the simulation technique explained in the text. Results are shown for three different values of the Hamaker constant below the wetting transition (red), almost at the wetting transition (green) and above the wetting transition yet below the critical prewetting point (blue). Results adapted from Ref.[54].

Taking into account a finite lateral system size as is achieved in computer simulation experiments by virtue of periodic boundary conditions provides yet another path for film stabilization.

Consider a finite system with lateral system size A, constraint to have a constant adsorption $\mathit{\Gamma} = \Delta\rho\,\ell$ far larger than that of the equilibrium thin film, which we assume $\ell_0 = 0$ for simplicity. The system has to choose whether to have the excess mass spread along the substrate forming a metastable film, or beading up to form a large droplet (Fig.1). In the first case, the free energy of the adsorbed film relative to the bare substrate is:

$$\Delta\Omega_f = \mathcal{A}(g_\mu(\ell) + \gamma_{lv}(1 - \cos\theta)) \tag{9}$$

In the second case, the free energy of formation of a droplet may be expressed in terms of classical nucleation theory as [57]:

$$\Delta\Omega_d = \frac{16\pi}{3}\frac{\gamma_{lv}^3}{\Delta p^2}\phi(\theta) + \frac{2\pi\tau\gamma_{lv}\sin\theta}{\Delta p} \tag{10}$$

where Δp is the Laplace pressure difference across the liquid–vapor interface and $\phi(\theta)$ is a function that describes the volume of a spherical cap relative to that of a sphere in terms of the macroscopic contact angle θ.

For the purpose of imposing the constraint of equal adsorption in both the droplet and film states, we must require the droplet to adsorb all the surface excess, such that $\frac{4\pi}{3}\phi(\theta)R^3 = \mathcal{A}\ell$. The ℓ dependence of Ω_d may be expressed by taking into account the Laplace equation and mass conservation. Thus, substitution of Δp in favor of ℓ, we conclude that a metastable film is actually stable against droplet formation whenever the following equation is satisfied:

$$g_{\mu_0}(\ell) + \gamma_{lv}(1 - \cos\theta) < \gamma_{lv}\left(\frac{36\pi\phi(\theta)}{\mathcal{A}}\right)^{1/3}\ell^{2/3} + \frac{\pi\tau\sin\theta}{\left(\frac{4\pi}{3}\mathcal{A}^2\phi(\theta)\right)^{1/3}}\,\ell^{1/3} \tag{11}$$

This result allows for a clear physical interpretation without any further simplification. For small enough lateral system sizes, the right hand side of the equation will be larger than the left hand side, thus allowing for stabilization of the adsorbed film. Positive contributions to the right hand side of the equation arise from different terms depending on the contact angle. For systems close to drying, the line tension term becomes irrelevant, but the bulk droplet term may still remain large for small surface areas. Close to the wetting transition, on the contrary, it is the bulk droplet term which vanishes, while the line tension term is found to exceed the left hand side always, due to the divergence of $\sin\theta/\phi(\theta)^{1/3}$.

This simple arguments show that indeed, the system size provides in principle a mechanism for the stabilization of films adsorbed on a flat substrate. The resemblance to the expected mean field description of the effective interface potentials shown in Fig.5 provides a plausibility test for this argument. It must be emphasized, however, that $\tilde{g}(\mathit{\Gamma})$ will show a system size dependence, at least above the wetting transition, with the maximum gradually disappearing in favor of a straight line. The region between zero adsorption and the equilibrium thin film, on the contrary, is expected to be robust to system size effects. The question is then, which system size is adequate here for extracting the sought form of $g(\mathit{\Gamma})$? A possible solution for this problem is to borrow ideas from liquid state theory in order to meaningfully extrapolate between the system size dependent and system size independent regions of $\tilde{g}(\mathit{\Gamma})$. Indeed, it is found that the decay of density profiles of fluids in contact with a substrate is dictated by bulk properties, and follows closely the asymptotic behavior of the total correlation function, at least for fluids with short range forces [58–60]. Not surprisingly, such correlations dictate also the spectrum of the interface potential, which is found to follow the short wave vector dependence of the structure factor.

