Simulations of Interfacial Phenomena in Soft Condensed Matter and Nanoscience

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Abstract. Computation of interfacial free energies between coexisting phases (e.g. saturated vapor coexisting with liquid) is a fundamental problem of classical statistical mechanics: the standard approach (dating back to van der Waals, Ginzburg-Landau, Cahn-Hilliard · · ·) is based on the continuation of the free energy of homogeneous states throughout the two phase coexistence region. Beyond mean field this continuation does not exist, nor does an “intrinsic profile” of the interface exist! These problems can be overcome by computer simulation: one popular method is based on sampling the order parameter distribution function in the two-phase coexistence region, which yields information on the surface tension of planar interfaces (from “slab configurations”) and of curved interfaces (from states containing “droplets”), elucidating the problem of the “Tolman length”. Another method (suitable also for solid-liquid interfaces) analyzes the capillary wave broadening or the capillary wave spectrum; all these methods require a careful assessment of finite size effects. Related problems occur for excess free energies due to walls, needed to describe wetting phenomena, capillary condensation, heterogenous nucleation, etc. As an example, a thermodynamic integration method (based on “mixing” systems with and without walls) will be described, and an application to understand phase separation in nanoconfinement will be mentioned.

1. Introduction
Interfacial phenomena are familiar from every day life: water droplets may spread on a glass surface, or they may not spread on a lotus leaf [1]. As we shall see, droplet spreading on surfaces reflect the wetting properties [2, 3, 4] of such substrates, and these wetting properties are ruled by the competition of three surface tensions [5]: the wall-vapor surface excess free energy, the wall-liquid surface excess free energy, and the liquid-vapor interfacial excess free energy (=interfacial tension). Very common and known to everybody also are interfacial phenomena in partially miscible more-component fluids (e.g. oil droplets in water, etc.). A less known system, which is nevertheless very popular for scientists because it is so well suited for experimental investigation, are colloid-polymer mixtures [6] (dispersed in a common solvent). Such systems are useful for the study of wetting phenomena, one can see individual colloidal particles in a microscope, and thus study the structure of wetting layers coating the walls of a container on the particle level [7, 8].

While some aspects of interfacial phenomena are understood since decades [5, 9] other aspects are not understood at all and have remained controversial until today [4, 10, 11, 12, 13, 14]. Only on a macroscopic level of description, the situation is clear-cut: the standard problem that
is considered is a saturated gas exposed to a flat planar wall. In the case of “partial wetting” (also called “incomplete wetting”) [1, 2, 3, 4, 5] the macroscopic droplet attached to the wall will not spread out but attain an equilibrium shape, namely (in the absence of gravity) a sphere cap. The liquid-gas interface that delineates the surface of this droplet then meets the wall along the “contact line” under the contact angle \( \theta \), which is given by the Young equation [15].

\[
\psi(3) = \gamma(1) \rho(1) \cos(\theta) .
\]

Of course, \( |\cos(\theta)| \leq 1 \), and hence partial wetting requires \( |\psi(3) - \psi(2)| < \gamma(1) \). When \( \psi(3) - \psi(2) \) tends towards \( \gamma(1) \), \( \cos(\theta) \to 1 \), and we encounter a wetting transition. For \( \psi(3) > \gamma(1) \), the wall is coated by a (macroscopically thick) wetting layer, and therefore the vapor avoids extending up to the wall. For this situation of “complete wetting” (where a droplet is unstable and spreads out into a wetting layer) one simply has [1, 2, 3, 4, 5]

\[
\psi(1) = \psi(2) + \gamma(1) .
\]

The fact that raising the temperature may cause a surface phase transition (i.e., a singularity of the surface excess free energy of the fluid) [16] from a partially wet to a completely wet state (where a droplet is unstable and spreads out into a wetting layer) one simply has [1, 2, 3, 4, 5]

\[
\psi(1) = \psi(2) + \gamma(1) .
\]

In order to deal with interfaces [5, 9] is useful. The first step always is what is a capillary wave and what is a bulk fluctuation [9, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28]. There occur large-scale fluctuations of the local interfacial height, the locally, such that one phase is below this interface and the other phase above it, still is a matter of debate [24, 25, 26, 27, 28]. Consequently, many aspects of wetting transitions are still under exploration today [4, 10, 11, 12, 13, 14].

Another important problem is the fact that viewing interfaces as purely geometrical objects, infinitely thin dividing surfaces between volume regions containing different phases, is a drastic simplification [9, 10, 18, 19, 20, 21, 22, 23]. Such a coarse-grained picture breaks down at the nanoscale, where interfaces may look very rough or diffuse depending on the resolution that is used [21, 24]. The local structure in which particles are arranged across an interface may be very irregular, and it may be rather difficult to identify where the local position of the interface actually is, and to distinguish genuinely interfacial fluctuations from bulk fluctuation in the phases close by the interface. Identifying a criterion that corresponds to the dividing surface locally, such that one phase is below this interface and the other phase above it, still is a matter of debate [24, 25, 26, 27, 28]. There occur large-scale fluctuations of the local interfacial height, the so-called capillary waves [29, 30]; for short wavelengths, however, it is again difficult to ascertain what is a capillary wave and what is a bulk fluctuation [9, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28].

Before these problems are discussed in depth, a reminder of the standard approach in statistical thermodynamics to deal with interfaces [5, 9] is useful. The first step always is the formulation of a mean field theory, and then one discusses how to improve it. For the vapor-liquid transition of a simple fluid this starting point is the van der Waals theory [31]. Near the critical temperature \( T_c \), the van der Waals theory can be reduced to the Landau theory [32], using the concept of an order parameter density \( \psi \), the reduced density difference from the critical density \( \rho_c \),

\[
\psi = (\rho - \rho_c)/(2\rho_c) ,
\]

so that the free energy density \( \Delta f_{\text{Landau}}(\rho, T) \) can be written as

\[
\Delta f_{\text{Landau}}(\rho, T) = \frac{3}{2} k_B T_c \rho_c \left[ \frac{T}{T_c} - 1 \right] \left[ \frac{1}{4} \psi^2 + \frac{1}{4} \psi^4 \right] .
\]

