Structures in fluids induced by interfaces

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Abstract. There are five mechanisms which can lead to mesoscopic interfacial structures: large interfacial fluctuations, the appearance of new length scales, the divergence of the bulk correlation length, long-range forces and the presence of massless Goldstone modes. The importance of the first four mechanisms for roughening, wetting, critical adsorption, and the orientational order in dipolar fluids, respectively, is discussed.

1. Introduction

If two phases of condensed matter are brought into spatial contact, an interfacial structure emerges which interpolates smoothly between the bulk properties of the two adjacent phases. In thermal equilibrium the thickness of such an interface is typically of the order of the bulk correlation lengths of the two bulk materials. This implies that over a wide range of pressure and temperature the length scale for the spatial variation of interfacial structures normal to their mean position is set by the sizes of the particles forming the two phases. For simple fluids these are a few ångstroms whereas in complex fluids such as colloidal suspensions or solutions of macromolecules they can reach several thousand ångstroms.

In spite of the low dimensionality of these interfacial sheets and their negligible contribution towards the global overall properties of the physical systems their presence is essential for a wealth of important processes in physics, chemistry, and biology. Therefore it is particularly interesting that either by tuning external thermodynamic variables such as temperature and chemical potentials or by tailoring the interaction potentials between the particles one can drastically increase the thicknesses of interfacial structures. Among the driving mechanisms for such a broadening are pronounced lateral fluctuations of the local interface positions, the appearance of length scales beyond the correlation lengths, the divergence of the bulk correlation lengths close to critical points, gapless excitations of Goldstone modes, and particularly long-range interaction potentials. In fluid systems these mechanisms are associated with capillary waves, wetting, critical adsorption, superfluidity, and dipolar interactions, respectively. The study of these phenomena is particularly stimulating because they play an important role in both technological applications and basic research where one can analyse the impact of broken translational invariance and the variation of structural properties between two and three spatial dimensions.

2. Capillary waves and roughening

If two phases are brought into contact under the condition of full thermodynamic equilibrium and connected to large reservoirs, there is no cost in free energy to shift rigidly the interface

position between the two phases so that the volume of one phase grows at the expense of the other. In practice this instability is offset by the discreteness of the lattice in the case of a solid–liquid interface or by gravity in the case of a fluid–fluid interface. Nonetheless its remnants are present in the form of pronounced lateral fluctuations of the interface position, which are known as capillary waves for fluid interfaces and lead to their broadening in particular under effective microgravity. Fluid interfaces turn rough for all temperatures above freezing in the limit of vanishing gravity. The rough state of an interface is characterized by the unlimited increase of the height–height correlation function of the local interface position $f(\mathbf{R})$, $\mathbf{R} \in \mathbb{R}^2$, with respect to a reference plane $z = 0$ and the corresponding unlimited broadening of the interface thickness (see, e.g. [1]). These results follow even within a Gaussian approximation by considering the correlation functions $G(\mathbf{R} - \mathbf{R}') = \langle f(\mathbf{R}) f(\mathbf{R}') \rangle$ and $G(0) = \langle f^2(\mathbf{R}) \rangle$ for a statistical weight $\exp(-\beta \mathcal{H}[f])$ with an effective interface Hamiltonian

$$\mathcal{H}[f] = \sigma_0 \int_{\mathbb{R}^2} d^2 R [\sqrt{1 + (\nabla f(\mathbf{R}))^2} - 1] = \frac{\sigma_0}{2} \int_{\mathbb{R}^2} d^2 (\nabla f(\mathbf{R}))^2 + \mathcal{O}(f^4) \qquad (2.1)$$

which measures the cost in free energy of increasing the area of the interface against the action of the surface tension σ_0 compared with a flat configuration; laterally the interface configurations are assumed to be asymptotically flat. The above picture can be refined by including curvature contributions which take into account, *inter alia*, that excursions of the interface into the vapour phase or into the liquid phase will in general be associated with different costs in free energy:

$$\mathcal{H}[f] = \int_{\mathbb{R}^2} d^2 R \, h_0(\mathbf{R}, [f]) \qquad (2.2)$$

with

$$h_0(\mathbf{R}, [f]) = \sigma_0(\sqrt{1 + (\nabla f(\mathbf{R}))^2} - 1) + \sqrt{1 + (\nabla f(\mathbf{R}))^2}\{c_H H + c_K K + c_{H^2} H^2 + \cdots\}$$
$$+ \tfrac{1}{2}(\rho_l - \rho_g) mg f^2(\mathbf{R}) \qquad (2.3)$$

where H and K denote the local mean and Gaussian curvature of the interface configuration, respectively. The mean interface position is $z = 0$, ρ_l and ρ_g are the number densities of the liquid and vapour bulk phases, m is the particle mass, and g is the gravitational constant. In the context of fluid membranes this phenomenological *ansatz* is known as the Helfrich Hamiltonian [2] with phenomenological constants c_H, c_K, and c_{H^2}. Equations (2.2) and (2.3) lead to the following form of the Fourier transform of the structure factor:

$$G(p) = \int_{\mathbb{R}^2} d^2 R \, e^{-i p \cdot (\mathbf{R} - \mathbf{R}')} \langle f(\mathbf{R}) f(\mathbf{R}') \rangle = \frac{k_B T / \sigma_0}{l_c^{-2} + [\sigma(p)/\sigma_0] p^2} \qquad (2.4)$$

where $l_c = (\sigma_0/(mg \, \Delta\rho))^{\frac{1}{2}}$, $\Delta\rho = \rho_l - \rho_g$, denotes the capillary length and $\sigma(p)$ is the momentum dependent surface tension which fulfills the requirement $\sigma(p \to 0) = \sigma_0$ and which in general is temperature dependent. $\sigma(p)$ contains a Gaussian contribution,

