Local orientations of fluctuating fluid interfaces

Klaus Mecke\textsuperscript{1} and Siegfried Dietrich\textsuperscript{2,3}

\textsuperscript{1} Institut für Theoretische Physik, Universität Erlangen-Nürnberg, Staudtstrasse 7, D-91058 Erlangen, Germany
\textsuperscript{2} Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany
\textsuperscript{3} ITAP, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany

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Thermal fluctuations cause the local normal vectors of fluid interfaces to deviate from the vertical direction defined by the flat mean interface position. This leads to a nonzero mean value of the corresponding polar tilt angle which renders a characterization of the thermal state of an interface. Based on the concept of an effective interface Hamiltonian we determine the variances of the local interface position and of its lateral derivatives. This leads to the probability distribution functions for the metric of the interface and for the tilt angle which allows us to calculate its mean value and its mean square deviation. We compare the temperature dependences of these quantities as predicted by the simple capillary wave model, by an improved phenomenological model, and by the microscopic effective interface Hamiltonian derived from density functional theory. The mean tilt angle discriminates clearly between these theoretical approaches and emphasizes the importance of the variation of the surface tension at small wave lengths. Also the mean two-point correlation function is determined which renders an additional structural characterization of interfacial fluctuations.

Various experimental accesses to measure the local orientational fluctuations are discussed.

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I. INTRODUCTION

If two phases of condensed matter, which coexist thermodynamically at first-order phase transitions, are brought into spatial contact under suitable boundary conditions, an interface is formed through which the system interpolates smoothly between the structural properties of the adjacent bulk phases. The formation of such an interface is accompanied by a cost in free energy given by the product of the mean interfacial area and the surface tension. Since the surface tension is always positive the system acts to minimize the interfacial area under given boundary conditions which gives rise to a plethora of capillary phenomena (for reviews see, e.g., Refs. \textsuperscript{1,2,3,4,5}). If the first-order phase transitions end at a critical point where the differences between the coexisting phases disappear, the interface broadens and ceases to exist; accordingly the surface tension vanishes there with a universal power law as function of temperature. There are numerous experimental and theoretical techniques to measure and to calculate surface tensions the knowledge of which allows one to tune capillary phenomena in a specific way \textsuperscript{1,2,3,4,5}.

With the advent of sophisticated spectroscopic techniques such as X-ray and neutron scattering under grazing incidence it has become possible to resolve the structural properties of interfaces at an atomic scale, paving the way for a microscopic understanding of interfacial properties in terms of mean density profiles, concentration profiles, and - in the case of nonspherical particles - orientational profiles (see, e.g., Ref. \textsuperscript{6} and references therein).

These mean profiles, i.e., one-point correlation functions, can be inferred from deviations of reactivity coefficients from the corresponding Fresnel formulae holding for steplike variations of the structural properties. The analysis of the diffuse scattering around the specular beam provides an even deeper insight into the structural properties of interfaces by probing the structure factor and thus the two-point correlation function in the lateral directions and close to the interface \textsuperscript{6}.

This interfacial structure factor is of particular interest because in addition to the bulk-like density fluctuations, which occur on length scales up to the bulk correlation length $\xi$ and reach the surface of each of the two semi-infinite phases, there are capillary wavelike fluctuations occuring at length scales larger than $\xi$ but tied to the interfacial region only. Without gravity or lateral confinement these capillary wavelike fluctuations lead to a unlimited thickening of the interface and to a unlimited increase in the spatial dependence of the two-point correlation function on the lateral distance, known as the roughening of the interface. If one of the two adjacent phases is a solid, this broadening occurs only above the so-called roughening transition whereas for interfaces between fluid phases it occurs at all temperatures. Thus, in the following we focus on fluid interfaces, in particular the liquid-vapor interface of a simple fluid.