Remember that this function describes the free energy density of a homogeneous system, although one passes the two-phase coexistence region, in between the saturated vapor density \( \rho_c = \rho_c(1 - 2\psi_{\text{coex}}) \) and the liquid density \( \rho_f = \rho_f(1 + 2\psi_{\text{coex}}) \), so \( \rho_c, \rho_f \) correspond to \( \pm \psi_{\text{coex}} \) with \( \psi_{\text{coex}} = \sqrt{T - T_c}/T_c \). Of course, the true free energy density in the regime \( \rho_c < \rho < \rho_f \) is not given by Eq. (4), but rather described by the double-tangent construction: i.e., \( \Delta f_{\text{Landau}}(\rho, T) \) is constant \( \left( = -\frac{3}{8} k_B T_c \rho_c \right) \) throughout the two-phase coexistence regime, and the hump described
by Eq. (4) in between the two minima is a mean field artefact [33, 34]. Similarly, the van der Waals loop for the reduced chemical potential

$$\frac{\Delta \mu}{k_B T} = \frac{\partial \Delta f}{\partial \rho} \propto \phi - \phi^3, \quad \phi = \psi/\psi_{\text{coex}}$$  \hspace{1cm} (5)

is a mean-field artefact as well, and interpreting the extrema ("spinodal points") of this loop as limits of metastability for the supersaturated vapor (or undersaturated liquid, respectively) is a "folklore" interpretation [33, 34, 35] which lacks any justification from statistical mechanics (for systems with short-range forces, as considered here) [36]. The true behavior is given by the Maxwell construction, which represents a description of a state of two-phase equilibrium [32]. The amounts of the two phases contained in these coexisting regions are given by the lever rule, and these regions are separated by an interface (e.g., a droplet surrounded by vapor) [32, 33, 34].

It is the description of this interface on which we now focus. When we continue to rely on Landau theory, we need to account for the cost of order parameter inhomogeneities across the interface. The traditional approach is to amend Eq. (4) by a \((\nabla \psi)^2\) term, to obtain the Landau free energy functional \([37] \Delta F\{\psi(\vec{x})\}\), namely

$$\Delta F\{\psi(\vec{x})\} = \int d^d \vec{x} [\Delta f_{\text{Landau}}(\psi) + (R^2/2d)(\nabla \psi)^2] \hspace{1cm} (6)$$

where \(d\) is the dimensionality of space, and \(R\) the range of interaction between the particles. The task is to find solutions \(\psi(\vec{x})\) that minimize \(\Delta F\{\psi(\vec{x})\}\). Of course, the trivial solution \(\nabla \psi \equiv 0\) yields the homogeneous phases, \(\psi = \pm \psi_{\text{coex}}\). To describe an interface, one looks for a solution \(\psi(z)\) that satisfies \(\psi(z \to \pm \infty) = \pm \psi_{\text{coex}}\) with \(\psi(z = 0) = 0\), such that \(z = 0\) describes the center of the interface. The condition that

$$\delta \Delta F\{\psi(z)\}/\delta \psi(z) = 0$$  \hspace{1cm} (7)

yields the Ginzburg-Landau equation \{recall \(\phi = \psi/\psi_{\text{coex}}\}\)

$$\phi - \phi^3 = 2 \frac{d^2 \phi}{dZ^2}, \quad Z = z/\xi, \hspace{1cm} (8)$$

where \(\xi\) is the correlation length for order parameter fluctuations, given as

$$\xi^2 = R^2/[d(1 - T/T_c)] \hspace{1cm} (9)$$

The solution of Eq. (8) is the well-known tanh-profile for the order parameter variation across the interface,

$$\phi(z) = \tanh(Z/2), \quad \psi(z) = \psi_{\text{coex}} \tanh(z/2\xi) \hspace{1cm} (10)$$

So the (intrinsic) width of the interface, according to this theory, is nothing but twice the correlation length. Using then this solution in \(\Delta F\{\psi(z)\}\), one obtains the interfacial tension from the normalized free energy excess (\(A\) is the interfacial area)

$$F_{\text{int}}/(k_B T A) = \frac{1}{3} \psi_{\text{coex}}^4 \xi \propto (1 - T/T_c)^{3/2} \text{ as } T \to T_c \hspace{1cm} (11)$$

Of course, the critical exponent \(\mu = 3/2\) is a mean field result, different from the correct value predicted by Widom’s scaling law, \(F_{\text{int}}/k_B T A \propto (1 - T/T_c)^\mu\) with \(\mu = (d - 1)\nu\), \(\nu\) being the critical exponent of the correlation length \(\{\xi \propto (1 - T/T_c)^{-\nu}, \text{ with } \nu \approx 0.63 \text{ in } d = 3 \text{ dimensions}\)\).

However, the failure of the Ginzburg-Landau theory of interfaces is more fundamental than just the fact that it predicts a wrong critical exponent: the problem is that the tanh(Z) profile
is a direct mathematical consequence of the double well free energy function, Eq. (4), or the equivalent van der Waals-type loops Eq. (5): neither of these functions are well defined!

It is illuminating to compute both the free energy density \( f(\rho) \) of the fluid (with short-range interactions among the particles) or its derivative \( \mu(\rho) = (\partial f(\rho)/\partial \rho)_T \) by more reliable methods of (classical) statistical mechanics. For a fluid phase where intermolecular interactions are simply modelled by the Lennard-Jones potential, Monte Carlo methods yield numerically exact results (apart from statistical errors, which can be made as small as desired, if enough computer time resources are invested). However, Monte Carlo simulations (as well as Molecular Dynamics simulations) always deal with finite systems, while analytical methods of statistical thermodynamics (as well as classical statistical mechanics) address the thermodynamic limit, the particle number \( N \) is taken to infinity. So the typical geometry of a simulated fluid is a \( L \times L \times L \) box (in \( d = 3 \) spatial dimensions), with periodic boundary conditions.

