Thermal fluctuations of thin liquid films

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Abstract
A surprising lowering of the surface energy of liquid surfaces was recently found
in x-ray scattering experiments which enhances thermal fluctuations of fluid
interfaces at microscopic scales and calls for a re-examination of small-scale
interfacial processes. This reduction was predicted for microscopic undulations
below a few nm by density functional theory taking into account the long-range
attraction of molecular interaction potentials. Here, a self-consistent theory is
proposed for the fluctuation of fluid interfaces in arbitrary potentials which can
significantly alter thermodynamical and structural properties of liquid drops,
thin films, or membranes near a substrate. The substrate-induced hindrance of
thermally excited capillary waves increases considerably the thickness of thin
liquid films, which cannot be neglected in the analysis of adsorption data. An
explicit expression for adsorption isotherms is given depending on temperature,
Hamaker constant A, and surface tension γ which takes into account the
influence of capillary waves on the thickness of the fluid film and removes
reported discrepancies with the Lifshitz theory of van der Waals forces. Also
the steric repulsion potential of a membrane at distance D from a hard wall
can be calculated self-consistently in excellent agreement with Monte Carlo
simulations.

1. Introduction

Liquid interfaces, in particular those involving water, are of fundamental importance in many
areas of science and technology. Although receiving continuous attention since the days
of van der Waals [1–3], they are still poorly understood—in particular, their structure and
conformation at sub-microscopic length scales, i.e. beyond the range of application of the
simple phenomenological description in terms of thermally excited capillary waves [4]. Since
the work of Mandelstam [5] considerable progress has been achieved in the study of fluctuating
capillary waves—reviews for a single interface are given, for instance, in references [2, 6, 7].
But, in contrast to the case for solid surfaces, the absence of relevant experimental information
even for the simplest liquid–vapour interfaces precludes the assessment of any of the existing
theoretical models, which considerably diverge in their conclusions. Recent developments
in grazing-incidence x-ray scattering experiments resolved this uncomfortable situation. The
results reported in reference [8] give the first complete determination of the structure and

fluctuations of a liquid–vapour interface and represent a significant improvement in the understanding of fluid interfaces. In particular, it is clarified by the x-ray experiments that the dominant effect below a few nm is a large decrease (up to 75%) of the surface energy due to dispersion forces (see figure 2, later). This calls for a re-examination of all small-scale interfacial processes involving fluids in physics, chemistry, or biology, since any interface deformation at these scales should be easier than was formerly expected.

At liquid interfaces two different types of fluctuation occur simultaneously which both require the same careful statistical analysis: namely density fluctuations in the bulk, which are present also in the absence of the interface, and secondly capillary waves of the interface position. Whereas the spatial extension of the bulk fluctuations varies between the molecular diameter r_0 of the species and the bulk correlation length ξ, the wavelengths of the capillary waves span the range between ξ and the capillary length $L_c = \sqrt{\gamma/E_0}$ with $E_0 = \Delta\rho\, G$ where γ is the macroscopic surface tension, $\Delta\rho = \rho_l - \rho_g$ the difference between the mass densities of the liquid and vapour phase, respectively, and G the gravitational constant.

Density fluctuations in the bulk can be well described by density functional theory even for inhomogeneous fluids and solids [9], but the statistical physics of capillary waves of fluid interfaces in a non-parabolic external potential is still a non-trivial task. Such capillary-mode fluctuations of fluid layers are ubiquitous in nature and play an important role in many physical and biological systems [6, 10, 11]. For instance, the thickness of wetting layers and adsorbed thin liquid films near a substrate depends essentially on these thermal undulations of the vapour–liquid interface [12–14]. Also the physics of lipid bilayers has received much attention during the last two decades since Helfrich proposed in his seminal paper 'Steric interaction of fluid membranes in multilayer systems' that soft membranes exhibit steric fluctuation-induced repulsions which are important in stabilizing vesicle suspensions [15]. Such interactions controlled by thermal undulations of the membrane are particularly relevant for biological cells such as red blood cells but also for microemulsions and lamellar liquid crystals [16, 17].

In figure 1 an undulating sharp interface above a substrate is depicted which may serve as a model system for both types of physical application considered here: thin liquid films and soft membranes close to a hard wall. Thermally excited bending modes $f(\boldsymbol{R})$ of interfaces can be decoupled by Fourier transformation which allows an exact treatment of the amplitudes $\tilde{f}(\boldsymbol{q})$ for sinusoidal undulations of the wave vector $\boldsymbol{q}$ in parabolic potentials. The usual approach taken to derive an effective Hamiltonian of an interface fluctuation $\tilde{f}(\boldsymbol{q})$ is the expansion of a free energy of an inhomogeneous fluid into powers of curvatures of the interface with the leading terms determined by special interface configurations, i.e., spherical and cylindrical ones (see references [18] and references therein). This approach yields the free energy [6, 15]

$$E(q) = E_0 + \gamma q^2 + \kappa q^4 + \mathcal{O}(q^6) \tag{1.1}$$

of a thermally driven undulation with wave vector q governed by the surface tension γ, the elastic curvature energy κ, and the gravitational energy $E_0 = \Delta\rho\, G$. Unfortunately, equation (1.1) is correct only for unhindered undulations of a freely fluctuating interface, and not for interfacial fluctuations in an arbitrary potential $U(z)$ depending on the excursion of the interface position at $z = f(\boldsymbol{R})$. But such interaction potentials are relevant whenever hard walls or steric hindrances are close by—in the cases of adsorption isotherms of liquid thin films and fluctuations of stacks of lipid bilayers, for instance.

In spite of this significant conceptual and practical importance of fluid layers near solid substrates, the structural properties of thermally undulating liquid films are still unresolved due to the dearth of rigorous theoretical results for realistic systems in three spatial dimensions. The reason for this uncomfortable situation is the fact that thermal fluctuations of fluid interfaces are governed by two different physical mechanisms or interaction energies which can be treated
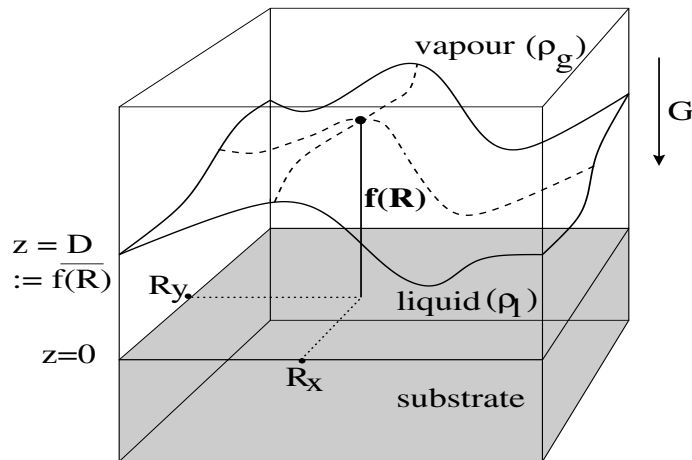
Figure 1. A schematic picture of a fluid film configuration with densities ρ_l and ρ_g, respectively. The substrate is flat at $z = 0$ and the interface between the coexisting liquid and vapour bulk phases does not contain overhangs or bubbles. Thus the local position of the liquid–vapour interface can be described by a single-valued function $f(\boldsymbol{R})$, where $\boldsymbol{R} = (R_x, R_y)$ denotes the lateral coordinates. Gravity $\boldsymbol{G}$ and fluid–substrate interactions $U(z)$ lead to a mean interface position at $D = \overline{f(\boldsymbol{R})}$. The statistical physics of one fluctuating interface such as a soft membrane or a liquid–vapour interface in the case of thin films is based mainly on the capillary-wave model given by equation (1.1) where the energy is comprised of the surface tension γ and the elastic bending rigidity κ.

theoretically only by complementary methods:

(i) The influences of surface tension and bending rigidities are usually treated by Fourier transformation of the interface position $f(\boldsymbol{R})$ yielding a decoupling of modes of fluctuating capillary waves.

(ii) The interaction of the interface with hard walls is usually treated in real space since the non-linearities of the substrate interaction potential $U(z)$ are relevant.

Whereas long-wavelength capillary waves of the interface position are mainly governed by the substrate interaction potential, microscopic ripples with wavelengths of a few nm are dominated by surface tension and bending rigidities which become larger with increasing wave vector q of the undulation. As shown below, this separation of length scales can be used for constructing an effective theory by combining Fourier-space and real-space techniques for the different modes in a self-consistent way.