The physical picture of the capillary wavelike fluctuations is that of an intrinsic profile - generated by bulklike fluctuations as if the interface would be flat - exhibiting local, laterally varying height positions. This picture reconciles van der Waals’ original idea of an interface \textsuperscript{7} and the purely capillary wavelike picture of a fluctuating steplike interface put forward by Buff, Lovett, and Stillinger \textsuperscript{8}.

Based on microscopic density functional theory one can determine the effective interface Hamiltonian, and thus the
The capillary wave approach to study liquid interfaces, which was put forward by Buff, Lovett, and Stillinger (BLS) [8], describes the actual smooth density profile as the thermal average of a locally fluctuating steplike interface between the two coexisting phases. The local position of the liquid-vapor interface is described by a single-valued function \( f(R) \) depending on the lateral coordinates \( R = (x, y) \) with \( R = [R] \) in the \( x-y \)-plane parallel to the mean interface at \( z = 0 \) (see Fig. 1). This so-called Mongé parametrization neglects overhangs of the interface as well as bubbles of one phase inside the other, i.e., domains topologically separated from the interface; apart from the close neighborhood of the critical point such configurations carry a sufficiently small statistical weight to be negligible. The orientation of the mean interface described by the unit-vector \( e_x \) is chosen to be parallel to the \( z \)-axis, i.e., perpendicular to the \( x-y \)-plane. This direction is determined either by corresponding boundary conditions or the direction of the gravitational

statistical weight for such a given configuration, which can be expressed in terms of a wavelength dependent surface tension; it equals the macroscopic surface tension at large wavelengths, attains a deep minimum at medium lengths, and increases for short wavelengths [9]. The ensuing theoretical predictions for the lateral interfacial structure factor have been confirmed quantitatively for water [10], OMCTS, CCl₄, squalane, glycol [11], and Ga [12] by using X-ray scattering under grazing incidence.

Given this successful agreement between theory and experiment one can turn to the question whether this wavelength dependent surface tension represents primarily a transparent parametrization of the interfacial structure factor or whether the corresponding effective interface Hamiltonian has the quality of transferability, i.e., predicts also other key features of fluid interfaces.

In this context we consider a snapshot of an interfacial configuration. The points in space, at which the local density equals, say, the mean value of the two bulk densities, form a two-dimensional isodensity surface which can be identified as the local interface position. This surface is characterized by giving its local and laterally varying height with respect to the mean flat interface position.

Alternatively, at each point of the surface one can attach its normal vector which forms the polar angle \( \theta \) with the vertical direction given, e.g., by the direction of gravity and which is the normal for the flat mean interface. The thermal fluctuations of the interface cause corresponding fluctuations of the surface normals and thus of the polar tilt angle \( \theta \). Since \( \theta \) is always positive its mean value \( \langle \theta \rangle \) is nonzero; \( \langle \theta \rangle = 0 \) would imply the complete absence of capillary wavelike fluctuations. Therefore, \( \langle \theta \rangle > 0 \) and the mean squared deviation \( \langle \theta^2 \rangle - \langle \theta \rangle^2 \) characterize the thermal state of the interface with a particular emphasis on the capillary wavelike fluctuations. Based on the aforementioned effective interface Hamiltonian one can derive the probability distribution function for \( \theta \) and thus calculate its mean value and its moments. Their increase with temperature \( T \) signals the unfreezing of capillary waves. In this sense \( \langle \theta \rangle \) \( (T) \) represents an additional characteristic quantity for defining the thermal state of interfaces, on equal footing with the surface tension. Moreover, the function \( \langle \theta \rangle \) \( (T) \) probes directly the concept of the wavelength dependent surface energy.