$$\sigma_G(p)/\sigma_0 = 1 + \frac{1}{2} \frac{c_{H^2}}{\sigma_0} p^2 + \mathcal{O}(p^4) \qquad (2.5)$$

and a non-Gaussian contribution $\sigma_{nG}(p)$ due to terms $\mathcal{O}(f^4)$ in equation (2.3) whose influence can be estimated, e.g., by mode coupling approximations [3]. Based on the *local* Hamiltonian in (2.2) and (2.3) $\sigma(p)/\sigma_0 - 1 = (\sigma_G(p) + \sigma_{nG}(p))/\sigma_0 - 1$ *increases* with p [3]. The square of the thickness of the interface is proportional to

$$G(R = 0) = (2\pi)^{-2} \int d^2 p \, G(p) = \frac{k_B T}{4\pi^2 \sigma_0} \int d^2 p \, \frac{1}{l_c^{-2} + [\sigma(p)/\sigma_0] p^2}. \qquad (2.6)$$

For physical reasons this momentum integration has an upper cutoff provided by the inverse of the thickness of the intrinsic density profile, which would be present in the absence of capillary waves: the interface model itself may become questionable for capillary wavelengths shorter than the thickness of the intrinsic profile. The presence of this momentum cutoff has the unpleasant feature that the physically observable quantity $G(R = 0)$ depends on this parameter, whose quantitative value is, however, not determined by the theory itself. For the interpretation of actual experimental data from fluid interfaces this latter conceptual problem was sidestepped by observing that, within the local model ((2.2) and (2.3)), the denominator of the integrand in (2.6) increases rapidly enough with p so that the momentum cutoff can be shifted to infinity without generating a divergence.

The density functional theory of inhomogeneous fluids offers the opportunity to check the above standard phenomenological line of argument on an atomic scale. Within a simple version of density functional theory this approach has yielded the following results [4]:

(i) Assuming a steplike density drop across the intrinsic density profile the local phenomenological Hamiltonian density h_0 (2.3) is replaced by the following *nonlocal* expression:

$$h_0(\boldsymbol{R}, [f]) = -\frac{(\Delta\rho)^2}{2} \int_{\mathbb{R}^2} \mathrm{d}^2 R' \int_0^\infty \mathrm{d}z \int_0^{f(\boldsymbol{R}')-f(\boldsymbol{R})} \mathrm{d}z'\, c(|\boldsymbol{r} - \boldsymbol{r}'|). \tag{2.7}$$

$c(r)$ denotes the bulk direct correlation function of a one-component fluid composed of spherically symmetric particles which interact according to a pair potential $w(r)$; $\boldsymbol{r} = (\boldsymbol{R}, z)$. For large distances one has $c(r \to \infty) = w(r) < 0$.

(ii) Imposing a gradient expansion onto (2.7) one recovers the structure of the Helfrich Hamiltonian (2.3) with the following microscopic expressions for the coefficients σ_0 and c_{H^2}:

$$\sigma_0 = -\frac{\pi}{2}(\Delta\rho)^2 \int_0^\infty \mathrm{d}r\, r^3 c(r) > 0 \tag{2.8}$$

$$c_{H^2} = \frac{\pi}{16}(\Delta\rho)^2 \int_0^\infty \mathrm{d}r\, r^5 c(r) < 0. \tag{2.9}$$

(Since the sharp-kink intrinsic density profile happens to be antisymmetric one has $c_H = 0$ and c_K remains undetermined, which is consistent with the fact that for asymptotically flat interfaces $\int_{\mathbb{R}^2} \mathrm{d}^2 R\, (1 + (\boldsymbol{\nabla} f(\boldsymbol{R}))^2)^{1/2} K = 0$.)

(iii) For actual fluids with dispersion forces one has $c(r \to \infty) \sim r^{-6}$ so c_{H^2} is infinite. Thus dispersion forces lead to a breakdown of the gradient expansion for the effective interface Hamiltonian.

(iv) If one models the long-range attractive part of the pair potential by $w_{lr}(r) = A/(r^2 + a^2)^3$, the Gaussian approximation for (2.7) yields

$$\sigma_G(p \to 0)/\sigma_0 = 1 - \left(\frac{ap}{2}\right)^2 \left[-\ln(ap) + \ln 2 + \frac{3}{4} - c_E \right] + \mathcal{O}(p^4 \ln p). \tag{2.10}$$

This demonstrates that the *nonlocality* of the effective interface Hamiltonian leads to a singularity of the momentum dependent surface tension. This singularity does not affect the *leading* behaviour $\sigma_G(p \to 0) = \sigma_0$ and thus does not alter the familiar predictions of the classical theory of capillarity, based on (2.1), on a macroscopic scale. However, the first correction to this theory is changed qualitatively. Moreover (2.10) shows that $\sigma_G(p)$ *decreases* for increasing values of p. If this behaviour would held in general, it would invalidate the reasoning put forward after (2.6) according to which $G(R = 0)$ is effectively independent of the momentum cutoff. This would raise serious conceptual challenges.

(v) It is intriguing to ask under what conditions the Helfrich Hamiltonian is an acceptable approximation for the actual nonlocal effective interface Hamiltonian. It turns out that if the pair potential decays as a power law r^{-n} with $n > 6$, e.g. due to retardation effects, c_{H^2} will remain finite (albeit very large) but higher-order terms such as H^4 will have an infinite prefactor. If the pair potential decays exponentially or as a Gaussian, all individual expansion coefficients remain finite, but the sum of the expansion series diverges. The necessary requirement for this series to converge is that the pair potential $w(r)$ has a strictly finite support.

(vi) The structure factor $G(p)$ (2.4) can be probed experimentally using diffuse scattering of x-rays or neutrons from fluid interfaces at grazing incidence as function of the lateral momentum transfer [5]. Whereas the *leading asymptotic* form $(G(p \to 0))^{-1} \sim l_c^{-2} + p^2$ has been already confirmed experimentally [5], the test of the subtle singular behaviour of the *next-to-leading asymptotic* behaviour $(G(p \to 0))^{-1} \sim l_c^{-2} + p^2 - (pa/2)^4 |\ln(ap)|$ with its negative sign has still to be carried out. Such experiments are very important for the conceptually correct understanding of the structure of fluid interfaces.