Whereas this theoretical result applies in principle only to the asymptotic decay, some results show that such a regime is achieved for just a few molecular diameters away from the substrate. Already Horn and Israelachvilli suggested that the wave length of oscillations and exponential behavior they observed in their surface force apparatus where most likely governed by liquid bulk properties [61]. Recent studies seem to confirm this suggestion. Henderson calculated density profiles and interface potentials using a density functional theory and observed indeed the asymptotic decay suggested from the total correlation function followed closely the DFT results [62]. Similarly, simulations and experiments with charge colloids point to the very fast attainment of the asymptotic regime for both the density profile and disjoining pressure isotherms [63].

Another matter of concern is that the method as proposed employs a global, rather than a local order parameter. As discussed previously, for unstable systems this might not properly discriminate between laterally homogeneous or inhomogeneous systems, and should therefore be restricted to small systems that can achieve overall homogeneity. Now, even for systems that are actually stable, there could be present smooth lateral inhomogeneities in the form of capillary waves. Thus, the free energy $\tilde{g}(\ell)$ is actually an average over wavy films $\ell(\mathbf{r}_{\|}) = \sum_{\mathbf{q}} \ell(\mathbf{q}) e^{i\mathbf{q}\cdot\mathbf{r}_{\|}}$ consistent with the fixed system's adsorption. In that sense, the results obtained from simulation may be considered as a partially renormalized mean field potential, that has adsorbed all capillary waves of amplitude $\lambda = L_x$. One could try to resolve these coarse grained free energy into a finer description by measuring the probability of observing locally $\ell(\mathbf{r}_{\|})$, rather than globally, an average ℓ. This attractive possibility has a caveat, however, as defining the local position of a film is not always simple and implies some degree of arbitrariness. Several definitions have been suggested [64–66], but it seems it is an important requirement to properly resolve bulk from interfacial fluctuations [22] as discussed in section 3. In practice, for small system sizes and long range forces the amplitude of capillary waves is not large unless close to a critical point, so it is expected that the difference between coarse grained and resolved free energies will not be large.

6 Conclusions

In this paper we have discussed the feasibility of extracting mean field like interface potentials from exact computer simulations. We have argued that the instabilities expected to hinder such attempt could be inhibited by simply imposing appropriate finite system size constraints which can be very naturally implemented. Metastable states will be certainly stabilized within a range of film thickness thanks to this device, but the stabilization of films that are actually unstable under the mean field picture might be more difficult. Yet, one can hope that, at least for simple fluids, some tools borrowed from liquid state theory could provide the clues for a suitable extrapolation of the interface potential when film stabilization is not possible.

As a final remark, it is interesting to comment on a related approach for the calculation of interface potentials that was reported very recently by Herring and Henderson [67]. In this approach, the stabilization of films of intermediate size is achieved by means of a geometrical constraint, rather than system size. Confining a condensed chunk of liquid into a slit pore with antisymmetrical walls, one achieves an equilibrium state where the liquid–vapor interface is inclined but flat. This is very advantageous with respect to the simulation of a drop, because the absence of curvature implies that Laplace pressure effects may be ignored. Having so stabilized films that vary continuously in thickness, the liquid–vapor interface may be described along a direction parallel to the wall as $\ell(x)$. For each value of x and hence, of $\ell(x)$ it is possible to measure a density profile $\rho(z;\ell(x))$ and exploit this result in order to measure directly the disjoining pressure as:

$$\Pi_{\mu_0}(\ell) = -\int_{-\infty}^{\infty} [\rho(z;\ell) - \rho(z;\infty)] \frac{\mathrm{d}}{\mathrm{d}z} V_{\mathrm{ext}}(z)\,\mathrm{d}z \tag{12}$$

where $\rho(z;\infty)$ is the density profile for a semi-infinite liquid layer adsorbed on that wall. The encouraging result found in this work is that the disjoining pressure isotherm that is obtained is fully consistent with the observed macroscopic contact angle predicted by the interface Hamiltonian of Eq. (4).

Hopefully similar positive conclusions might be obtained for several open issues that need to be considered before validation of the method proposed in this work: Is a system size constraint enough to fully stabilize adsorbed films of widely different sizes on a flat substrate? Are the free energies measured for such constraint films able to describe condensates of different morphology according to an interface Hamiltonian? Are such free energies consistent with independent calculations for the disjoining pressure as obtained from Eq. (12)?

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