When one obtains the true free energy density \( f_L(\rho, T) \) and its derivative \( \mu_L(\rho, T) = (\partial f_L(\rho, T)/\partial \rho)_T \) from such a simulation, one does find a double-well potential but the shape of the hump in between the two minima at \( \rho_v \) and \( \rho_t \) is not described by Eq. (4): in particular the height of the maximum scales like \( 1/L \), and as \( L \to \infty \) the whole part of \( f_L(\rho, T) \) for \( \rho_v < \rho < \rho_t \) smoothly converges toward the horizontal straight line provided by the double-tangent construction. Conversely, the parts of \( f_L(\rho, T) \) for \( \rho \leq \rho_v \) and \( \rho \geq \rho_t \) rapidly converge towards size-independent results, as soon as \( L \gg \xi [33, 34] \).

The loop of \( \mu_L(\rho, T) \) as function of \( \rho \) tells the same story: while it resembles the van der Waals loop (Eq. (5)) for \( L \leq \xi \), its shape is very different from Eq. (5) for \( L \gg \xi \); both extrema positions shift with increasing size towards the coexistence curve location \( (\rho_v, \rho_t) \), the height (depth) of the extrema (as well as the whole loop) systematically decrease as \( L \) increases: for \( L \to \infty \), the straight line of the Maxwell construction results automatically [33, 34].

In fact, both \( f_L(\rho, T) \) and \( \mu_L(\rho, T) \) reflect the true equilibrium behavior of the system, one must not interpret the part of the loop where \( \mu_L(\rho, T) \) decreases with increasing \( \rho \) as being due to “unstable states”, as is commonly done in the context of the van der Waals equation: rather this peculiar behavior of \( f_L(\rho, T) \) and \( \mu_L(\rho, T) \) is simply due to interfacial phenomena. As we shall see in the next section, such data do yield direct information on the interfacial tension between the coexisting phases, and there is no need to locate the interface on the particle level for this purpose.

2. Extracting Interfacial Free Energies from the Order Parameter Distribution

We now discuss in more detail the behavior of the loop \( \mu_L(\rho) \) versus \( \rho \) that is observed in a simulation when one crosses the vapor-liquid two-phase coexistence region of a fluid (see figures two, three and four of Ref. [34] for illustrative explicit examples). In the thermodynamic limit (\( L \to \infty \)), two-phase coexistence starts immediately when \( \rho \) exceeds \( \rho_v \); in the finite simulation box, however, the system stays homogeneous up to some density \( \rho_1 > \rho_v \), where \( \mu_L(\rho) \) has a maximum (which becomes singular in the limit \( L \to \infty \), while \( \rho_1(L \to \infty) \to \rho_v \)). The physical significance of this maximum is the “droplet evaporation/condensation transition” [38, 39, 40, 41, 42, 43, 44]. For \( \rho \geq \rho_1 \) the state of the system now is inhomogeneous, for \( \rho_1 < \rho < \rho_2 \) a droplet (with on average spherical shape) coexists with surrounding vapor (which is supersaturated in comparison to the saturated vapor that occurs for \( L \to \infty \) at \( \rho = \rho_v \)). At \( \rho = \rho_2 \) the shape of the droplet changes from spherical to cylindrical (stabilized by the periodic boundary conditions), and this shows up via a (rounded) kink in the \( \mu_L(\rho) \) vs. \( \rho \) curve. Most important in the present context, however, is the region in between \( \rho_3 \) and \( \rho_4 \), in which \( \mu_L(\rho) \) is a constant, independent of \( L \), and this is the chemical potential characteristic for two-phase coexistence in the thermodynamic limit. The rounded kinks in the \( \mu_L(\rho) \) vs. \( \rho \) curve that occur near \( \rho_3 \) and \( \rho_4 \) are due to the transition from a cylindrical droplet (or bubble, for \( \rho > \rho_4 \)) to a “slab configuration”, where the periodic boundary conditions stabilize a liquid-slab, separated
from saturated vapor by two planar interfaces. Note that the area of these interfaces is just $L^2$, and so the total free energy cost associated with these interfaces is (in $d$ dimensions)

$$\Delta F/k_B T = 2L^{(d-1)}\gamma_{\ell v}(L) .$$

Here we have taken into account that the periodic boundary conditions on the length scale $L$ constrain the interfacial fluctuations, and so the interfacial tension associated with these interfaces may deviate from the associated bulk value by some finite size correction. This finite size dependence of the interfacial tension $\gamma_{\ell v}(L)$ in practice is rather weak, and carrying out simulations over a range of values of the linear dimension $L$ and an extrapolation of $\gamma_{\ell v}(L)$ versus $1/L$ allows to estimate $\gamma_{\ell v} \equiv \gamma_{\ell v}(\infty)$.

At this point it is useful to recall how $f_L(\rho, T)$ and $\mu_L(\rho, T)$ are obtained from the simulations in practice. Typically it is most convenient to work in the grand-canonical $\mu VT$ ensemble ($V = L^d$ is the volume of the $d$-dimensional simulation box). Using successive umbrella sampling [45] and histogram reweighting [46] methods the distribution function $P_{\mu VT}(N)$ of the particle number $N$ can be sampled very accurately [45]. Then the free energy $V f_L(\rho, T)$ discussed above is given by

$$V f_L(\rho, T) = F(N, V, T) \equiv -k_B T \ln P_{\mu VT}(N) + \mu N + F_0 ,$$

where $F_0$ is an unimportant constant. The chemical potential function $\mu_L(\rho, T)$ simply is the derivative

$$\mu_L(\rho, T) = \left( \frac{\partial F(N, V, T)}{\partial N} \right)_{T, V}$$

as usual. Phase coexistence (yielding the chemical potential $\mu_{\text{coex}}(\rho, T)$ to which $\rho_c$ and $\rho_t$ belong) simply is obtained from the equal weight rule for $P_{\mu VT}(N)$ [47, 48]. Even simpler is the problem for symmetric binary (A,B) Lennard-Jones mixtures, where one works in the semi-grandcanonical ensemble, carrying out identity switches between the particles ($A \rightarrow B$ or $B \rightarrow A$, respectively) [49, 50, 51], in addition to standard displacement moves of particle coordinates ($\vec{r}_i \rightarrow \vec{r}_i' = \vec{r}_i + \delta \vec{\delta}$, $\vec{\delta}$ being a random small displacement), as usually done in NVT simulations [52]. Then phase coexistence between segregated A-rich and B-rich phases of such a mixture occurs automatically at chemical potential difference $\Delta \mu = 0$ between the particles, due to the symmetry of the model.