(vii) For a proper theoretical interpretation of such experiments, which focus on correction terms, one first needs a detailed theory for the scattering of x-rays and neutrons at grazing incidence. This is available [5]. As for the statistical mechanics of the capillary waves the following improvements beyond the results mentioned above are required: (a) replacement of the sharp-kink intrinsic profile by a realistic smooth one, (b) consideration of the distortion of this intrinsic profile due to curvatures, (c) introduction of normal coordinates, and (d) calculation of the structure factor with a statistical weight which incorporates both the nonlocal and the non-Gaussian character of $h_0(\mathbf{R}, [f])$ [6].

3. Wetting phenomena

In practice gravity reduces the roughening of fluid interfaces between two phases α and γ typically to a mild broadening of the interface thickness except e.g. for mass density matching of two coexisting fluid phases of a suitable binary liquid mixture by tuning its isotopic composition. The broadening of the α–γ interface can, however, be drastically enhanced if a coexisting third phase β becomes thermodynamically stable and can, from a reservoir, intrude into the α–γ interface and wet it. For this wetting transition to occur the bulk free energy of the β phase must become equal (or at least very close) to the bulk free energies of the α and γ phases, which are already equal to each other because they form the α–γ interface. (If α happens to be an inert spectator phase such as a container wall only the balance of the bulk free energies of the γ (e.g. vapour) and β (e.g. liquid) phase matters.) With the bulk free energies (nearly) balanced the structure of the α–γ interface is determined by the interplay between the three surface tensions $\sigma_{\alpha\beta}$, $\sigma_{\beta\gamma}$, and $\sigma_{\alpha\gamma}$. In thermodynamic equilibrium one always has the inequality

$$\sigma_{\alpha\gamma} \leqslant \sigma_{\alpha\beta} + \sigma_{\beta\gamma} \tag{3.1}$$

known as Antonov's rule. If $\sigma_{\alpha\gamma} < \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$ the thickness of the intruding β-like film between the α and γ phase remains finite. Turning this inequality into an equality, $\sigma_{\alpha\gamma} = \sigma_{\alpha\beta} + \sigma_{\beta\gamma}$, causes the α–γ interface to split into two independent surface structures α–β and β–γ which must therefore be macroscopically far apart from each other. This divergence of the thickness l of the β-like wetting film reflects the occurrence of a wetting transition. The wetting transition can be encountered along two distinct thermodynamic paths. (i) If the β and γ phases are off coexistence and l diverges by raising, e.g., the

chemical potential of the species towards β–γ coexistence one finds so-called *complete wetting*. (ii) If the β and γ phases are in equilibrium it may be that l is finite below a so-called wetting transition temperature T_w but infinite for $T \geqslant T_w$. This wetting transition along β–γ coexistence may be continuous (*critical wetting*) or discontinuous (*first-order wetting*). In the latter case this discontinuity is present even off coexistence, forming a so-called *prewetting line*, which joins the β–γ coexistence line at T_w tangentially. Upon crossing this prewetting line along a complete wetting path the thickness l undergoes a first-order thin–thick transition so that this discontinuity diverges on approaching T_w along the prewetting line and vanishes continuously on approaching the critical point of the prewetting line, where it disappears.

The ubiquity of wetting phenomena, their technological importance, and the richness of these interfacial phase transitions have led to a steadily sustained increase of theoretical and experimental investigations, which are documented in several review articles [7–11]. Among the systems and phenomena for which wetting has been observed are one-component fluids at a wall, binary liquid mixtures, liquid metals, quantum fluids, liquid crystals, polymers, microemulsions, surface melting, grain-boundary melting, wetting in pores, interface dynamics of volatile and nonvolatile fluids, order–disorder phenomena in binary alloys, superconductivity, and wetting in disordered systems.

The concept of the effective interface potential $\Omega(l)$ [12] provides an effective and transparent theoretical framework for the description of the diverse phenomena mentioned above. $\Omega(l)$ is the free energy cost per area to maintain a wetting film of a prescribed thickness l. The actual equilibrium thickness l_0 minimizes $\Omega(l)$ and renders $\sigma_{\alpha\gamma} = \Omega(l_0) = \min_l \Omega(l)$. $\Omega(l)$ is composed of the surface tensions $\sigma_{\alpha\beta}$ and $\sigma_{\beta\gamma}$, which survive if the wetting film becomes macroscopically thick, and the interaction contribution $\omega(l)$ which vanishes for $l \to \infty$ and at β–γ coexistence and which describes the interference between the two interfacial structures α–β and β–γ if they only are a finite distance l apart:

$$\Omega(l) = \sigma_{\alpha\beta} + \sigma_{\beta\gamma} + \omega(l). \tag{3.2}$$

In the case of complete wetting $\omega(l)$ contains a linearly increasing term which penalizes the buildup of a phase which is not yet thermodynamically stable in the bulk. The theoretical task consists of computing $\Omega(l)$ from a microscopic Hamiltonian based on appropriate techniques of statistical mechanics and monitoring how the minimum at l_0 moves to infinity as a function of the thermodynamic variables such as the pressure and the temperature and as a functional of the underlying microscopic interaction potentials. Using density functional theory for inhomogeneous fluids this programme has been carried out [9, 13] for simple one-component fluids and binary liquid mixtures [14] and can serve for the quantitative understanding of the recent experimental discoveries of first-order wetting and prewetting [15, 16] and of critical wetting [17] in such systems.