Although the problem of evaluating thermal undulations near hard walls is easy to formulate, an accurate determination of the fluctuation spectrum is almost impossible. In view of the absence of rigorous results, the structure of fluid interfaces near substrates has been investigated using approximate schemes. To this end, one approach has emerged which is used frequently in the literature: in addition to the substrate potential $U(z)$ an effective steric interaction potential $U_s(z; E_0, \sigma, \kappa)$ is derived which describes the hindrance of thermal undulations by the substrate $U(z)$ and depends therefore on the interfacial parameters such as the bending rigidity κ. But in the standard *ansatz* for $U_s(z; E_0, \sigma, \kappa)$ only interactions with a hard step-like wall are taken into account, which therefore does not capture the details of an arbitrary potential $U(z)$. In particular, the dependence of thermal undulations on local minima in the substrate potential and the influence of soft repulsion cores are neglected in $U_s(z; E_0, \sigma, \kappa)$. Since recent experiments can actually measure the details of the structure of

fluid interfaces near substrates, an improved self-consistent *ansatz* for $U_s(z)$ which depends also on $U(z)$ may be useful in interpreting experimental data and to determine surface tensions of thin adsorbed films [14] or bending rigidities of lipid bilayers [19, 20], for instance.

1.1. Surface tension of liquid interfaces

Whereas for fluctuating membranes the free energy given by equation (1.1) works well, one has to be careful when applying it to vapour–liquid interfaces. As early as 1893, van der Waals [1] showed that an intrinsic density profile across the interface interpolates smoothly between the densities of the bulk liquid and vapour phases, respectively. The relevant fluctuations are density fluctuations in the bulk phases in contrast to capillary waves of the interface position, which have no counterpart in the bulk. Thus, one has to distinguish two different types of fluctuation at all length scales, i.e., the undulations of the interface position and the bulk density fluctuations. This means that the intrinsic density profile should take into account only bulk fluctuations but no undulations of the interface position, which are described in a second step by a statistical theory for capillary waves on all scales even for wave vectors larger than the inverse correlation length.

To this end one may start from a microscopic density functional theory for inhomogeneous simple fluids, which is a successful approach for the description of non-uniform fluids [9]. One can separate the different kinds of density fluctuation—bulk bubbles and interface undulations—by determining the intrinsic density profile via minimizing the functional under the constraint of a locally prescribed interface position $f(\boldsymbol{R})$, i.e., the location of the isodensity contour of the mean density is given as function of the lateral coordinates. Thus, by construction the profile does not take into account fluctuations of the interface position. In the second step the complete structure of the interface is obtained by weighting the unfreezing of these interface fluctuations by the cost in free energy of maintaining a given interface configuration as determined from the density functional. For this separation of the fluctuations, density functional theory is particularly suited because the forms of the density functional which are actually available do not contain these large interface fluctuations which lead to the roughening of fluid interfaces in the absence of gravity.

Such a density functional theory of fluid interfaces which takes into account the non-local features of any molecular interaction potential predicts a drastic decrease of surface tension on microscopic length scales [21, 22], as shown by the solid line in figure 2. The effective surface energy $\gamma(q)$ depends on the wave vector $q = 2\pi/L$, i.e., on the length scale L of the undulation of the interface. It should first decrease from its macroscopic value at $q = 0$ due to the effect of attractive long-range forces, reach a minimum, and then in fact increase $\propto q^2$ at large q due to the distortion of density profile when the surface is bent. The effective theoretical surface tension

$$\gamma(q) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathrm{d}z \, \mathrm{d}z' \, W(q, z - z') \rho(q, z) \rho(q, z') \tag{1.2}$$

can be written as an integral over a function $W(q, z-z'; r_0)$ describing the molecular interaction potential and a q-dependent density profile $\rho(q, z; \xi)$ where z, z' denote the distances perpendicular to the surface [21]. Using grazing-incidence x-ray scattering, reference [8] reported in 2000 for the first time the complete determination of the free-surface structure and of the size-dependent surface energy $\gamma(q)$ for water and organic liquids. Anomalous amplitudes of the sub-micrometre modes were observed which cannot be explained by the standard capillary-wave theory [4], and are attributed to the long-range effect of molecular interactions.
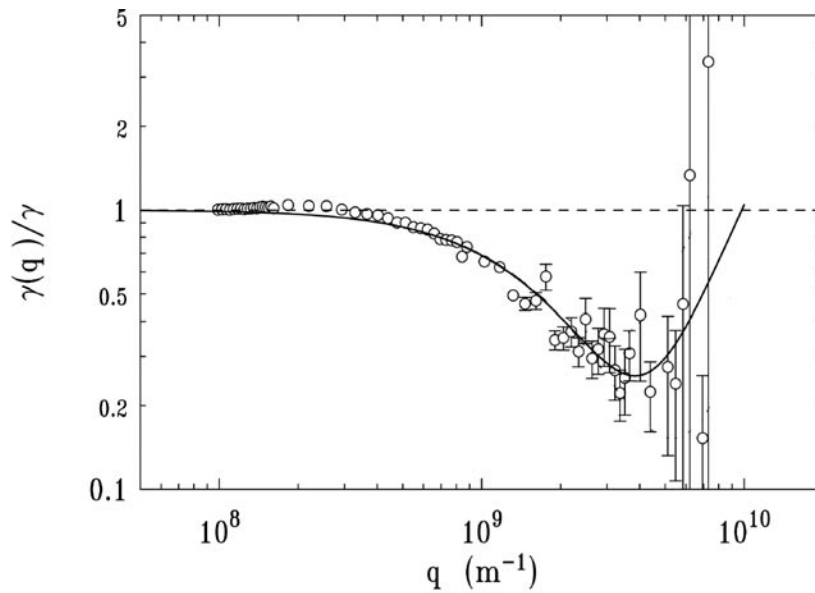
Figure 2. The wave-vector-dependent surface energy $\gamma(q)$ of water normalized to the macroscopic surface tension γ [8]. The line is the analytical result from the density functional theory (see equation (1.4) and reference [21]) without any adjustable parameter. The agreement with the experimental x-ray grazing-incidence data (circles) is excellent in the range $q \lesssim 3 \times 10^9$ m^{-1}. Only the amplitude $0 < \delta \lesssim 1$ of the density distortion is unknown (here $\delta = 0.35$) but its value is not relevant for the results at $q < 3 \times 10^9$ m^{-1}. The decrease of the surface energy $\gamma(q)$ does not depend sensitively on the molecular size r_0 and the correlation length ξ for values within a physically reasonable range.

An explanation for this surprising lowering of the surface energy can be found by taking into account the long-range power-law decay of the dispersion forces always existing between molecules. Assuming standard expressions for dispersion forces and density profiles in equation (1.2), the surface tension $\gamma(q)$ depends only on the size r_0 of the molecules (hard-core diameter), on the correlation length ξ, and on the amplitude δ of the curvature corrections of the density profile for thermally excited capillary modes. Whereas values for r_0 and ξ are experimentally accessible, for the parameter δ only the limiting values $0 < \delta < 0.5$ can be given. The effective theoretical surface tension $\gamma(q)$ obtained using reasonable parameter values for water is given in figure 2. The shape of the measured curve is perfectly described by the calculations where no fit parameter is used. Let us note that a similar effect of the dispersion forces was recently observed in the bulk structure factor of rare gases [23].

For practical purposes one may derive a more convenient formula than the full theoretical expression, equation (1.2). Considering particles which interact via dispersion forces for the attractive part of the interaction potential $w(r)$, one can adopt the form [22]

$$w(r) = -\frac{w_0 r_0^6}{(r_0^2 + r^2)^3} \tag{1.3}$$

reflecting the correct large-distance behaviour $w(r) \sim r^{-6}$. The length r_0 corresponds to the diameter of the particles and thus serves as a lower limit for the length scale of the density fluctuations and of the capillary waves considered below. Following reference [21] the full

expression for $\gamma(q)$, equation (1.2), can be reduced for this interaction potential to

$$\frac{\gamma(q)}{\gamma} = (2 - \delta(\xi q)^2) \frac{\tilde{w}(qr_0)}{(qr_0)^2} + 0.74\,\delta^2(\xi q)^2 \left(\frac{1}{2} + \left(\frac{\xi}{r_0}\right)^2 \tilde{w}(qr_0)\right) + \mathcal{O}((qr_0)^4) \qquad (1.4)$$

with $\tilde{w}(x) = 1 - (1 + x)e^{-x}$ [21].

The predicted and experimentally confirmed reduction in the surface energy of liquid interfaces at short length scales makes it mandatory to re-examine fluctuation phenomena of liquid surfaces—in particular, of small droplets and thin films where the relevant length scales are microscopic. The decrease of the surface tension may directly influence the contact angle of small liquid drops on substrates as well as enhance the nucleation of small water droplets in the upper atmosphere. Here, only two examples are discussed where an increase of thermal fluctuations plays an important role: (i) the increase of the thickness of an adsorbed fluid layer due to the hindrance of thermal fluctuations (steric repulsion) and (ii) the decrease of the thermal roughness of a fluid membrane between two hard walls.