In all such systems one observes a flat horizontal region of $f_L$ in the center of the two-phase coexistence region, and $\mu_L$ is constant, equal to the bulk value of the chemical potential at two-phase coexistence. The fact that the plateau of $f_L(T, \rho)$ must be strictly horizontal is due to the fact that a variation of the order parameter in this region just means that the amount of liquid phase in the liquid slab changes, but as long as the two planar interfaces are far enough apart from each other, so they have only a negligible interaction, the free energy density does not change. Since $f_L(\rho, T) = F(N, V, T)/L^d$, one obtains from Eq. (12)

$$\gamma_{\ell v}(L) = L f_L(\rho, T)/2 .$$

This method was first invented for the two-dimensional Ising (lattice gas) model [53] and now is established as a first principles approach that has proven useful for large variety of models of fluids [10, 20, 24, 34, 51, 54, 55]. This method is particularly useful near the critical point, where $\gamma_{\ell v}$ vanishes, and traditional methods advocated in the textbooks [5, 52], such as using the anisotropy of the pressure tensor $p_{\alpha \beta}(z)$ across an interface, are difficult to apply, because the anisotropy then is small, and fluctuations are huge. Defining normal ($p_n(z)$) and tangential components ($p_T(z)$) as
\[ p_n(z) = p_{zz}(z) , \quad p_T(z) = \frac{1}{2} (p_{zz}(z) + p_{yy}(z)) , \]  

(16)

and for a system with periodic boundary conditions, containing a liquid slab with two liquid-vapor interfaces oriented along the \( z \)-axis, one has

\[ \gamma_{\ell v} = \frac{1}{2} \int_0^L dz \left[ p_n(z) - p_T(z) \right] \ . \]  

(17)

Eq. (17) is only preferable to Eq. (15) at low temperatures (e.g. close to the triple point), where the grand-canonical Monte Carlo algorithms become less efficient, or when one uses Molecular Dynamic methods [52, 56].

Eq. (15) was tested for the Ising (lattice gas) model since there the interfacial tension is known exactly from transfer matrix methods in \( d = 2 \) dimensions [57]. The rigorous approach to interfacial free energies for such lattice models considers the ratio of partition functions of two systems, one containing an interface, the other containing no interfaces. In the Ising model, we can enforce the presence of an interface by flipping the sign of the exchange constant between the spins in two adjacent rows (in \( d = 2 \)) or planes (in \( d = 3 \)), respectively, still using periodic boundary conditions; denoting the partition sum of such a system as \( Z_- \), while the partition sum of the system with only ferromagnetic bonds and no interfaces is \( Z_+ \), we obtain (\( A \) is the interfacial area, and the limit \( A \to \infty \) is considered)

\[ \gamma_{\ell v} = \frac{1}{k_B T A} \ln \left( \frac{Z_-}{Z_+} \right) \ . \]  

(18)

Alternatively, one can also use systems with fixed spin boundary conditions, where in one case (\( Z_{++} \)) all boundary spins are fixed as \( S_i = +1 \), while in the other case (\( Z_{+-} \)) only the boundary spins along the left half of the system are \( S_i = +1 \) while the boundary spins along the right half are all \( S_i = -1 \). Then

\[ \gamma_{\ell v} = \frac{1}{k_B T A} \ln \left( \frac{Z_{+-}}{Z_{++}} \right) \]  

(19)

Clearly, the merit of Eq. (15), for \( L \to \infty \), is that it is a generalization of such first principle approaches that can be carried over to phase coexistence in any systems, off-lattice models, and is also not restricted to liquid-vapor type systems, but can also be used for phase coexistence in liquid crystalline systems (interfaces between isotropic and nematic phases [58]), solid-liquid interfaces [59], etc.

3. Interfacial Profiles and Capillary Waves

In the previous section, we have emphasized that one should not rely on the van der Waals-Ginzburg Landau-Cahn Hillard mean field theory to compute interfacial tensions between coexisting phases reliably, avoiding uncontrolled errors. In this section we focus on another aspect of interfacial phenomena, namely interfacial profiles.

For this problem, the failure of mean field theory is much worse: it is very doubtful, whether an “intrinsic” interfacial profile can be observed at all; and if such an intrinsic profile can be defined, it does not have the simple tanh-form of Eq. (10). The problem is to understand precisely the broadening of the profile due to capillary waves [9, 10, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30]. This broadening has first been seen in simulations of various Ising-type lattice models [19, 60] and models for symmetrical binary polymers [20], and particular extensive studies were carried through for colloid-polymer mixtures, both experimentally [7, 8, 61] and by model simulations [24]. These effects can also be seen in model studies of nematic-isotropic
interfaces \[62\] of liquid-crystalline systems, and even for interfaces between the fluid and the crystal at the melting transition \[63, 64, 65, 66, 67, 68, 69\]. Here we shall focus on the work on symmetrical polymer blends \[20\], since there a very complete study was performed, including also an estimation of the interfacial tension with the method based on the order parameter probability distribution, as explained in Sec. 2. Simulations were performed \[20\] for the bond fluctuation model of polymers \[70, 71\], using chain lengths of \(N_A = N_B = N = 32\) monomers, and interactions of square-well type, of strength \(\varepsilon_{AA} = \varepsilon_{BB} = -\varepsilon_{AB} = \varepsilon\) and range \(\sqrt{6}\) lattice spacings. In separate work it had already been found that the model exhibits phase separation into A-rich and B-rich phases when \(\varepsilon\) exceeds a critical value \(\varepsilon_c \approx 0.14\) (a factor \(1/k_BT\) is absorbed in the definition of \(\varepsilon\) here). Most calculations were done in the strongly segregated case \(\varepsilon = 0.3(T/T_c \approx 0.48)\). Choosing a system geometry \(L \times L \times D\) with \(D = 128\) lattice spacings the lateral linear dimension \(L\) was varied from \(L = 16\) to \(L = 256\). The system simulated contained 50% A chains and 50% B chains, with a single interface (in \(z\)-direction a variant of an “antiperiodic” boundary condition was used, i.e. A monomers leaving the box at one side reenter as B-monomers at the opposite side, or vice versa). Recording the interfacial profile, a very pronounced broadening of the profile with increasing lateral linear dimension \(L\) is observed, and it is clear that one suspects that this size-dependent broadening needs to be attributed to the capillary waves. In order to study them systematically, the interfacial configurations of the model system in the course of the simulation need to be carefully analysed. A view of snapshot pictures of the system, where the positions of all monomers of one kind are drawn, reveals the fact already mentioned above, that the interface on the single particle level is very rugged, and that it is difficult to distinguish what is a fluctuation of the local height of the interface, and what is a bulk composition fluctuation \[20\]. So it normally is decided \[20, 24, 25\] to use a block analysis method to coarse-grain the interface. I.e., if the interface normally is the \(z\)-axis, one divides the \(L \times L\) planes normal to the \(z\)-axis into \(n_B^2\) squares of linear dimension \(B \times B\) each, with \(B = L/n_B\). One then considers rectangular columns \(B \times B \times \Delta z\), with \(\Delta z = z_+ - z_-\) and the values \(z_+, z_-\) are chosen such that the interface position \(z_G\) is in between \(z_-\) and \(z_+\) for all blocks. Here \(z_G\) is then defined as a Gibbs dividing surface in each block. In this way a local height variable \(h(x,y) = z_G\) is obtained, but it turns out that the snapshots of those coarse-grained interfacial configurations depend very much on the resolution of the “microscope” with which the interface is viewed: choosing a small block size, \(B = 2\) lattice spacings, so that one is able to see small local details of the interface configuration, the picture is extremely rugged; choosing a larger block size, e.g. \(B = 8\) (a length comparable to the gyration radius \(R_g \approx 7\) of the polymer chains considered in this study), one obtains smoother variations, the picture looks like a hilly landscape with mountain ridges and valleys. Still it is clear, that strong fluctuations of the local height \(h(x,y)\) are present, with many wavelengths \(\lambda\) (with \(\lambda \geq B\), of course; smaller-scale structures by construction cannot be resolved).