The effective interface potential offers also a helpful tool to decide to what extent the presence of capillary waves on the emerging α–β and β–γ interfaces as discussed in the previous section will affect the wetting transitions and their corresponding thermal singularities. It turns out that the answer to this question depends sensitively on the range of the underlying molecular interaction potentials. If they are dominated by dispersion forces as in basically all fluid systems, $\omega(l \to \infty)$ decays *algebraically* and thus the exponentially small entropic contributions in spatial dimension $d = 3$ from the capillary wave fluctuations are irrelevant for large l. Therefore in $d = 3$ continuous wetting transitions are described correctly by mean-field theory, which ignores the capillary waves [18]. However, for first-order wetting the capillary waves are important even for fluid systems with dispersion forces because in this case the modifications of $\omega(l)$ for small l due to capillary waves do matter

[19]. If there were a system dominated by short-range forces its wetting transitions would display a very rich fluctuation dominated behaviour [9, 11, 20].

Although a thorough discussion of recent developments in the fields mentioned above would be rewarding, it would be beyond the scope of the present article. Instead I shall pick one particular issue and focus on wetting phenomena on laterally structured substrates. This is an area in which technological applications and interesting problems of basic research come particularly close to each other. There is a wide range of possible lateral structures which can be classified as chemical or geometrical as well as combinations thereof. The most obvious structures of that sort are either disordered chemical defects or geometrical grooves which lead to a rough substrate. In these cases one strives for an effective description by averaging appropriately over the lateral disorder. Whereas this issue has already received both experimental [21] and theoretical [22] attention, the number of studies of wetting on highly ordered lateral structures has surged upwards only recently. The following examples highlight this interest.

Janus beads are colloidal particles whose surfaces are treated chemically such that one hemisphere is hydrophobic and the other hydrophilic [23]. This allows their use as artificial surfactants for dissolving oil in water. Whereas traditional molecular surfactants are so densely packed at the oil–water interface that it is impenetrable to ions, these artificial surfactants leave enough space between them even when densely packed that ion transport between the oil- and water-rich phases remains possible. It is interesting to monitor the increase of the local wetting film thickness from a microscopic value to a macroscopic one upon crossing the chemical heterogeneity at the equator. Replacing such a Janus bead by a semi-infinite flat substrate ($z < 0$) which comprises two halves $x > 0$ and $x < 0$, composed of different species, this crossover has been studied in detail as function of the temperature T, and the chemical potential μ of a simple fluid adsorbate, and as functional of the interaction potentials involved [24]. If the latter decay for large distances as $r^{-(3+\sigma)}$, where $\sigma = 3$ corresponds to Lennard-Jones potentials, then the thickness $l_+(\Delta\mu)$ of the wetting film far to the right of the heterogeneity diverges as $(\Delta\mu)^{-1/\sigma}$ for complete wetting ($\Delta\mu \to 0$ above T_w^+) of the corresponding homogeneous substrate; $\Delta\mu = \mu_0 - \mu$ denotes the deviation from gas–liquid coexistence $\mu_0(T)$. For the spatial variation of the local wetting film thickness along the lateral coordinate x one finds a scaling behaviour

$$l(x > 0, \Delta\mu \to 0) = l_+ f(x/\xi_\perp) \tag{3.3}$$

with $\xi_\perp(\Delta\mu \to 0) \sim (l_+)^{(\sigma+1)/2}$, $f(\infty) = 1$, and $f(y \to 0) \sim y^{2/(\sigma+1)}$, so that for $\sigma = 3$ the film thickness diverges as $\sqrt{x}$; the prefactor is also known analytically. (For a detailed analysis of the film morphology along various thermodynamic paths see [24].) *Inter alia*, it turns out that the *local* interface Hamiltonian (2.1) significantly underestimates the width of the lateral transition region of $l(x)$ as compared to the *nonlocal* version, which in turn yields rather good agreement with the predictions of a full density functional approach which avoids an effective interface description. Obviously for both technological and scientific reasons it is promising to extend the study of the adsorption of fluids to the case of more complex chemical surface structures, as they can be provided, e.g., by microcontact printing [25].

Substrates can also be endowed with a rich regular topography. Among the numerous possibilities the thickness of a wetting film exposed to a periodic array of trapezoidal grooves has been studied experimentally by x-ray reflectivity [26]. Although a realistic theoretical description of such a system has not yet emerged, some basic features can be learned from the study of the simpler case of wetting in a single wedge [27]. If the wedge is exposed to the vapour phase of a simple fluid whose chemical potential is raised towards

$\mu_0(T)$ the outer parts of the sides of the wedge are covered by a complete wetting film whose thickness l diverges $\sim (\Delta\mu)^{-1/\sigma}$ provided T is above T_w of the corresponding flat substrate. Towards the centre $x = 0$ of the symmetric wedge the thickness of the wetting film increases, reaching a maximum for $x = 0$. For $l \to \infty$ this maximum value diverges as l^σ and the excess coverage within the wedge as compared with the coverage of two independent semi-infinite substrates meeting each other diverges as $l^{2\sigma}$. Thus the filling of the wedge occurs rather rapidly and is governed by a single diverging length scale $\sim 1/\Delta\mu$. The shape of the meniscus, which is determined by the *line contribution* to the free energy of the system, attains for $|x| \to \infty$ its asymptotic constant distance l from the sides of the wedge according to van der Waals tails $\sim |x|^{-3}$ ($\sigma = 3$) whose amplitudes are known analytically; the local effective interface Hamiltonian (2.1) underestimates these amplitudes as compared to the nonlocal version (2.7). On the basis of macroscopic arguments it has been suggested [28] that for $\Delta\mu \to 0$ the unlimited filling of a wedge with opening angle α occurs not only for $T > T_w$ but also for $T_\alpha < T < T_w$ where T_α is given implicitly by $\Theta(T = T_\alpha) = (\pi - \alpha)/2$ with $\Theta(T)$ as the contact angle of the fluid on the planar substrate. This would imply that the line contribution to the free energy of the wedge exhibits its own thermodynamic singularities, which are independent and distinct from those of the surface and bulk contributions of this system. This interesting feature still awaits explicit confirmation by solution of a microscopic model in statistical physics. Experimentally it would also be challenging to detect the onset of the transition at T_α by analysing the aforementioned x-ray reflectivity data for the periodic array of grooves, for which, however, this transition would be smeared out due to their finite depth.