1.2. Adsorption isotherms of thin liquid films

The technique of adsorption has recently given rise to a lively discussion about the interpretation of data for thin-film adsorption since experiments claimed significant discrepancies with theory [24–27]. Although measurements of monolayer adsorption have been extensively analysed [28], few theoretical approaches have emerged for interpreting data recorded for thicker films [12, 13]. It was generally accepted for a long time that the theory of Frenkel, Halsey, and Hill (FHH), which is based on the Lifshitz theory of dispersion forces [29, 30], accurately describes the shape of adsorption isotherms sufficiently close to saturation, i.e., in the thick-film regime [31, 32]. It predicts that the adsorption energy should scale as the inverse third power of distance z of the molecule yielding an effective substrate potential $U(D) = k_B T A D^{-2}/2$ for a thin liquid film of thickness D (see equation (5.1) below) where A is related to the Hamaker constant of the layer system (for details of the substrate potentials $U(z)$ see reference [33]). Therefore, the thickness D of the adsorbed film measured in units of the monolayer thickness r_0 varies as

$$D = \left(\frac{A}{\ln(p_s/p)}\right)^{1/3} \qquad (1.5)$$

with the gas pressure p below the saturated vapour pressure p_s of the film material.

However, improvement of the experimental techniques for determining the adsorbed film thickness revealed considerable deviations from equation (1.5) for virtually all systems studied [13, 25–27]. Early measurements on flat substrates moreover remain a matter of discussion, with recent experiments claiming significant discrepancies with Lifshitz theory (see references in reference [13]). Although it has been mentioned before that thermal fluctuations may be the cause for the observed discrepancies [13, 27], an expression for adsorption isotherms which is comparable in simplicity to equation (1.5) but is nevertheless consistent in detail with experimental data has not been derived yet. Such an expression would be very useful to experimentalists for analysing and interpreting their data—for instance, for film adsorption on rough substrates [34, 35]—in order to study whether the substrate is fractal or self-affine. Just because of the lack of an improved version of equation (1.5) including thermal fluctuations hindered by the substrate, experimental data have been interpreted wrongly and this has steered the discussion in a misleading direction by leading to interpretation of the thermal fluctuations as surface roughness of the substrate [13].

The suppression of fluctuating capillary waves in thin liquid films may also affect the contact angle Θ of a liquid drop which is simply related to the excess free energy of the film surface [36, 37]:

$$\cos \Theta = 1 + \Delta f(\gamma)/\gamma$$

where $\Delta f(\gamma)$ depends on the surface tension γ. In the case of thick films the value of Δf is too small to affect the contact angle, but for thin films the effective repulsion may make a considerable contribution to the value of the film contact angle.

1.3. A fluctuating membrane near a wall

A similar problem occurs when studying fluid floating bilayers, which are often used as an experimental model system for studying membranes. Biophysical studies of membrane–membrane and membrane–protein interactions require such well controlled model systems [17, 38]. A typical example of a fluid membrane is a lecithin bilayer in water, which does not show shear resistance, only showing elastic bending energies due to curvatures of the layer. In contrast to the adsorption layer mentioned above where the increase of thickness due to thermal fluctuations is a few nm, shape fluctuations of vesicles are visible already in optical microscopy.

That thermal undulations or ripples induce a repulsive steric interaction between membranes was first addressed theoretically [15, 39, 40], but steered in the meantime a number of experiments. The statistical physics of membranes and the importance of thermal undulations for vesicles [41, 42] or multi-lamellar systems [43, 44] has been reviewed in many articles [6, 45]. To determine the fluctuation-induced free energy as a function of κ, for instance, is a non-trivial task and many theoretical approaches have been applied: Monte Carlo simulations [46–49], renormalization group analysis [50], Flory theory [51], mean-field theories of lattice models and self-consistent numerical calculation [47, 52]. Here, the focus of the paper is limited to a subtle but nevertheless important point: the fluctuations of one single interface (membrane) close to a flat solid substrate. We are not interested in unbinding transitions [17, 45], nor in universal scaling behaviours close to critical transitions or in complex phase diagrams, but only in the non-universal dependence of the thermal undulations on the details of the molecular interaction potential with the substrate. A discussion of interaction energies between molecules and substrates can be found in reference [33].

For biophysical applications the knowledge of the precise pressure law is essential, i.e., the steric repulsion potential [15]

$$U_s(D) = c_H \frac{(k_B T)^2}{\kappa D^2} \tag{1.6}$$

as a function of distance D and temperature T which keeps the membranes apart due to steric repulsion. Usually, one assumes that the surface tension $\gamma = 0$ and the gravitational energy $E_0 = 0$ vanishes for a lipid bilayer although stress-induced forces and external parabolic potentials may be relevant in some cases. This steric repulsion potential with the dimensionless prefactor $c_H = 3\pi^2/128 \approx 0.231$ was first derived by Helfrich in 1978, but the precise value of the prefactor $c_H(\gamma, E_0)$ remained an unsolved puzzle—in particular, its dependence on γ and E_0. Computer simulations yield smaller prefactors, namely $c_H = 0.116$ [46], $c_H = 0.074$ [47], and $c_H = 0.0798$ [48]. The value $c_H(\gamma = 0) \approx 0.08$ derived here from the self-consistent theory for vanishing surface tension is in excellent agreement with the Monte Carlo simulations. Additionally the theory proposes a strong dependence for non-zero but small values of γ (decrease) and E_0 (increase) which may resolve the problems related to disagreement of experimental data and predictions from Monte Carlo simulations. Of course,

the functional shape of the steric repulsion potential $U_s(D)$ also changes with increasing values of γ and E_0 which can be calculated within the self-consistent theory, as well as the dependence on the substrate potentials $U(D)$.

Thermally excited bending modes of interfaces can be decoupled by a Fourier transformation which allows an exact treatment for parabolic potentials (see section 2). But hard walls are non-parabolic constraints in real space which cannot be converted easily into constraints on the amplitudes of Fourier modes. The main idea for solving this problem is presented in section 3 where short-wavelength fluctuations are distinguished from large-scale undulations. Whereas the former are governed mainly by surface tension γ and bending rigidity κ and can be treated in Fourier space, the long-wavelength fluctuations are constrained by hard walls and the interaction potential $U(z)$. These fluctuations can be calculated in real space in a self-consistent way by assuming a mean squared width σ_f of the fluctuations due to the short-wavelength fluctuations which depends not only on γ and κ but also on the mean interface position D. Averaging over the long-wavelength fluctuations yields a mean average position $\bar{f}(D, \sigma_f) = D$ as a function of D and σ_f which should equal D.

An accurate determination of the steric repulsion potential $U_s(D)$ (see equation (1.6)) based on this self-consistent theory is presented in section 4 and a more accurate adsorption isotherm than equation (1.5) is derived in section 5. Since recent experiments are able to measure in detail the thickness D of thin liquid films (adsorption isotherms, [13, 14]) as well as the distance and fluctuation width σ of liquid bilayers (membranes [19, 20]), for instance, it may be possible to extract values for surface tension and bending rigidities once the influence of the functional shape of the substrate potential $U(D)$ can be determined.

2. The freely fluctuating interface: relevant length scales

At low temperatures, i.e., far below the critical point of the two coexisting bulk phases, the intrinsic thickness of the interface is of the size of the particles and the dominant fluctuations are capillary waves which are promoted entropically but opposed by gravity and by the surface tension which penalizes the increase of the interfacial area generated by the capillary waves. The approach put forward by Buff, Lovett, and Stillinger [4] describes the actual smooth density profile of the film as a fluctuating step-like interface between the liquid and vapour phase assuming that capillary waves of the interface are the relevant thermal fluctuation for the formation of a smooth profile at low temperatures.

The local position of the liquid–vapour interface can be described by $z = f(\mathbf{R})$, where $\mathbf{R} = (x, y)$ with $R = |\mathbf{R}|$ is the lateral reference point in the xy-plane parallel to the mean interface at $z = D$ and the substrate at $z = 0$ (see figure 1). Overhangs of the interface and bubbles of one phase inside the other, i.e., domains topologically separated from the interface, are neglected so that one can proceed analytically by treating a single-valued function $f(\mathbf{R})$. A convenient starting point for the statistical physics of an interface is the effective Hamiltonian $\mathcal{H} = \mathcal{H}^{(G)} + \mathcal{H}^{(W)}$ with the energy of a freely fluctuating interface

$$\mathcal{H}^{(G)}[f(\mathbf{R})] = \frac{1}{2}\int_{\mathbb{R}^2} \mathrm{d}^2\mathbf{R} \; E_0 f(\mathbf{R})^2 + \gamma(\nabla f(\mathbf{R}))^2 + \kappa(\Delta f(\mathbf{R}))^2 \qquad (2.1)$$

governed by surface tension γ and bending rigidity κ and with the non-linear interaction potential $U(z)$

$$\mathcal{H}^{(W)}[f(\mathbf{R})] = \int_{\mathbb{R}^2} \mathrm{d}^2\mathbf{R} \; U(f(\mathbf{R})) \qquad (2.2)$$

describing the influence of the wall due to a non-parabolic interaction potential $U(z)$. The term $E_0 = \Delta\rho\, G$ takes into account the gravitational energy of a fluid layer where $\Delta\rho = \rho_l - \rho_g$

denotes the difference between the mass densities of the liquid and vapour phase, respectively, and G the gravitational constant.