The standard assumption now is that such fluctuations of the interfacial height \(h(x,y)\) can be described by the capillary wave Hamiltonian,

\[
\mathcal{H}_{CW} = \frac{1}{2}k_BT\tilde{\gamma} \int_0^L dx \int_0^L dy |\nabla h(x,y)|^2, \tag{20}
\]

where the “interfacial stiffness” \(\tilde{\gamma}\) for a liquid-vapor interface simply can be identified with the interface tension \(\gamma_{lv}\), and for a fluid binary (AB) mixtures \(\tilde{\gamma} = \gamma_{AB}\), the interface tension between coexisting A-rich and B-rich phases.

Due to the periodic boundary conditions in the \(x,y\)-direction parallel to the interface, introduction of Fourier transforms
\[ h(x, y) = \sum_{\vec{q}} h(\vec{q}) \exp[i(q^2 x + q y)] \]  

(21)

diagonalizes the capillary wave Hamiltonian, reducing it to a problem analogous to independent harmonic oscillators,

\[ \mathcal{H}_{CW} = \frac{1}{2} k_B T \tilde{\gamma} \sum_{\vec{q}} q^2 |h(\vec{q})|^2 \].

(22)

For such problems we can immediately invoke the equipartition theorem \[32\]

\[ \frac{k_B T}{2} \langle |\vec{q}|^2 \rangle_T = \frac{1}{2} k_B T \]

(23)

and hence we conclude that the capillary wave spectrum is described by

\[ \langle |h(\vec{q})|^2 \rangle = 1/(\tilde{\gamma} q^2) \].

(24)

Numerical tests of this relation [20, 24] have shown very good agreement with this relation, over all accessible wavelengths \(\lambda = 2\pi/q\) from \(\lambda_{\text{min}} = B\) to \(\lambda_{\text{max}} = L\). Eq. (24) can also be used to predict the mean-square width of this coarse-grained interface, using the convention that \(\langle |h(x, y)|^2 \rangle = 0\),

\[ s_L^2 = \langle |h(x, y)|^2 \rangle = \sum_{\vec{q}} \langle |h(\vec{q})|^2 \rangle = \frac{1}{\tilde{\gamma}} \sum_{\vec{q}} q^{-2} \].

(25)

Converting the sum over discrete values of \(\vec{q}\) to an integral yields

\[ s_L^2 = (2\pi\tilde{\gamma})^{-1} \int_{2\pi/L}^{2\pi/B} dq/q = \ln(L/B)/(2\pi\tilde{\gamma}) \].

(26)

When we wish to compare this result to actual observations of averaged interfacial profiles and their widths, we need to take into account that the above calculation includes only the contribution of the fluctuations in height of the dividing surface, but not a possible “intrinsic width” \(w_0\) (which is attributed to fluctuations on length scales smaller than the cutoff length \(B\)). This intrinsic width \(w_0\) is included in terms of a convolution approximation of the intrinsic profile with the Gaussian distribution, \(P_L(h) = (2\pi s_L^2)^{-1/2} \exp(-h^2/2s_L^2)\), to find [18]

\[ w^2 = w_0^2 - (4\tilde{\gamma})^{-1} \ln B + (4\tilde{\gamma})^{-1} \ln L \].

(27)

This logarithmic variation of \(w^2\) with the lateral linear dimension \(L\) has been verified experimentally and for various models [19, 20, 21, 22, 23, 24, 60]. The prefactor \((4\tilde{\gamma})^{-1}\) of the \(\ln L\) term has also been nicely confirmed [20, 24], for a broad range of temperatures. But we emphasize that there is no possibility whatsoever to distinguish in the term \(w_0^2 - (4\tilde{\gamma})^{-1} \ln B\) what is \(w_0\) and what is the cutoff contribution \(-(4\tilde{\gamma})^{-1} \ln B\): since the choice of the cutoff \(B\) to some extent is arbitrary, more or less of the short wavelength fluctuation spectrum of the interface is attributed to the intrinsic width. Of course, when the cutoff \(B\) is of the order of a few particle diameters, there is no reason to expect that Eq. (20) is still accurate; it has been discussed [24, 73, 74] that Eq. (24) may need a generalization in terms of a wavevector-dependent interfacial stiffness \(\tilde{\gamma}(q)\); but this generalization is still controversial, and it seems to depend on the way in which the fluctuating interface as a “dividing surface” is defined [26, 28]. So while the long wavelength fluctuations of interfaces can be understood quantitatively in terms
of capillary wave excitations very well, their short wavelength fluctuations are still much less well understood.