As the above example shows x-ray and neutron reflectivity measurements offer the opportunity to determine the thickness of wetting films, i. e. *one*-point correlation functions, on an atomic scale. Moreover, the diffuse scattering around the specular beam gives access to the structure factor of such liquid-like films, i.e., to their *two*-point correlation functions $G(\boldsymbol{R} - \boldsymbol{R}', z, z') = \langle \rho(\boldsymbol{r})\rho(\boldsymbol{r}') \rangle - \langle \rho(\boldsymbol{r}) \rangle \langle \rho(\boldsymbol{r}') \rangle$ where $\rho(\boldsymbol{r})$ denotes the fluctuating local number density of the fluid. These experiments probe the Fourier transform of G with respect to $\boldsymbol{R} - \boldsymbol{R}'$ and the Laplace transform with respect to z and z' [5]. In the case of the formation of a liquid-like wetting film G is determined by (i) the perturbation of the liquid bulk structure factor due to the presence of a substrate, (ii) the fluctuations of the depinning of the emerging liquid–vapour interface (see section 2), and (iii) the interference between these two interfaces. Based on a weighted density functional theory progress has been made in understanding (i) for a hard-sphere fluid [29]. This allows one to understand how a wall perturbs the local packing effects in a simple atomic liquid. It also gives access to the local structural properties of a colloidal suspension close to a wall which can be probed by light scattering.

4. Critical phenomena

The phases considered in the previous sections were considered to be thermodynamically far from critical points of gas–liquid coexistence or demixing in the case of binary liquid mixtures so that the correlation length is of the molecular order. However, upon approaching such critical points T_c the correlation length ξ diverges as $\xi_\pm(\tau = |T - T_c|/T_c \to 0) = \xi_0^\pm \tau^{-\nu}$ with a universal exponent $\nu \simeq 0.632$ and nonuniversal amplitudes $\xi_0^\pm$, which depend on whether T_c is approached from below $(-)$ or above $(+)$ and are of the order of 3 Å; the ratio of the true correlation lengths $\xi_0^+/\xi_0^- \simeq 1.73$ is universal. Since a planar wall perturbs an adjacent fluid at least over a distance z on the scale of ξ one can anticipate that for $T \to T_c$ the wall perturbation proliferates into the bulk without limit. A sizeable

body of theoretical and experimental research has explored this local modification of bulk driven critical phenomena [30] and revealed a surprisingly rich and subtle structure. Due to their universality these phenomena have a rather general character and occur both in solids (surface magnetism, order–disorder transitions) and fluids. For the latter the so-called critical adsorption and the Casimir effect play a particularly interesting role.

4.1. Critical adsorption

The container walls of a binary liquid mixture have a preference for one of the two components leading to a concentration profile which decays towards its bulk value on the scale of ξ. Close to the demixing transition into an A-rich and a B-rich liquid phase the concentration difference turns into the order parameter Φ for which one finds the following scaling form:

$$\Phi_\pm(z, \tau) = a\tau^\beta P_\pm(z/\xi_\pm); \tag{4.1}$$

a is the nonuniversal amplitude of the bulk order parameter, $\Phi_-(z = \infty, \tau \to 0^-) = a\tau^\beta$ with $\beta \simeq 0.328$, and $P_\pm(\zeta)$ are universal scaling functions which have been computed by various techniques [31]. For large ζ they decay exponentially whereas for small ζ they diverge:

$$P_\pm(\zeta \to 0) = c_\pm \zeta^{-\beta/\nu} \qquad \beta/\nu \simeq 0.519 \tag{4.2}$$

where $c_\pm$ are universal surface amplitudes with $c_+/c_- = (\xi_0^+/\xi_0^-)^{-\beta/\nu}$. Thus at criticality the order parameter leads to a *mesoscopic* interfacial structure,

$$\Phi(z \to \infty, \tau = 0) = ac_\pm \left(\frac{z}{\xi_0^\pm}\right)^{-\beta/\nu} \tag{4.3}$$

whose zeroth moment $\int_0^\infty dz\, \Phi(z, \tau = 0)$ does not exist. As function of $\tau \to 0$ it diverges,

$$\int_0^\infty dz\, (\Phi(z, \tau) - \Phi(\infty, \tau)) = a\, \xi_0^\pm g_\pm \frac{\tau^{-(\nu-\beta)} - 1}{\nu - \beta} \tag{4.4}$$

with universal surface amplitudes $g_\pm = (\nu - \beta) \int_0^\infty d\zeta\, (P_\pm(\zeta) - P_\pm(\infty))$ [32].

The surface behaviour of a large number of binary liquid mixtures has been studied by ellipsometry and light reflectivity, confirming the above picture [32, 33]. For example, it is encouraging to find satisfactory quantitative agreement between the theoretical values of the universal amplitudes $c_\pm$ in (4.3) and the corresponding experimental values inferred from seven different binary liquid mixtures (see figure 7 in [32]). This strongly supports the theoretical concept of surface universality and provides confidence in the perturbative calculation schemes for universal surface quantities. Experiments using x-ray or neutron reflectivity are expected to yield an even more detailed picture due to their spatial resolution, much higher than that of light [34]. With such techniques one may be able to study quantitatively the conceptually important crossover between universal critical adsorption and nonuniversal complete wetting behaviour along isotherms close to T_c as advanced in figure 8 in [12].