It is transparent to study the Gaussian part of the Hamiltonian $\mathcal{H}^{(G)}$ which is quadratic in the amplitudes of the fluctuating interface $f(R)$ in Fourier space in which the bending modes $\tilde{f}(q)$ of the interface decouple. Therefore, introducing the Fourier-transformed functions

$$\tilde{f}(q) = \int_{\mathbb{R}^2} d^2R \, e^{-iq \cdot R} f(R) \qquad \text{and} \qquad f(R) = \int_{\mathbb{R}^2} \frac{d^2q}{(2\pi)^2} \, e^{iq \cdot R} \tilde{f}(q) \qquad (2.3)$$

describing the interface position and the interaction between the molecules, the Hamiltonian $\mathcal{H}^{(G)}$ reads

$$\mathcal{H}^{(G)}[\tilde{f}(q)] = \int_{R^2} \frac{d^2q}{(2\pi)^2} \frac{1}{2} |\tilde{f}(q)|^2 E(q) \qquad (2.4)$$

with $E(q) = \sigma_f^{-2}(q) = E_0 + \gamma q^2 + \kappa q^4$ given by equation (1.1), γ the surface tension, and κ the bending rigidity. Equations (1.1) and (2.4) describe the cost in free energy $E(q)$ of bending an interface with wave vector q.

The probability of a surface wave $\tilde{f}(q)$ of wave vector q is then

$$P[\tilde{f}(q)] = \sqrt{\frac{E(q)}{2\pi k_B T}} \exp\left(-\frac{1}{2} \frac{E(q)}{k_B T} |\tilde{f}(q)|^2\right). \qquad (2.5)$$

In contrast, the probability $P[f_0]$ of finding the interface position $f_0 = f(\mathbf{0})$ at a specified position $R = \mathbf{0}$ is given by the integral over all fluctuating modes $\tilde{f}(q)$ of the interface

$$P[f_0] = \prod_q \int d\tilde{f}(q) \, \exp\left(-\frac{1}{2} \int \frac{d^2q}{(2\pi)^2} \frac{E(q)}{k_B T} |\tilde{f}(q)|^2\right) \delta\left(f_0 - \int \frac{d^2q}{(2\pi)^2} \tilde{f}(q)\right)$$

$$= \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{1}{2} \frac{|f_0|^2}{\sigma^2}\right) \qquad (2.6)$$

with the mean squared width

$$\sigma^2 = \xi_\perp^2 = \int \frac{d^2q}{(2\pi)^2} \frac{1}{E(q)} = \frac{k_B T}{4\pi} \int_0^\infty dx \, \frac{1}{E_0 + \gamma x + \kappa x^2}. \qquad (2.7)$$

Of course, in order to separate short and long wavelengths one needs the probability of the difference $\delta f_R = f(r+R) - f(r)$ between the interface position at distance R which is given by equation (2.6) if σ is replaced by $\sigma(R)^2 = 2(g(0) - g(R))$ where

$$g(R) = \langle f(r+R)f(r)\rangle = \int_0^\infty \frac{dq}{2\pi} \frac{q J_0(qR)}{E(q)} \qquad (2.8)$$

denotes the correlation function and $J_0(x)$ the Bessel function. The correlation function describes the influence of the interface at $f(r)$ on the fluctuating interface at distance R in terms of the bending energy $E(q)$. This function is needed when an average position $f(r) = D$ is assumed and the average position $\bar{f} = \langle f(r+R)\rangle = D$ at distance $|R| = \xi_\parallel$ is determined self-consistently where $\xi_\parallel$ denotes the lateral correlation length. Defining the perpendicular correlation length by $\xi_\perp = \sigma(\xi_\parallel)$ one finds $\xi_\perp \approx \sigma$, so σ can be used instead of $\xi_\perp$.

Using the definition (2.8) for the correlation function with the parallel correlation length $\xi_\parallel$ defined by $\lim_{R\to\infty} g(R) = e^{-R/\xi_\parallel}$ and the mean squared width $\sigma^2 = g(R = 0)$, one obtains the exact relation

$$\sigma^2 = \frac{k_B T}{2\pi\gamma} \frac{1}{\sqrt{|1 - 4E_0\kappa/\gamma^2|}} \begin{cases} \arctan\sqrt{4E_0\kappa/\gamma^2 - 1} & \text{for } \gamma^2 < 4E_0\kappa \\[2mm] \dfrac{1}{2}\log\dfrac{1 + \sqrt{1 - 4E_0\kappa/\gamma^2}}{1 - \sqrt{1 - 4E_0\kappa/\gamma^2}} & \text{for } \gamma^2 > 4E_0\kappa \end{cases} \qquad (2.9)$$

with the limiting expressions

$$\sigma^2 \to \begin{cases} \dfrac{k_B T}{8\sqrt{E_0 \kappa}} & \text{for } \gamma^2 \ll 4E_0\kappa \\[3mm] \dfrac{k_B T}{2\pi\gamma} \log \dfrac{\gamma}{\sqrt{E_0\kappa}} & \text{for } \gamma^2 \gg 4E_0\kappa. \end{cases} \tag{2.10}$$

The relation between the perpendicular and parallel correlations length may be approximated as follows:

$$\xi_\parallel^2 = \frac{\kappa}{\gamma}\left(\exp\left(\frac{4\pi\gamma}{k_B T}\sigma^2\right) - 1\right) \to \begin{cases} \dfrac{4\pi\kappa}{k_B T}\sigma^2 = \dfrac{\pi}{2}\sqrt{\dfrac{\kappa}{E_0}} & \text{for } \gamma^2 \ll 4E_0\kappa \\[3mm] \dfrac{\kappa}{\gamma}\exp\left(\dfrac{4\pi\gamma}{k_B T}\sigma^2\right) = \dfrac{\gamma}{E_0} & \text{for } \gamma^2 \gg 4E_0\kappa \end{cases} \tag{2.11}$$

yielding the two exact limiting cases for vanishing surface tension γ and bending rigidity κ, respectively. Note that in the former the factor 4π is often replaced by 16, a difference which is not relevant in the following.

As shown in figure 2 and equations (1.2)–(1.4), the actual surface energy of liquid interfaces at microscopic scales $L_\parallel$ can be considerably smaller than the macroscopic surface tension γ used in equations (1.1) and (2.9)–(2.11). The corresponding increase of thermal undulations, i.e. of the mean squared width σ, increases also the influence of hard walls, i.e., the hindrance of capillary waves by substrate potentials. Therefore the following focus on two possible effects: the increase of the thickness D of thin liquid films, improving in section 5 the adsorption isotherm, equation (1.5), and the change of the coefficient c_H in equation (1.6) describing the fluctuation width σ^2 of a membrane between two hard walls at distance $2D$ (see section 4).

3. Hindrance by a substrate: self-consistent theory

The statistical physics of a single membrane between two parallel hard walls is quite a difficult problem—though easy to formulate. Whereas in the last section a freely, i.e., unhindered fluctuating membrane can be treated exactly by a Fourier transformation of the interface position $f(R)$ (see equation (2.3)) yielding the mean squared width σ and the parallel correlation length $\xi_\parallel$ (see equations (2.9) and (2.11), respectively), an analogous approach is not possible as soon as interaction potentials $U(z)$ are involved which are not parabolic.

An intriguing heuristic solution assumes that soft membranes exhibit an effective steric interaction potential $U_s(z)$, which works amazingly well for many applications [15]. An undulating interface can be considered as a surface with random humps of typical height $\sigma = \xi_\perp$ extending over an area $\sim\xi_\parallel$. One may assume that these humps can be interpreted in terms of independent particles that exert an ideal-gas pressure, $P_s = k_B T/(2DL_\parallel^2)$. The typical length $L_\parallel = c_\xi \xi_\parallel$ is of the order of the parallel correlation length, so one may choose $c_\xi \approx 1$. Using equation (2.11) for the parallel correlation length and assuming a relationship

$$\sigma^2 = \mu D^n \qquad \text{with } n = 2 \tag{3.1}$$

between the roughness σ and the separation distance D to the wall, one finds the steric interaction energy per area [53]

$$U_s(D) = \frac{\gamma k_B T}{2\kappa c_\xi^2} \int_D^\infty dx \Big/ \left[x\left(\exp\left(\frac{4\pi\gamma}{k_B T}\mu x^n\right) - 1\right)\right] \to c_H \frac{(k_B T)^2}{\kappa D^2} \qquad \text{for } \gamma \ll 4E_0\kappa \tag{3.2}$$

with $P_s = -\partial U_s(D)/\partial D$. Here, $c_H = 1/(16\pi c_\xi^2 \mu)$ denotes a dimensionless prefactor which determines the strength of the fluctuation-induced interaction. Despite many attempts to

determine the value of c_H exactly, there is still a lively debate as regards how to calculate it accurately. In the limit $\gamma \rightarrow 0$ one can assume a linear relationship $D \sim \sigma$, i.e., $n = 2$. Of course, the mean-field argument cannot capture the correct behaviour $n = 1$ for surface-tension-dominated interfaces yielding the steric potential $U_s(D) \sim \exp(-D/D_0)$ which was predicted by renormalization group transformation [54] and confirmed by Monte Carlo simulations [55].