Particularly useful is this capillary wave method for solid-liquid interfaces, since there the method based on the free energy hump to the slab configuration is difficult to apply. First successful analyses of the capillary wave spectrum were done for liquid-solid interfaces of metallic systems [63, 64, 65, 66, 67, 69] and later work addressed colloidal crystals [67, 68]. Also evidence for the size-dependence of the mean square interfacial width \( w^2 \) could be obtained [67, 68], and it could be shown that meaningful estimates of the interfacial stiffness \( \gamma \) can be extracted [67, 68].

However, for solid-liquid interfaces there clearly enters another problem, namely the interface tension depends on the orientation of the interface normal relative to the axes of the crystal lattice. As a consequence, there is a systematic distinction to be drawn between interfacial tension and interfacial stiffness (see e.g. Privman [75] for a pedagogic account of this problem). This problem is already well-known for lattice models such as the Ising/lattice gas models, where (in \( d = 3 \) dimensions) one can show that \( \gamma \) diverges to infinity when the temperature \( T \) approaches the roughening transition temperature \( T_R \) [76], while \( \gamma \) at \( T_R \) is only weakly singular (it exhibits the so-called “essential singularity”, i.e. at \( T = T_R \) the radius of a Taylor expansion of \( \gamma \) in powers of \( T - T_R \) is zero). For \( T < T_R \), there are no longer long wavelength capillary waves present, and the interfacial width \( w \) no longer diverges with increasing \( L \). However, these phenomena are outside the scope of the present paper, and we only mention these problems to warn the reader that the extension of concepts for interfaces between fluid phases to fluid-solid interfaces need to be considered with caution. Also the identification of the local height \( h(x, y) \) of a fluid-solid interface in terms of local order parameters for the solid is difficult [63, 64, 65, 66, 67, 68, 69].

4. Curved Interfaces

Let us return in this section to the vapor to liquid transition of fluids, and the estimation of the associated interfacial tension. So far (Sec. 2) only the slab configuration of two-phase coexistence in cubic simulation boxes with periodic boundary conditions was exploited; but the descending part of the loop of the \( \mu_L(\rho, T) \) versus \( \rho \) curve contains information on the interfacial free energy of droplets or bubbles. The droplets in the region \( \rho_1 < \rho < \rho_2 \) have on average a spherical shape, while the rounded kink in this function at \( \rho_2 \) is due to a transition to a cylindrical shape of the droplet (facilitated by the periodic boundary condition in the direction of the cylinder axis). This cylindrical morphology in fact is stable in the regime \( \rho_2 < \rho < \rho_3 \), while near \( \rho_3 \) a rounded step of \( \mu_L(\rho, T) \) towards a constant indicates the onset of the slab configuration, see Sec. 2.

Similar observations can be stated with respect to bubbles for the liquid-rich part of the two-phase coexistence region. As described in details elsewhere [10, 34, 43, 77, 78, 79] one can use the knowledge on \( \mu_L(\rho, T) \) and \( f_L(\rho, T) \) to extract information on the curvature-dependence of the surface tension of spherical droplets and bubbles with radius \( R \). The standard description of this problem is due to Tolman [80]

\[
\gamma_{\ell_0}(T, R) = \gamma_{\ell_0}(T, \infty)/\{1 + 2\delta(T)/R + 2[\ell(T)/R]^2\}, \quad R \to \infty
\]  

(28)

where \( \gamma_{\ell_0}(T, \infty) = \gamma_{\ell_0}(T) \) is the standard interface tension of a planar interface, and \( \delta(T), \ell(T) \) are two (phenomenologically introduced) characteristic lengths. Tolman (1949) proposed three hypotheses: (i) the length \( \delta(T) \), now commonly referred to as the “Tolman length”, should be positive for droplets (and hence negative for bubbles: note that in a two-phase droplet and vapor configuration an interchange of the phases means a change in sign of the radius of curvature \( R \) of the interface). (ii) \( \delta(T) \) should be of the same order as \( \sigma \), the molecular diameter. (iii) The length \( \ell(T) \) appearing in the second-order term should be of the same order, \( \ell(T) \approx \delta(T) \).

These hypotheses have remained controversial until recently; however, the analysis of \( \mu_L(\rho, T) \) and \( f_L(\rho, T) \) due to Block et al. [77, 78, 79] based on the finite size effects modifying the “lever
rule" of two-phase coexistence yielded compelling evidence that all three hypotheses in fact are wrong. Thus, the finding that $\gamma_{\text{bd}}(T, R)$ for bubbles is always smaller than $\gamma_{\text{bd}}(T, R)$ for droplets already shows that $\delta(T) > 0$ for bubbles and hence $\delta(T) < 0$ for droplets. Secondly, $\delta(T)$ is an order of magnitude smaller than $\ell(T)$. While $\ell(T)$ far below the critical point is of order of molecular lengths, it has been shown [78] that near $T_c$ this length is proportional to the correlation length, $\ell(T) \propto \xi(T)$, while $|\delta(T)|$ increases much slower when $T \to T_c$. This is due to the fact that $\delta(T) = 0$ in symmetric systems (such as the Ising-lattice gas model), and the asymmetry of the liquid-vapor phase diagram near criticality is only related to a correction to scaling, and not the leading scaling behavior [81]. So the term $\delta(T)/R$ in Eq. (28) does not enter the universal scaling function for $\gamma_{\text{bd}}(T, R)$ in the critical region, and was estimated in Ref. [78]. A further interesting consequence of these findings [77, 78, 79] concerns the theory of homogeneous nucleation [33, 35, 82]: according to the standard “capillarity approximation” of the conventional theory of nucleation, the curvature dependence of $\gamma_{\text{bd}}(T, R)$ is neglected altogether when one predicts the free energy barrier $\Delta F^*/k_B T$ that needs to be overcome in a nucleation event. For typical supersaturations $S(S = \rho/\rho_\infty < 1$ for bubble nucleation while $S = \rho/\rho_\infty > 1$ for droplet nucleation), for which the barrier $\Delta F^*/k_B T$ is in the range from 20 to 50, one finds an error of about 20 for bubbles and 10 for droplets, i.e. the error is of the same order as the barrier itself [77, 78, 79]. Of course, the simulation data are consistent with the expectation that for $R \to \infty$ the capillarity approximation becomes valid; but it becomes numerically accurate only for barriers $\Delta F^*/k_B T = 100$ or larger, i.e. a regime that is not practically relevant.