At this stage it is worth pointing out that such critical adsorption phenomena play an important role for more complex fluids such as polymers exposed to nonplanar geometries. For example if colloidal particles or fibres are immersed in a dilute polymer solution one can study interesting adsorption–desorption phase transitions on their surfaces [35]. For an attractive interaction energy between the polymer monomers and these curved particles one finds a threshold for its strength above which a single polymer with one end fixed at a finite

distance from the surfaces will coil around a particle. This means that in the limit of an infinite polymer a *finite* portion of it will adhere to the curved surfaces. Whereas on spheres this phase transition will be observable only on large particles for which the finiteness of the surface area is not yet effective, there is a true phase transition on fibres or rodlike particles. (For a detailed analysis of this transition as well as for additional structural properties such as the profiles of the monomer density or of the end density of the polymer chains see [35].)

4.2. The Casimir effect

In the previous subsection the perturbation of a fluid by a single wall was discussed. If the fluid is confined by an additional parallel wall at a distance l qualitatively new effects appear as soon as ξ becomes comparable to l. If l is still large compared to the size of the fluid particles the free energy of this film of area A decomposes as

$$\frac{F(T,l)}{k_B T_c A} = l f_b(T) + f_{s,1}(T) + f_{s,2}(T) + \delta f(T,l) \tag{4.5}$$

where f_b, $f_{s,1}$, $f_{s,2}$, and δf are the bulk free energy per volume, the surface free energies per area at the two plates, and the finite-size contribution, respectively, in units of $k_B T_c$. Close to T_c all four terms contain singular contributions such that [36]

$$\frac{F_{sing}(T,l)}{k_B T_c A} = \left\{ \frac{-a_b^{\pm}}{\alpha(1-\alpha)(2-\alpha)} y_{\pm}^d - \frac{a_{s,1}^{\pm} + a_{s,2}^{\pm}}{\alpha_s(1-\alpha_s)(2-\alpha_s)} y_{\pm}^{d-1} + \Theta_{\pm}(y_{\pm}) \right\} l^{-(d-1)} \tag{4.6}$$

where $y_{\pm} = l/\xi_{\pm}$, $\alpha = 2 - d\nu$ and $\alpha_s = \alpha + \nu$ are standard bulk and surface critical exponents [30], $a_b^{\pm}$ and $a_s^{\pm}$ are universal bulk and surface amplitudes, and $\Theta_{\pm}(y_{\pm})$ is the universal finite-size scaling function. For large $y_{\pm}$ the scaling functions $\Theta_{\pm}(y_{\pm})$ decay exponentially and their value at $y = 0$ is known as the universal Casimir amplitude $\triangle = \Theta_{\pm}(y = 0)$. Since for large l the actual phase transition in the film occurs at a temperature $T_c(l)/T_c = 1 - \kappa(l/\xi_0^-)^{-1/\nu}$ with a universal amplitude κ so that F_{sing} is analytic at $T_c = T_c(l = \infty)$, one has $\Theta_{\pm}(y_{\pm} \to 0) = \sum_{i \geqslant 0} \triangle_i^{\pm} y_{\pm}^{i/\nu} +$ (the first two terms in the above curly brackets (4.6) with opposite sign) with universal numbers $\triangle_0^{\pm} \equiv \triangle$ and $\triangle_i^{\pm}$. These universal amplitudes as well as the universal scaling functions $\Theta_{\pm}(y_{\pm})$ depend on the universality class of the bulk system and on the surface universality classes [30] of *both* confining boundaries. These quantities have been determined theoretically by various techniques [36]. It turns out that for equal boundary conditions on both sides Θ is negative whereas Θ can be positive if they are different [36]. In the first case the corresponding critical Casimir force $-\partial F_{sing}/\partial l$ is attractive and acts to thin the film whereas it is repulsive in the second case.

In fluid systems close to T_c this critical Casimir force adds to the dispersion forces which are present at all temperatures. For large l the finite-size contribution of the free energy due to the dispersion forces scales as $\delta f_{reg}(T,l) = [W(T)/(k_B T_c)]/l^2$ where $W(T)$ is the Hamaker constant of the film whereas $\delta f_{sing}(T,l) = \Theta_{\pm}(l/\xi_{\pm})/l^2 \xrightarrow{T \to T_c} \triangle/l^2$. Thus at T_c both contributions follow the *same* power law and one obtains an effective Hamaker constant

$$W_{eff}(T_c) = W(T_c) + k_B T_c \triangle \tag{4.7}$$

containing a universal contribution $\triangle$. For $T \neq T_c$ $\delta f_{sing}(T, l \to \infty)$ is exponentially small so that outside the critical region it can be neglected as compared with the dispersion forces. It is worth noting that at T_c, however, the Casimir contribution is ultimately the dominant contribution, because the dispersion forces will become retarded for $l \to \infty$, leading to

$\delta f_{reg}(T, l \to \infty) \sim l^{-3}$, whereas the power law $\sim l^{-2}$ for the critical Casimir contribution remains valid for any l.

There are two experiments with fluids for which this critical Casimir force is accessible. The first is based on measuring the force between two parallel plates filled with a fluid with a force microscope apparatus which enables one to monitor a force anomaly upon crossing T_c. The fluid can be a one-component liquid close to its liquid–vapour critical point, a binary liquid mixture close to its critical or tricritical demixing transition, or ^{4}He or ^{4}He/^{3}He mixtures close to their critical or tricritical transitions to superfluidity. According to (4.7) the critical effect is particularly pronounced if T_c is sufficiently large and $W(T_c)$ sufficiently small. (For a more quantitative discussion see the fourth article of [36].)