Note that this heuristic approach does not take into account the details of the interaction potential $U(z)$ of the interface with the substrate, only considering its strong repulsion at short distances. The dependence of the steric repulsion potential $U_s(z)$ on $U(z)$ may be determined using a self-consistent theory presented here. Applying a Fourier transformation, the bending modes of the membrane decouple yielding a Gaussian distribution of the amplitudes of the waves. The main problem in evaluating the partition sum is that the hard walls cannot be treated exactly in Fourier space. On the other hand, in real space hard walls are simply constraints on the integration range of the membrane position which can be implemented straightforwardly, but one cannot integrate exactly over the coupled bending modes of the interface. One may overcome this uncomfortable situation by evaluating the partition sum both in Fourier space and real space, applying in the two cases similar approximations by introducing an unknown parameter σ_f. To do this one has first to separate the long-wavelength bending modes governed by substrate potentials from the microscopic ripples influenced mostly by bending rigidities and surface tension.

3.1. Separation of large and small wave vectors

One may parametrize the interface position $f(\mathbf{R}) = f_s(\mathbf{R}) + f_l(\mathbf{R})$ into a function describing the short-wavelength contribution

$$f_s(\mathbf{R}) = \int \frac{d^2q}{(2\pi)^2} \, e^{iq \cdot R} \tilde{f}(\mathbf{q}) \tilde{S}(|\mathbf{q}|) \tag{3.3}$$

and the remaining part

$$f_l(\mathbf{R}) = \sum_{i,j} f_{ij} S_{ij}(\mathbf{R}) \tag{3.4}$$

parametrized by amplitudes f_{ij} in real space and a window function $S_{ij}(\mathbf{R})$. Choosing a step function $S_{ij}(\mathbf{R}) = S_i(R_x)S_j(R_y)$ with

$$S_i(R) = \begin{cases} 1 & iL_\parallel \leqslant R < (i+1)L_\parallel \\ 0 & \text{otherwise} \end{cases} \tag{3.5}$$

one introduces a soft cut-off $\tilde{S}(q) \sim (\sin qL_\parallel)/qL_\parallel$ for the modes $\tilde{f}(\mathbf{q})$ in Fourier space. Of course, one may introduce a sharp cut-off

$$\tilde{S}(q) = \begin{cases} 1 & q > q_\parallel = 2\pi/L_\parallel \\ 0 & q < q_\parallel = 2\pi/L_\parallel \end{cases} \tag{3.6}$$

where the integrations over the Fourier modes are restricted strictly to wave vectors larger than $q_\parallel$, yielding a smooth window function $S_{ij}(\mathbf{R})$ instead of equation (3.5). Another choice would be a Gaussian function

$$S_{ij}(\mathbf{R}) = \frac{1}{2\pi L_\parallel} \exp\left(-\left[\mathbf{R} - \binom{i}{j}L_\parallel\right]^2 \Big/ (2L_\parallel^2)\right) \qquad \text{and} \qquad \tilde{S}(q) = e^{-L_\parallel^2 q^2/2}$$

but the details of $S_{ij}(\mathbf{R})$ and $\tilde{S}(q)$ are not relevant here, so equations (3.5) and (3.6) are chosen, respectively. Uncertainties of the definition are taken into account by a dimensionless factor

$c_\xi \approx 1$ relating the size $L_\parallel = c_\xi \xi_\parallel$ of fluctuating patches to the parallel correlation length $\xi_\parallel$. Note that due to the quadratic window function in equation (3.5), one may have to introduce a geometric factor $\alpha^2 = \pi/4$ defined by

$$4q^2 = \int_{-q}^{q} dq_x \int_{-q}^{q} dq_y = \int_{|q|<q/\alpha} d^2q = \frac{\pi}{\alpha^2} q^2$$

which accounts for the area ratio of a disc to a square of the same size. Integrating over wave vectors q it may be more convenient to introduce this geometric factor and transform integrals to spherical symmetric coordinates for the independent modes. The geometric factor α is always necessary if one integrates in Fourier space over a finite area, i.e., including a cut-off for large values of q (compare the factors 16 and 4π in equation (2.11)). Of course, a more thorough treatment is required when details of the microscopic structure are relevant, but here one may assume that the factors c_ξ and α are sufficient to capture the relevant features.

3.2. Fourier space

Applying a Fourier transformation, one may approximate analogously to equation (2.9) the total width σ of an interface by an integral over all modes

$$\sigma^2 = \int \frac{d^2q}{(2\pi)^2} \sigma(q)^2. \tag{3.7}$$

But in contrast to the case for equation (2.9) for an unhindered fluctuating interface, the width $\sigma(q)$ of each mode depends on the substrate potential $U(z)$. The intrinsic width σ_l of the single large-scale mode $f_l(R)$ of wavelength $q_\parallel = 2\pi/L_\parallel$ is mainly governed by the steric interactions with the hard walls and depends on the substrate potential $U(D)$. The steric hindrance due to hard walls may therefore be approximated by a wave-vector-independent Gaussian distribution of width $\sigma_l(q)$:

$$\frac{1}{\sigma(q)^2} = \frac{1}{\sigma_f(q)^2} + \int_0^{q_\parallel} \frac{d^2q}{(2\pi)^2} \frac{1}{\sigma_l(q)^2} = \frac{E_0^{(steric)} + E_0 + \gamma q^2 + \kappa q^4}{k_B T} \tag{3.8}$$

for the modes $q < q_\parallel$ which are added to the inverse width $\sigma_f(q)^{-2}$ of an otherwise freely fluctuating interface position $f_s(R)$ given by equation (1.1). The width of small-scale fluctuations $\tilde{f}_s(q)$ has to be decreased according to the fluctuation width σ_W of a patch on large scales $f_l(R)$ governed by the interaction potential $U(z)$. Assuming that the width $\sigma_s^2(q) = \sigma_W^2 = \langle \tilde{f}_l^2(q) \rangle$ is constant for each mode f_l for $q < q_\parallel = 2\pi/L_\parallel$, one obtains

$$E_0^{(steric)} = \frac{k_B T}{\sigma_W^2} \frac{1}{c_\xi \xi_\parallel^2} \qquad \text{with } L_\parallel = c_\xi \xi_\parallel. \tag{3.9}$$

Thus, integrating over all modes between $q_{min} = 2\pi/L_{max}$ and $q_\parallel = 2\pi/L_\parallel$ results in a factor $\xi_\parallel^2$, where the system size L_{max} is set to infinity. In addition, a factor $c_\xi \approx 1$ is introduced to account for uncertainties in the definition of the relevant size of fluctuating patches. Of course, results should not depend sensitively on the value of c_ξ. The change of the fluctuation width $\sigma(q)$ due to the interaction with the hard wall is assumed to be equal for each wave vector q which seems to be reasonable even at small wavelengths where q becomes large.

In other words, one approximates the hindrance by a wall, i.e., by a substrate potential $U(z)$, by adding a constant contribution $E_0^{(steric)}$ to the energy which is needed to generate an undulation of wave vector q. This approach corresponds to approximating a hard wall by a parabolic potential $\frac{1}{2} E_0^{(steric)} f(R)^2$ where $E_0^{(steric)}$ depends on the size $L_\parallel$ of typical undulations $f(R)$ and the strength σ_W has to be determined self-consistently. However, one has to note that $E_0^{(steric)}$ is not just the second derivative of the substrate potential $U(z)$.