5. Wall Tensions

As a last topic of this paper, we discuss the estimation of surface excess free energies due to walls. This is necessary to allow us to deal with problems such as wetting phenomena (mentioned already in the introduction) and heterogeneous nucleation [83]. There exists an enormous range of methods that have been developed to deal with such problems (see e.g. [10] for references). Here we shall focus on a single approach that was recently developed by Winkler et al. [84, 85]. It is a variant of a thermodynamic integration method (see also [86]) and has been termed “ensemble switch method”.

One considers a fluid in the canonical NVT ensemble, assuming a volume $V = L \times L \times D_w$, with two walls a distance $D_w$ apart, and at the same time one considers a system with the same particle number $N$ (at the same temperature) and the same linear dimensions but now without any walls, taking periodic boundary conditions in all three directions. The free energies of these two systems will just differ by twice the wall excess free energy, their bulk free energies being the same.

Now the idea is to construct the free energy difference between these systems by finding a path in configuration space $\{\vec{X}\}$ that leads from the one system to the other. Such a path can be constructed in terms of a mixed Hamiltonian: using a parameter $\kappa$, we take $\kappa$ times the Hamiltonian $H_{\text{bulk}+\text{walls}}(\vec{X})$ of the system with walls and adding $(1 - \kappa)$ times the Hamiltonian $H_{\text{bulk}}(\vec{X})$ of the system without walls,\n
$$H(\vec{X}) = (1 - \kappa)H_{\text{bulk}}(\vec{X}) + H_{\text{bulk}+\text{walls}}(\vec{X}) \quad . \tag{29}$$

Since the microstates (phase space points) $\vec{X}$ for both systems are the same, Eq. (29) is a well-defined Hamiltonian, suitable for Monte Carlo-simulation, even though such a system never can be created by an experimentalist in the laboratory. However, such possibilities of simulation to go beyond experiment are a particular strength of Monte Carlo simulation.

Discretizing then the interval $[0, 1]$ in which $\kappa$ is defined into 100 discrete steps $\kappa_i$, it makes sense to treat $\kappa_i$ as a dynamical variable which is included in the Monte Carlo sampling. Apart
from the usual Monte Carlo moves in the canonical ensemble, where one attempts to displace particles from their old position in the simulation box to a new one, one also considers “switches” where $\kappa_i$ changes to a neighboring value ($\kappa_{i-1}$ or $\kappa_{i+1}$). The corresponding free energy differences between these states then can be gotten by Wang-Landau sampling [87].

In the following we shall briefly review an application example [84, 85], namely the Asakura-Oosawa model [88] of colloid-polymer mixtures [6]. In this model, colloids are described as hard spheres of radius $R_c$, which must neither overlap themselves nor the polymers which are treated as soft spheres of radius $R_p$. Originally the polymers were just treated as ideal gas-like (since random-walk like polymer coils can interpenetrate each other with little energy cost), but it is also possible to use a slightly different model with a soft polymer-polymer repulsion [89]. Using a ratio $q = R_p/R_c = 0.8$, the model exhibits a phase separation into a vapor-like polymer-rich phase and a liquid-like colloid-rich phase, if the normalized polymer fugacity (denoted as “polymer reservoir packing fraction” $\eta^p$ [6, 89, 90]) exceeds a critical value $\eta^p_{\text{crit.}} = 0.767$ [90]. Note that $\eta^p$ is an intensive thermodynamic variable, analogous to inverse temperature for an ordinary binary mixture.

To avoid any problems due to large correlation lengths associated with the critical point, the methodology was tested deeply in the strongly segregated regime, e.g. for $\eta^p = 0.94$, choosing colloid packing fractions $\eta_c$ outside the coexistence curve. Free energy differences between neighboring states $\kappa_i, \kappa_{i+1}$ are obtained from observations of the probabilities $P(i)$ to find the state $i$, $\Delta F(\kappa_{i+1}) - \Delta F(\kappa_i) = k_B T \ln P(i) - \ln P(i+1)$, and for typical choice of parameters (e.g. $L = 6.735$ colloid diameters at $\eta_c = 0.319$) one finds $\Delta F(1) - \Delta F(0) \approx 125 k_B T$, but there is a distinct dependence on the distance $D_w$ between the walls, which repel the particles with a Weeks-Chandler-Andersen potential [91]; the range ($\sigma_w$) of this potential is used as a control parameter. However, it was shown that this size-dependence is due to a $1/D_w$ correction [84, 85] and carrying out an extrapolation towards $D_w \to \infty$ very precise results for the wall tensions $\gamma_{uv}$ and $\gamma_{wv}$ of both liquid-like and vapor-like phase could be obtained [84, 85]. For this model, both the colloid packing fractions $\eta_{c,v}, \eta_{c,ell}$ at the “vapor-liquid” coexistence curve and the interface tension $\gamma_{uv}$ are accurately known [90]. Thus, using Young’s equation [15], Eq. (1), the contact angle could be reliably predicted. It turns out that varying $\sigma_w$ one can change the wetting behavior of the system all the way from complete wetting (for $\sigma_w < 0.59$ colloid diameters) to complete drying (for $\sigma_w > 0.79$).

6. Application to Nanoconfinement

The knowledge on the phase behavior of the Asakura-Oosawa model in the bulk [90] together with the knowledge of its walls tensions [84] can be used to clarify the properties of this model system under conditions of confinement in a spherical cavity [85]. Phase behavior of various systems under conditions of confinement on the nanoscale has become a topic of widespread interest, and hence the present system allows to carry out a corresponding model study.