A more indirect but elegant method is to monitor the thickness of wetting films under the action of the critical Casimir force. This requires continuous phase transitions in fluids which leave the depinning liquid–vapour interface (as one of the confining walls of the critical film) sharp; the other wall is provided by a substrate. This situation can be found for critical end points in binary liquid mixtures [14], where the line of critical points of demixing hits the first-order liquid–vapour phase transition, or at the critical end point at which the line of continuous transitions to superfluidity in ^{4}He or ^{4}He/^{3}He mixtures hits the gas–liquid coexistence curve at T_λ. In both cases the substrate and the vapour act as inert spectator phases confining a fluid which is at the verge of becoming critical. The equilibrium thickness of the wetting film is determined by the minimum of (3.2) where $\Omega(l)$ is the sum of the regular contribution due to dispersion forces and the singular contribution $F_{sing}(T, l)/A$ (4.6). This implies that along a thermodynamic path within the gas phase and parallel to the gas–liquid coexistence curve the thickness of the wetting film shrinks (expands) upon passing the critical end point if the critical Casimir force is attractive (repulsive). The depth of this minimum relative to the noncritical state yields the universal Casimir amplitude $\triangle$ whereas its shape $l(T)$ around T_c yields the universal scaling functions $\Theta_\pm(l/\xi_\pm)$ (see the fourth article of [36] for a detailed analysis). It should be pointed out that classical fluids and the superfluidity transition in ^{4}He and ^{4}He/^{3}He belong not only to different bulk universality classes (Ising and XY models, respectively) but also to different surface universality classes: classical fluids are exposed to surface fields which are conjugate to their order parameter, whereas in ^{4}He and ^{4}He/^{3}He there are no surface fields acting on the order parameter of the superfluidity transition, so in this case the Casimir effect belongs to the case of Dirichlet boundary conditions at both walls. Such experiments would provide detailed quantitative tests of the present understanding of wetting phenomena, surface critical behaviour, finite-size scaling, and of the relation between them.

5. Dipolar fluids

Correlation functions cannot decay faster than the pair potential $w(r)$ between the particles involved. Thus one can anticipate that long-range forces will lead to significant structural perturbations of fluids induced by interfaces.

Dispersion forces with $w(r \to \infty) \sim r^{-6}$ lead to the so-called van der Waals tails according to which perturbations of the number densities in fluids at interfaces decay toward their bulk values $\sim z^{-3}$. The amplitudes of these van der Waals tails are known analytically [12, 13].

The vast majority of microscopic model calculations for fluids are based on the approximation that the underlying interaction potentials between the particles are spherically symmetric. However, only atomic fluids fulfill this assumption whereas all molecules deviate from this spherical symmetry and introduce orientational degrees of freedom.

Consequently interfacial structures of molecular fluids are characterized not only by density profiles but also by *orientational profiles*. At elevated temperatures, however, the molecules are expected to rotate rapidly so that from a distance they appear as spheres which allows one to describe their properties approximately by effective, temperature dependent spherically symmetric interaction potentials [37], but this simple picture is no longer valid if external fields, spatial inhomogeneities, or high densities hinder this rotation.

I shall focus on bulk and interfacial properties of *dipolar* fluids for which the anisotropy is rather pronounced due to the long range of the dipole–dipole interaction potential. This is motivated, *inter alia*, by the experience that the range of forces plays a crucial role for interfacial properties in general and wetting phenomena in particular [9] and the fact that many fluids used for experiments in this field comprise of molecules with a permanent electric dipole. Consequently one should be prepared for significant differences in their interfacial properties compared with those of simple fluids.

The so-called Stockmayer model serves as a starting point for this kind of theoretical analysis; it assumes spherical particles interacting according to Lennard-Jones interaction potentials and carrying a permanent point dipole of strength μ in their centres. The advantage of this model is that it is also provides an acceptable effective description of ferrofluids which are emulsions of spherelike magnetized colloidal particles dissolved in a solvent comprising much smaller molecules. If these colloidal particles do not carry permanent dipole moments but gain them under the influence of external fields, one is dealing with electrorheological or ferrorheological fluids which are technologically important. The line of attack consists in studying first the bulk properties of these fluids and then turning to their interfacial structures. This task can be accomplished using appropriate versions of density functional theory [37, 38], the results being compared with simulation data [39]. The objectives are to calculate phase diagrams, density distributions, and the orientational order as functions of temperature, chemical potential, and external fields and to monitor the dependence of these quantities on the strength μ of the dipole moment. The Lennard-Jones interaction potential parameters set the scale for the temperature and the density.

5.1. Bulk properties

Beyond quantitative aspects the Stockmayer model allows one to address also an interesting conceptual issue. It is known that a sufficiently anisotropic particle shape leads to the possibility of forming *liquids* with *long-range* orientational order. These liquid crystalline phases are promoted primarily by short-range steric interactions. The study of the Stockmayer model can answer the question of whether in the complete absence of steric interactions, i.e. for spheres, the anisotropy of the dipolar interaction alone is able to support long-range orientational order in a fluid state.

The above question can be answered positively [38]. For sufficiently high densities these dipolar fluids do form a ferromagnetic liquid phase which is separated by a line of critical points from the isotropic liquid. This line of critical points ends both at the liquid-vapour and at the liquid–solid transition with critical end points. In the solid phase this line continues as a line of Curie points. The dipole moment must be sufficiently large to prevent the formation of the ferromagnetic liquid phase being undercut by freezing. For increasing values of the dipole moment the critical end point at the liquid–vapour transition turns into a tricritical point, which detaches from the liquid–vapour coexistence curve and opens a first-order transition region between the isotropic and ferromagnetic liquid. For large dipole moments the critical point of the liquid–vapour transition disappears so one is left with a

single coexistence region between an isotropic and a ferromagnetic fluid (for phase diagrams see [38]). The occurrence of a ferromagnetic liquid phase in the Stockmayer model as well as in related models is supported by simulations [40]. Whereas the quantitative agreement between density functional theory and simulation data is satisfactory for small dipole moments [37] it deteriorates for larger values. This may reflect the increasing difficulty of existing density functional theories in properly capturing the pronounced chain formation in these dipolar fluids for large dipole moments. Nonetheless even in this parameter range the analytic approach provides an important overview of the rich phase behaviour of these systems which is also in line with phenomenological approaches [41].