Taking equations (2.11), (3.7)–(3.9), one finds with E_0 replaced by $E_0 + E_0^{(steric)}$ a relationship $\sigma_W(\sigma)$ shown in figure 3. In particular, one obtains

$$\sigma_W = \sqrt{k_B T/\gamma}$$

in the surface-tension-dominated regime $\gamma \gg 4E_0\kappa$ and

$$\sigma_W = (4/\sqrt{\pi})\sigma \approx 2.257\sigma$$

in the bending-rigidity-dominated regime $\gamma \ll 4E_0\kappa$, when $c_\xi = 1$ and the gravity term $E_0 = 0$ has been neglected for convenience.
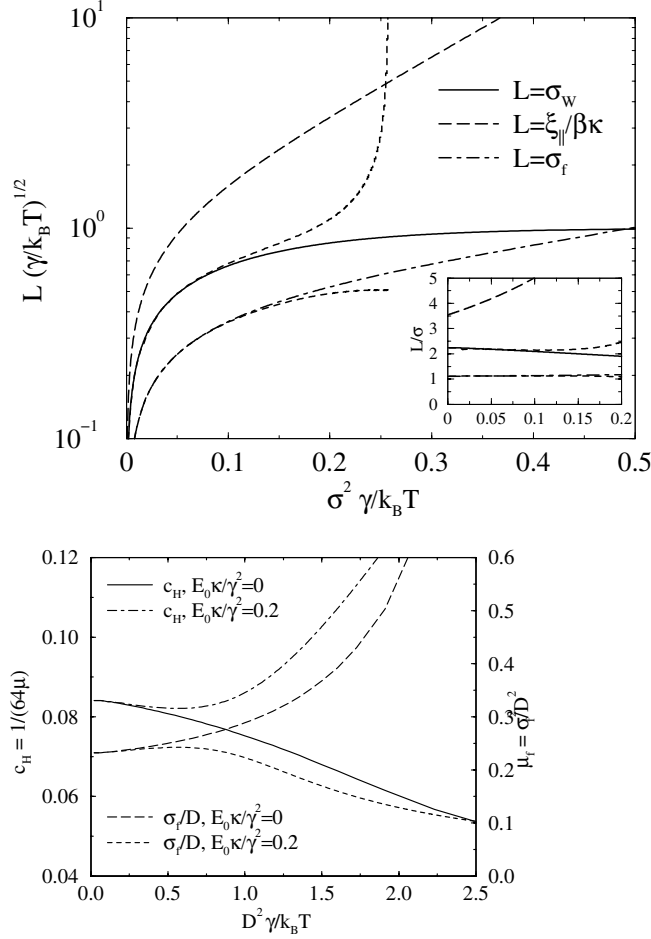

Figure 3. Top: dependences of σ_W (solid line), $\xi_\parallel$ (dashed), and σ_f (dot–dashed) on the total width σ which has to be determined self-consistently using equations (3.10)–(3.13) in order to take into account the details of the substrate potential $U(z)$. The dotted lines are for $E_0\kappa/\gamma^2 = 0.2$ whereas the other curves show the values for $E_0\kappa/\gamma^2 = 0$. One finds the limiting values $\sigma_W = (4/\sqrt{\pi})\sigma = 2.25\sigma$, $\xi_\parallel = 3.55\sigma\beta\kappa$, and $\sigma_f = 1.115\sigma$ for vanishing surface tension $\gamma = 0$. Bottom: for a fluctuating membrane between two hard walls, the dependence of $c_H = 1/(64\mu) = D^2/(64\sigma^2)$ and σ_f^2/D^2 on the distance $2D$ of the two walls calculated self-consistently using equation (4.3) and using the values shown in the top panel for σ_f. One finds the limiting values $c_H = 0.084$ ($\mu = 0.19$) and $\sigma_f^2 = \mu_f D^2$ with $\mu_f = 0.23$ for vanishing surface tension $\gamma = 0$.

It remains to find an expression for $\sigma(\sigma_W)$ in order to determine self-consistently the still unknown parameter σ_W and therefore σ as a function of $U(z)$. One may repeat the same line of argument in real space, yielding a second set of equations where the explicit expression $U(z)$ for the substrate potential can be taken into account.

3.3. Real space

In contrast to equation (3.7) for Fourier space, one can calculate the mean squared width σ in real space from

$$\sigma^2 = \frac{1}{Z} \int_{-\infty}^{\infty} \mathrm{d}z \, z^2 \mathrm{e}^{-\beta U(z) L_\parallel^2} P_f(z - D) \tag{3.10}$$

with $L_\parallel = c\xi_\parallel$ the size of a fluctuating patch $f_l(\boldsymbol{R})$ of the interface where D denotes the mean distance from the interface to the wall, $U(z)$ is the potential of the interaction with the substrate, and

$$Z = \int \mathrm{d}z \, \mathrm{e}^{-\beta U(z) L_\parallel^2} P_f(z - D)$$

is the normalizing partition sum. The probability $P_f(z)$ of a deviation z of the membrane position $f_l(\boldsymbol{R})$ from its mean value D is approximated by a Gaussian distribution

$$P_f(z) = \sqrt{\frac{2\pi}{\sigma_f^2(\sigma)}} \exp\left(-\frac{z^2}{2\sigma_f^2(\sigma)}\right) \tag{3.11}$$

with a width

$$\frac{1}{\sigma_f^2(\sigma)} = \frac{1}{\sigma^2} - \frac{1}{\sigma_W^2(\sigma)} \tag{3.12}$$

due to the bending modes $f_s(\boldsymbol{R})$ at small scales. From the total width σ, one has to subtract the width σ_W of a single mode for $q \to 0$ which is about to be added by the integration in equation (3.10). Note that $\sigma_f^2 \neq \int \mathrm{d}^2q \, \sigma_f(q)^2$ with $\sigma_f(q)$ given by equation (1.1). The back-reaction of the potential $U(z)$ on σ_f is already included, since σ_f is defined self-consistently by equations (3.10) and (3.12), so σ_f is not given by the width of a freely fluctuating interface. Equation (3.12) corresponds in real space to the analogous approximation of equation (3.8) in Fourier space where σ_f and σ_W are auxiliary variables defined solely by the self-consistent determination of the total width σ. Assuming that the two expressions (3.7) and (3.10) for σ are equal, one obtains an implicit equation for σ_W and thus for σ once the mean distance D is determined by the self-consistent implicit equation

$$D = \frac{1}{Z} \int_{-\infty}^{\infty} \mathrm{d}z \, z \exp\left(-\beta U(z) L_\parallel^2(\sigma) - \frac{(z - D)^2}{2\sigma_f^2(\sigma)}\right) \tag{3.13}$$

where the parallel correlation lengths $\xi_\parallel(\sigma)$ are given by equation (2.11) and the interfacial widths $\sigma_f^2(\sigma)$ by equation (2.9).

Of course, these self-consistent equations are based on a crude mean-field type approximation, but the argument does not depend on the special choice of the probability $P_f(z)$ in equation (3.11), and the advantage compared to renormalization group techniques, for instance, is the applicability for arbitrary substrate potential $U(z)$ and the possibility of determining the dependence of σ even on details of $U(z)$. Let us discuss some elementary examples for the potential $U(z)$ (section 4) before the self-consistent equations (3.10) and (3.13) are applied in section 5 to calculate adsorption isotherms.

4. Symmetric potentials: fluctuation width σ

Applying equation (3.13) for a symmetric potential $U(z) = U(-z)$, one immediately finds $D = 0$, so one only has to solve the self-consistent equation (3.10) for the total width σ.

4.1. The freely fluctuating interface

An unbounded fluctuating membrane, i.e., for a vanishing potential $U(z) = 0$ one can perform the Gaussian integral yielding $\sigma = \sigma_f$ (see equation (3.10)). Using the relation $\sigma_f^{-2} = \sigma^{-2} - \sigma_W^{-2}$ one finds $\sigma_W^{-1} = 0$ and therefore $\sigma = \xi_\perp$ given by equation (2.9). That is trivial but at least the self-consistent approach does not fail.

4.2. The parabolic potential: gravitational field

For a liquid–vapour interface which fluctuates in a parabolic external potential

$$U(z) = \frac{1}{2}\bar{E}_0 z^2 \tag{4.1}$$

in addition to a gravitational field $E_0 = \Delta\rho\, G$, one finds with

$$\sigma^{-2} = \sigma_f^{-2} + \frac{\bar{E}_0 \xi_\parallel^2}{k_B T}$$

(see equation (3.10); $c_\xi = 1$) and the relation $\sigma_f^{-2} = \sigma^{-2} - \sigma_W^{-2}$ the expression

$$\sigma_W^2 = \frac{k_B T}{\bar{E}_0} \frac{1}{\xi_\parallel^2}$$

(compare with the width of the most probable mode $q = 2\pi/\xi_\parallel$). Therefore, one finds $E_0^{(steric)} = \bar{E}_0$ (see equation (3.9)) and with equations (3.7) and (3.8) the exact result

$$\sigma(\xi_\parallel)^2 = \xi_\perp^2 = \frac{k_B T}{8\sqrt{(E_0 + \bar{E}_0)\kappa}}$$

given by equation (2.9) where E_0 is replaced by $E_0 + \bar{E}_0$. Thus, the self-consistent approximation is consistent with the analytically known result for an interface fluctuating in a parabolic potential.

4.3. A membrane between hard walls

Let us consider an interface fluctuating between two hard walls of separation $2D$. The asymptotic behaviour of the steric repulsion is given by the effective interaction potential (1.6) with the dimensionless prefactor c_H describing the strength of the fluctuation-induced interaction between two membranes. Computer simulations indicate a value $c_H \approx 0.08$ [46–48] although heuristic arguments yield a much larger value, $c_H \approx 0.231$ [15]. However, to determine the fluctuation-induced free energy of an interface in an arbitrary substrate potential as a function of the surface tension γ remained a non-trivial task—in particular, for van der Waals forces (see equation (5.1) below) and large values of D and σ [50, 51]. The central quantity $\mu = (\sigma/D)^2$ is always assumed to be constant, with estimated values of $\mu = 1/6$, 0.183, or 1/4 according to heuristic arguments, Monte Carlo simulations, or self-consistent numerical calculations [47, 52], respectively. But when a fluid interface is strongly bound close to a substrate where the steric hindrance becomes dominant, the value of μ depends on the details of the interaction potentials $U(z)$.