When one chooses a radius $R = 10$ colloid diameters, and complete wetting conditions ($\sigma_w = 0.5$), under very strong segregation conditions ($\eta^p = 1.4$) one finds that nevertheless there is no wetting layer at the surface of the vapor-like polymer rich phase [85]. This surprising result is due to the fact that under nanoconfinement it can happen that the relevant particle number simply is too small: for $R = 10$ in the vapor-like phase at coexistence only $N_c = 177$ colloids are present in the whole volume of the nanocavity (while in the liquid-like phase $N_c = 2909$). There are simply too few colloids in the vapor-like phase to allow the formation of a wetting layer in such a system. When one studies the free energy $F(N_c)$ as a function of the number of colloids $N_c$ in the system, one finds a double-well structure. However, again it does not mean that we have a Landau-type free energy: still the peak is due to interfacial effects, the system forms a core-shell structure (the polymer-rich phase forms a core, which on average is spherical and in the center, the colloids form the shell). Conversely, if we consider neutral walls, the
peak of $F(N_c)$ is due to a “Janus particle” structure, the system forms an essentially planar interface, with one hemisphere formed by the colloid-rich phase and the other hemisphere by the polymer-rich phase. In both cases the chemical potential $\mu(\eta_c)$ of the colloids exhibits loops, again reflecting two-phase coexistence, and hence must not be interpreted as van-der-Waals-type loops. It is remarkable that in this situation of nanoconfinement the loops of $\mu(\eta_c)$ do not develop any sharp peaks and rounded kinks, as is the case with the periodic boundary conditions: these features were due to discontinuous transitions in the geometry of the coexisting phases (from the droplet to the slab configuration, etc.) These structures were stabilized by the periodic boundary conditions, and do not occur for experimentally more relevant boundary effects considered in the present section.

It is very interesting to analyze how these finite size effects on phase coexistence change when one varies the radius $R$ of the spheres. One then finds that the loops in the $\mu(\eta_c)$ curves get gradually flatter, so the system also converges to an isotherm, with a horizontal part from the pure vapor-like to the pure liquid-like phase as $R \to \infty$. A very interesting aspect is that for finite $R$ the different ensembles of statistical mechanics yield different results, although they become equivalent for $R \to \infty$. A loop in the $\mu(\eta_c)$ curve is only seen when $\eta_c$ is the control parameter and $\mu_c$ is obtained from the Monte Carlo sampling. However, carrying out a simulation in the grand-canonical ensemble, $\mu$ is the control parameter and $\eta_c$ is sampled: then one finds the isotherm $\eta_c(\mu_c)$ is monotonous; while in the thermodynamic limit this isotherm has a perpendicular part, for finite $R$ the slope of the isotherm is finite but large, the maximum slope scales like $R^3$. In contrast, the shift of the inflection point of the isotherm (where this maximum slope occurs) relative to the location of the bulk scales like $1/R$. Thus for phase coexistence the finite size effects behave very differently from what one knows about finite size effects on critical phenomena (where shift and rounding scale with the same exponent, $R^{-1/\nu}$ where $\nu$ is the critical exponent of the correlation length [92]).

A consequence of the fact that isotherms in the grand-canonical ensemble are monotonic, while isotherms (plotting the same variable) in the canonical ensemble are nonmonotic (due to their loops) also means that they are not simply related by a Legendre transformation, as in the thermodynamic limit.

The fact that the shift of the transition scales like $1/R$ can easily be understood from the surface excess contributions to the free energy. For spherical geometry one obtains for the location of the transition [84, 85]

$$\mu_c(R) - \mu_c(\infty) = \frac{3}{R} \frac{\gamma_{\text{w}l} - \gamma_{\text{w}v}}{\rho_{c,l} - \rho_{c,v}}, \quad R \to \infty \tag{30}$$

where $\rho_{c,l}$ and $\rho_{c,v}$ are the colloid densities at the coexisting liquid-like and vapor-like phases in the bulk colloid-polymer mixture. Analyzing the shift observed in the simulation hence is a second method for estimation of the wall free energy difference $\gamma_{\text{w}l} - \gamma_{\text{w}v}$, that also enters the Young equation for the contact angle. It was found [85] that for $0 < \theta < 180^\circ$ the agreement with the thermodynamic integration method (the “ensemble switch method”) of the previous section is very good. Interestingly, for the regime of complete wetting one simply finds the result

$$\gamma_{\text{w}v} = \gamma_{\text{w}l} + \gamma_{\ell v} \tag{31}$$

due to the liquid wetting layer intruding in between the wall and the vapor region in the thermodynamic limit. Thus, the analysis confirms the location of the wetting transition, at least roughly. Thus, we see that for simple systems, like the Asakura-Oosawa model, one can understand all aspects of phase coexistence in nanosystems in terms of an interplay of surface vs. bulk behavior and finite size effects.
These studies have been carried over to liquid-solid coexistence in the confined hard sphere system and the Asakura-Oosawa model (at high colloid density) [93, 94]. The “ensemble switch method” was found to be useful also in this case, and together with estimations of the interfacial free energy between coexisting fluid and solid phases (obtained from interfacial broadening due to capillary waves, see Sec. 3) predictions for the contact angle could be made [94]. This prediction was found to be in reasonable agreement with direct observations of the contact angle of wall-attached crystalline “droplets” at planar structureless walls. Although these results clearly are encouraging, they can be considered as a promising first step only, and a much more complete study is required.

7. Concluding remarks

In this paper, it was emphasized that interfaces between coexisting phases in condensed matter are important for many phenomena: nucleation, wetting, phase separation kinetics, phase coexistence in nano-materials; etc. It was also emphasized that analytical theories are quite misleading: concepts such as van der Waals loops, Landau double well free energies, intrinsic interfacial profiles of tanh form, etc., all are mean field artefacts.

Interfaces have structure from the atomistic-scale to the mesoscopic scale: but well-equilibrated large-scale interfaces are a challenge for simulation. The interfacial profiles depend on the system geometry, and it is difficult to disentangle interfacial from bulk fluctuations, and to give the “intrinsic profile” a precise meaning. This issue has been controversial over decades and still is today. Particularly many open problems concern solid-liquid interfaces (faceting transitions; equilibrium shape of nanocrystals in different environments, etc.) and also the “line tension” associated with the contact line where three interfaces meet. Thus, the subject will remain active and exciting for many years to come.

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