Density functional theory offers moreover the possibility of investigating the nature of the ferromagnetic liquid phase. If this phase were spatially homogeneous, i.e. with a parallel alignment of the dipoles, the long range of the dipolar forces would lead to a dependence of the bulk free energy and thus of the phase diagram on the shape of the sample. However, dipolar systems have a proper thermodynamic limit, so the bulk free energy is independent of the shape of the sample [42]. This independence is accomplished by forming spatially inhomogeneous orientational distributions which vary on the scale of the sample size and *do* depend on the shape of the sample although the phase diagram *does not*. Thus there is long-range orientational order in the sense that the orientation of a dipole on one side of the sample fixes the orientational order across the sample on the other side. However, this orientational order is no longer a simple parallel alignment but much more complex and critically dependent on the shape of the sample boundaries. This is the most drastic influence surfaces can have, because their presence determines the structural order throughout the sample. In these systems the range of influence of surfaces is equal to the size of the system. (Similar results are known for the phase behaviour of defects in elastic media [43].) Although first achievements in characterizing the spatial arrangement of the orientational order in such dipolar fluids have been made [38, 44], a thorough microscopic analysis is still missing.

5.2. Interfacial properties

In the previous subsection it was reported that the container walls influence the structure of the orientationally ordered phase on the scale of the sample size. For orientationally disordered phases the influence of interfaces is less drastic insofar as its range does not scale with the system size but leads to variations on the scale of the bulk correlation length with a crossover to van der Waals tails $\sim z^{-3}$ governed by an *effective* temperature dependent isotropic pair potential decaying $\sim r^{-6}$ [37].

The local structural properties at interfaces for fluids comprising rigid molecules with a single preferred axis is given by the number density $\hat{\rho}(\boldsymbol{r}, \omega)$ of particles at point $\boldsymbol{r}$ with orientation ω. For laterally isotropic interfaces $\hat{\rho} = \hat{\rho}(z, \vartheta)$ where ϑ is the orientational angle of the molecules relative to the normal coordinate z. This number density can be factorized into the total number density $\rho(z)$ integrated over all orientations and a dimensionless orientational order parameter $\bar{\alpha}(z, \vartheta)$:

$$\hat{\rho}(z, \vartheta) = \rho(z)\frac{1}{2\pi}\bar{\alpha}(z, \vartheta) \qquad \int_0^\pi \mathrm{d}\vartheta \, \sin\vartheta \, \bar{\alpha}(z, \vartheta) = 1. \tag{5.1}$$

Accordingly $\bar{\alpha}(z, \vartheta)$ can be expanded into Legendre polynomials, $\mathcal{P}_l(\cos\vartheta)$,

$$\bar{\alpha}(z, \vartheta) = \sum_{l=0}^{\infty} \alpha_l(z)\mathcal{P}_l(\cos\vartheta) \tag{5.2}$$

so that the coefficient $\alpha_l(z)$ describes the spatial variation of the orientational order at the interface whereas $\rho(z)$ describes the total density variation. Due to the normalization one has $\alpha_0(z) = \frac{1}{2}$. For disordered dipolar fluids $\alpha_l(z) = 0$ for l odd. Considering the interface between disordered phases one has $\alpha_{l \geq 2}(|z| \to \infty) = 0$. For the interface between the isotropic liquid and the isotropic gas the higher-order coefficients $|\alpha_{l \geq 4}(z)|$ are much smaller than $|\alpha_2(z)|$ so that for this interface the orientational order is described primarily by $\alpha_2(z)$ [37]. From density functional calculations $\alpha_2(z)$ is negative on the liquid side of the interface and positive on the vapour side with two extrema [37, 45]. This means that, although there is no net polarization, the dipoles are preferentially oriented in the plane on the liquid side and normal to the interface on the vapour side. The amplitude of this orientational profile depends strongly on the dipole strength μ and vanishes $\sim \mu^4$ for $\mu \to 0$. For $T \to T_c$ this interface structure must disappear and scaling requires also a broadening $\sim \xi$ for $\tau \to 0$. For the total number density one has

$$\rho(z, \tau \to 0) = \rho_c^+ A_\rho \tau^\beta F_\rho(z/\xi_-) \tag{5.3}$$

where ρ_c is the density at criticality, A_ρ the amplitude of the bulk order parameter, and $F_\rho(\zeta)$ a universal scaling function. There is evidence that the orientational profile $\alpha_2(z, \tau)$ also exhibits a scaling behaviour for $\tau \to 0$ although it cannot be expressed in terms of the order parameter of the gas–liquid transition:

$$\alpha_2(z, \tau \to 0) = A_\rho \tau^{\beta + 2\nu} F_\alpha(z/\xi_-); \tag{5.4}$$

$F_\alpha(\zeta)$ is another universal scaling function, which vanishes for $|\zeta| \to \infty$ and has a zero at $\zeta = 0$, a minimum at about $\zeta \simeq -1$, and a maximum at about $\zeta \simeq +1$. It would be interesting to probe these predictions either by optical methods such as second-harmonic generation or by x-ray or neutron scattering techniques with molecules labelled suitably by a sufficient internal charge or isotope contrast so that their orientation becomes indirectly visible.

Density functional theory also allows one to pinpoint the contribution of this anisotropy at the interface to the surface tension. One finds (see the last article in [37]) that the anisotropic contribution is negative but much smaller than the isotropic contribution so the sum remains positive. This is also displayed in the critical behaviour of both quantities which must vanish for $\tau \to 0$. The anisotropic contribution vanishes $\sim \tau^{2(\beta + \nu)}$ whereas the isotropic part vanishes $\sim \tau^{2\nu}$ and thus is also the leading term in the total surface tension. These predictions still await tests by numerical simulations.

Acknowledgments

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