The self-consistent theory separates the short-wavelength fluctuations governed by bending rigidity from long-wavelength fluctuations determined by the hard-wall potential. In particular, for vanishing surface tension $\gamma = 0$ and in the limit $E_0 \to 0$, the implicit equation (3.10) reduces to

$$\sigma^2 = \frac{1}{Z} \int_{-\infty}^{\infty} dz\, z^2 \exp\left(-\frac{16\kappa}{(k_B T)^2} U(z)\sigma^2 - \frac{3z^2}{8\sigma^2}\right) \tag{4.2}$$

with $\sigma_f^2 = 1.243\sigma^2 \approx \frac{4}{3}\sigma^2$ and the partition sum Z defined below equation (3.10). Equation (4.2) determines the mean squared width for an arbitrary wall potential $U(z)$. Assuming two parallel hard walls at separation $2D$, the self-consistent equation (3.10) for the total mean squared width reads

$$\sigma^2 = \sigma_f^2 \left(1 - \frac{D}{\sigma_f}\sqrt{\frac{2}{\pi}}\frac{e^{-D^2/(2\sigma_f^2)}}{\Phi(D/(\sqrt{2}\sigma_f))}\right) \tag{4.3}$$

with the error function

$$\Phi(x) := \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \tag{4.4}$$

and σ_f depending on surface tension γ and E_0 as given by equations (2.9), (2.11), (3.9), and (3.12). The solution $\sigma^2 = \mu(\gamma, E_0)D^2$ of the implicit equation (4.3) is identical to the assumed *ansatz* in equation (3.1) but with a parameter-dependent coefficient $c_H(\gamma, E_0)$. For vanishing surface tension $\gamma = 0$ and in the limit $E_0 \to 0$, one obtains the value $\mu = 0.186$ and therefore $c_H = 1/(64\mu) \approx 0.084$ in excellent agreement with Monte Carlo simulations [48].

In figure 3 the coefficient $c_H(\gamma, E_0)$ as well as $\mu_f(\gamma, E_0) = \sigma_f^2(\gamma, E_0)/D^2$ are shown as functions of surface tension γ for two different gravitational terms E_0. Note that for non-vanishing E_0 the value of c_H is increasing with surface tension γ which might be relevant for interpretations of experimental data. Of course, these results are only relevant for small values of the surface tension $\gamma D^2/k_B T < 1$ and $E_0\kappa/\gamma^2 < 1$ where the surface-tension-dominated fluctuations can be considered as perturbations. Since the self-consistent theory introduces a length scale $L_\parallel$ for the smallest possible wave vector $q_\parallel = 2\pi/L_\parallel$, fluctuations at larger scales are suppressed, so $E_0^{(steric)}$ does not vanish for large distances $D^2\gamma/k_B T \gg 1$.

Calculating self-consistently the total width σ within a Gaussian approximation in both Fourier and real space, one finds that the value μ depends on interface parameters such as surface tension γ and the in-plane correlation length $\xi_\parallel$ of the interface as well as on the details of the external potential $U(z)$. For a membrane between two hard walls, one obtains the value $\mu \sim 0.186$ for rigid membranes ($\xi_\parallel$ larger than the microscopic length scale) in very good agreement with Monte Carlo simulations [48]. A more precise prediction of μ and c_H seems to be necessary, since recent experiments indicate that the actual values of D and σ became sensitive to details of the inter-bilayer interactions $U(z)$ [19, 20]. Thus, extracting values of κ from measurements of D and σ is sensitive to approximations and model assumptions regarding μ and c_H, so only a reliable theory allows for comparison with recent independent measurements of κ for vesicles [56, 57], for instance.

5. The asymmetric potential: adsorption isotherm D

The self-consistent determination of thickness D and fluctuation width σ may help one to derive a more accurate adsorption isotherm than the FHH isotherm, equation (1.5). Let us assume that $\sigma^2 = \mu D^2$ is valid, i.e., that the equilibrium width σ which solves the second

self-consistent equation (3.10) depends linearly on the mean distance D of the interface from a hard wall. Let us further assume that the interaction potential is given by van der Waals forces:

$$U(D) = \frac{\Delta\mu D}{r_0^3} + \frac{1}{2}\frac{A}{D^2}k_B T \qquad (5.1)$$

where $\Delta\mu = -k_B T \log(p/p_s)$ is the difference of the chemical potentials of the vapour and liquid phase, respectively, at pressure p below the saturation pressure p_s. If fluctuations in the thickness of the film D are not relevant, one can minimize the energy given by equation (5.1) in order to find the most probable thickness $D_{FHH} = (A/\Delta\mu)^{1/3}$ as a mean thickness in accordance with the Frenkel–Halsey–Hill adsorption isotherm given in equation (1.5) and in perfect agreement with certain experimental data [32]. But many experimental data for thin-film adsorption showed significant discrepancies with the FHH isotherm (see [24–27] and figure 4). In contrast, the data can be very well represented as an adsorption isotherm, which is obtained from a refined statistical model taking into account thermal fluctuations in film thickness [13].
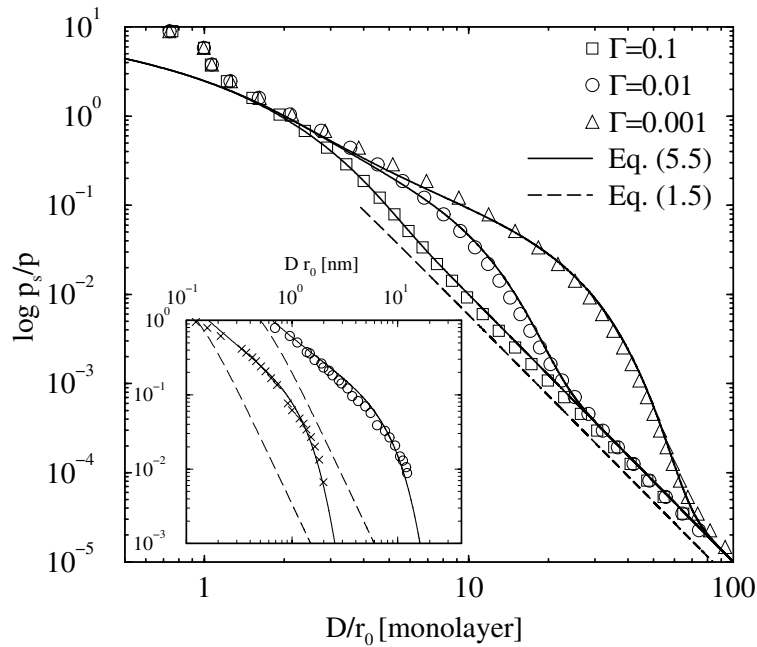

Figure 4. Comparison of the effective adsorption isotherm 5.5 (solid line) with isotherms obtained by the solid-on-solid (SOS) model (symbols) at the same parameters for Hamaker constant $A = 10$ and surface tensions $\Gamma = 4\pi\mu\gamma/k_B T$. The agreement is very good, except of the monolayer adsorption which cannot be captured by an effective isotherm such as equation (5.5) based on a continuous description of the fluid layer. Comparison with experimental data is shown in the inset, namely for hexane (circles, reference [26]) with $A = 1$, $\Gamma = 0.005$, $r_0 = 0.6$ nm and water (crosses, reference [25]) with $A = 1$, $\Gamma = 0.015$, $r_0 = 0.15$ nm, respectively. The thicknesses D of liquid layers are considerably larger due to thermal fluctuations than one would expect for the FHH isotherm (dashed line).

5.1. Comparison with the SOS model

The statistical approach is based on the SOS model which has extensively been applied to multilayer-stepped adsorption isotherms [58]. The substrate consists of a square lattice of

N adsorption sites $i = 1, \ldots, N$ and thickness $d_i = r_0 n_i$ of the adsorbed film at the site i, allowing $n_i \geqslant 0$ to be any non-negative integer where the monolayer thickness is chosen to be the molecular diameter r_0. The restriction of gas molecules to certain lattice sites is well proven for a monolayer and seems to be justified for films only a few layers thick. The vapour is considered to be a homogeneous reservoir of molecules with chemical potential $\Delta \mu = k_B T \log(p_s/p)$ and the adsorbed molecules are assumed to pile up at each site in columns, without forming overhangs or vapour bubbles, which is reasonable for thin films and temperatures well below the critical point. The statistics of the film thickness is then given by the partition sum

$$Z = \sum_{\{n_i\}} \exp[-\beta \mathcal{H}(\{d_i\})]$$

where the sum runs over all configurations, i.e. integers n_i ($i = 1, \ldots, N$), for the film. The Hamiltonian reads then [13]

$$\mathcal{H}(\{n_i\}) = \sum_i^N \left(n_i k_B T \log \frac{p_s}{p} + \frac{1}{2} \frac{A}{n_i^2} k_B T \right) + \Gamma \sum_{\langle ij \rangle} (n_i - n_j)^2 \tag{5.2}$$

where sum runs over nearest-neighbour sites $\langle ij \rangle$ only. The parameter Γ takes into account the molecular interactions within the film and corresponds to an effective surface tension of the film–vapour interface.

Assuming that fluctuations in the film thickness are not relevant, one may minimize the energy (5.2) yielding the most probable thickness D_{FHH} given by the FHH isotherm, equation (1.5). But the film–vapour interface is always undulating due to thermal fluctuations which become important for thin films where fluctuations are hindered by the substrate. Thus, in order to perform the partition sum, one can apply a mean-field approximation, replacing d_j in equation (5.2) with its mean value D. One obtains a self-consistent equation for the mean thickness, which can be solved by standard numerical procedures and can be applied straightforwardly to the experimental data (see figure 4 and reference [13]). The solution is the adsorption isotherm $D(\Delta \mu; A, r_0, \gamma)$ depending on the Hamaker constant A, the monolayer thickness r_0, and the surface tension γ. Of course, $\gamma(D)$ depends itself on the mean film thickness and may be determined experimentally when the vapour pressure p and thickness D are measured.

This SOS model reproduces the results of the Brunauer–Emmett–Teller and the Frenkel–Halsey–Hill models in the monolayer and thick-film regimes, respectively, but for intermediate coverage a qualitatively different behaviour occurs which is governed by thermal fluctuations of the film thickness and therefore determined by the surface tension Γ. As one can see in figure 4 it is found that the substrate-induced hindrance of such fluctuations significantly increases the mean thickness D compared to the most probable thickness D_{FHH} given by the FHH isotherm, equation (1.5). For convenience, one may wish to have an explicit adsorption isotherm which is as simple as the expression (1.5) but does capture the influence of thermal fluctuations. To this end, the self-consistent equation (3.13) is approximated for large distances D in the following section.

5.2. The effective adsorption isotherm

The partition sum

$$Z = \sum_{n=0}^{\infty} e^{-\beta \Delta \mu n} = (1 - e^{-\beta \Delta \mu})^{-1}$$

for adsorbed molecules without any interactions yields the mean thickness $D^{-1} = e^{\beta \Delta\mu} - 1$ with $\Delta\mu = -k_B T \log(p/p_s)$, i.e., the so-called BET isotherm. The same result can be obtained in a continuous-film approximation by replacing the sum in the partition sum Z by an integral

$$Z = \int_0^\infty e^{-Bx} \, dx = B^{-1}$$

if the chemical potential $\Delta\mu$ is replaced by

$$B = e^{\beta \Delta\mu} - 1. \tag{5.3}$$

Thus the term $e^{\beta \Delta\mu} - 1$ is due to the discreteness of the sum over adsorption layers and cannot be recovered by any continuous-film approximation such as those used in the previous sections 2–4. Since we are not interested in the first-layer thickness which is determined mainly by a local contact potential, we nevertheless use the continuous approximation and replace $\beta \Delta\mu$ by B in the Hamiltonian given by equation (5.1).

The reason for the observation of the FHH isotherm governed by the van der Waals potential (5.1) for large film thickness (see figure 4) instead of the BET isotherm is the suppression of fluctuations of the thickness by surface energies. Let us assume that $\sigma^2 = \mu D^2$ as was found in section 4 for small surface tensions $\gamma D^2/k_B T \ll 1$ at small distances D from a hard wall. Expanding the van der Waals potential (5.1) at the mean distance D of the vapour–liquid interface,

$$\frac{A}{z^2} = \frac{A}{D^2} - 2\frac{A}{D^3}(z - D) + 3\frac{A}{D^4}(z - D)^2 + \mathcal{O}((z - D)^3)$$

the self-consistent equation (3.13) reduces to

$$\bar{B}\sqrt{2\pi\sigma_f^2} \, e^{-\bar{B}D + \bar{B}^2\sigma_f^2/2} \frac{1 - \Phi(\bar{B}\sigma_f/\sqrt{2}) - D/(\sqrt{2}\sigma_f))}{2} = e^{-D^2/(2\sigma_f^2)} \tag{5.4}$$

with the error function $\Phi(x)$—see equation (4.4)—$\bar{B} = (B/r_0^3 - A/D^3)L_\parallel^2$, $\sigma_f^2 = \mu_f D^2$, and $L_\parallel^2 = r_0^2 e^{-4\pi\gamma\mu D^2/k_B T}$. Here, the molecular diameter r_0 is set as a lower cut-off for the parallel correlation length, but otherwise expression (2.11) is used. Since the width σ_f is determined self-consistently, one has to neglect the quadratic term in the expansion of A/z^2. The parameter $\bar{B}$ denotes the deviation from the FHH isotherm due to fluctuations, so one may expand in $\bar{B}$ for large distances $D\sqrt{\gamma/k_B T}$ yielding

$$(e^{\beta \Delta\mu} - 1)D/r_0 = \frac{Ar_0^2}{D^2} + c_\gamma \exp\left(-\frac{4\pi\gamma}{k_B T}\mu D^2\right) \tag{5.5}$$

in the lowest order of the deviation $e^{-\gamma D^2}$ from the FHH isotherm. Of course, in the limit of large surface tension $\gamma D^2 \gg 1$ at large distances, one recovers the FHH isotherm given by equation (1.5). The parameter c_γ depends on the details of the approach, i.e., on the values of c_ξ and μ_f, for instance. Note that with $c_\gamma = k_B T \gamma r_0^2/(2c_\xi^2\kappa)$ our final result, the self-consistently determined effective adsorption isotherm equation (5.5) is equal to the derivative

$$\frac{\partial}{\partial z}(U(z) + U_s(z)) = 0$$

as one would expect for an effective potential theory where the steric repulsion potential $U_s(z)$ is given by equation (3.2). However, equation (3.13) is more general and can be used for cases where a linear addition of an effective repulsion potential $U_s(z)$ is not valid any longer. In figure 4 the effective adsorption isotherm (5.5) is compared with the mean-field approximation of the SOS model as described in the previous section and in reference [13]. One finds without

any fit parameters a very good agreement over the whole range of distances D and chemical potentials $\Delta\mu$. Of course, the behaviour of the monolayer adsorption cannot be modelled by an adsorption isotherm which is based on a continuous description of the fluid layer. If the coverage is low (monolayer regime) or high (asymptotic scaling regime), the surface tension has no influence on the isotherm, whereas at intermediate thickness, there is a strong dependence of the layer thickness D on the value of γ. Experimental data showing significant discrepancies with Lifshitz theory, i.e., the FHH isotherm (1.5) [25, 26], can be re-analysed by using the adsorption isotherm (5.5). Figure 4 (inset) shows that these data are at least consistent with Lifshitz theory if thermal fluctuations are taken into account which effectively increase the thickness of the fluid film. Since only the monolayer thickness r_0 was known, the value $A = 1$ is chosen for both data sets. But one has to emphasize that any other value for A only yields a shift of the dashed line, which can never fit the bent data curves—in particular, the slope of apparently less than -3 of the measured adsorption isotherm. This is only possible by taking thermal fluctuations into account, i.e., finite values for the surface tension γ in equation (5.5).

6. Conclusions

In a recent density functional theory a surprising lowering of the surface energy of any liquid interface was found if one took into account the long-range nature of the dispersion forces always existing between molecules (see equation (1.4) and figure 2). The reduction of the energy cost of increasing the interfacial surface area leads to an anomalously large increase of thermal fluctuations at short length scales which could be measured by grazing-incidence x-ray scattering experiments. These findings make it mandatory to re-examine thermal fluctuations of fluid interfaces close to substrates—for instance, of thin liquid films or membranes near a wall. Applying a self-consistent theory which separates the short-wavelength fluctuations governed by bending rigidity from long-wavelength fluctuations determined by the substrate potential, one can derive the fluctuation-induced free energy, i.e., the steric repulsion potential $U_s(z)$ of a membrane as a function of surface tension γ, bending rigidity κ, and substrate potential $U(z)$, respectively. The total mean squared width $\sigma^2 = \mu D^2$ with $\mu = 0.19$ for hard walls is in good agreement with Monte Carlo simulations (see equation (4.2) and figure 3). Also, it is possible to derive an effective adsorption isotherm which includes the steric hindrance of thermal fluctuations yielding much better agreement with experimental data than comparisons with the FHH isotherm based on Lifshitz theory (see equation (5.5) compared with equation (1.5) and figure 4). Further refinements of density functional theory and self-consistent theory for fluctuations of fluid interfaces interacting with hard walls are necessary in order to study in detail the thermodynamical and structural properties of membranes, liquid drops, and thin films on substrates.

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