Unrelated to this latter aspect, in a series of papers Simpson and Rowlen studied the surface roughness contributions to measurements, based on linear dichroism, of the molecular orientations of optically active molecules adsorbed on rough solid surfaces [13, 14, 15]. In order to infer from such data the local molecular orientation they must be corrected by the effects due to the frozen orientational fluctuations of the rough supporting substrate. Thus in this context the tilt angle distribution of the interface plays an important role. Other experiments consider orientational fluctuations in monolayers or thin multilayer films of non-spherical particles adsorbed on fluid interfaces [16, 17, 18, 19, 20]. These orientational fluctuations are determined by fixed relations between the orientations of the adsorbed molecules and the fluctuating local orientations of the supporting fluid interface. Here we focus on the latter contribution. There is a wide range of experimental techniques which provide access to the molecular orientations at interfaces [14] such as fluorescence, second-harmonic generation (SHG), sum-frequency generation (SFG), linear dichroism (LD), and angle-resolved photoacoustic spectroscopy (ARPAS). For instance, in Ref. [21] the spectroscopically determined orientation of complex molecules such as proteins attached to rough solid substrates is studied. If adsorbed with low concentrations at fluid interfaces such tracer molecules probe the orientational fluctuations of the interface normals. Promising further perspectives are provided by studying fluid interfaces of colloidal suspensions by laser scanning confocal microscopy which allows one to observe, down to the scale of the colloidal particles, thermally induced capillary waves in real space and to analyze the distribution of the local interface orientations [22].

In Sec. II we introduce the geometry of the local orientations of fluid interfaces followed in Sec. III by a discussion of the various theoretical approaches describing capillary wavelike fluctuations as they are used for calculating the Gaussian interfacial fluctuations in Sec. IV. The dependence of the mean tilt angle and its mean squared deviation on physical parameters is analyzed in Sec. V. The relation of these results with experiments is discussed in Sec. VI. We summarize our results in Sec. VII.

II. LOCAL ORIENTATIONS OF FLUID INTERFACES
force. Although the mean orientation $e_z$ is fixed one does observe local variations of the interfacial orientation due to thermal fluctuation of $f(R)$. These deviation may be described by a local tilt angle 

$$\theta(R) = \arccos (e_z \cdot n(R))$$

(1)

where

$$n(R) = \frac{1}{\sqrt{1 + f_x^2 + f_y^2}} \begin{pmatrix} -f_x \\ -f_y \\ 1 \end{pmatrix}$$

(2)

denotes the normal vector of the interface at the lateral position $R$ which is given by the partial derivatives $f_i := \frac{\partial f(R)}{\partial i}$, $i = x, y$, of the interface position $f(R)$. In addition to the polar angle $0 \leq \theta(R) \leq \pi/2$ one may define

$$\phi(R) = \arccos \left( \frac{n(R) \cdot e_x}{\sin \theta(R)} \right),$$

(3)

i.e., the azimuthal angle between the projection of the normal vector $n$ onto the $x$-$y$-plane and the $x$-direction in the $x$-$y$-plane. The local tilt angle $\theta(R)$ and $\phi(R)$ describe uniquely the interface orientation because

$$n(R) = \begin{pmatrix} \cos \phi(R) \sin \theta(R) \\ \sin \phi(R) \sin \theta(R) \\ \cos \theta(R) \end{pmatrix}$$

(4)

can be reconstructed from the knowledge of the angles $\theta$ and $\phi$.

FIG. 1: Schematic picture of an interface configuration between the coexisting liquid and vapor bulk phases with number densities $\rho_l$ and $\rho_g$, respectively. The interface does not contain overhangs or bubbles. Thus the local position of the liquid-vapor interface can be described by a single-valued function $f(R)$, where $R = (R_x, R_y)$ denotes the lateral coordinates. The dashed curves indicate the intersections between the two-dimensional manifold $f(R)$ and planes $x = R_x = \text{const}$ and $y = R_y = \text{const}$, respectively. Gravity $G$ leads to a mean interface position at $z = 0$ (dotted lines). The volume of the sample is $V = AL$ where $A$ is the lateral area and $L$ is the vertical height. The local orientation of the interface is described by the normal vector $n(R)$ characterized by the angles $\Theta(R)$ and $\phi(R)$ (see Eq. (1)–(4)).
An important motivation to study the local tilt angle \(0 \leq \theta(R) \leq \pi/2\) is the non-vanishing thermal average
\[
\langle \theta \rangle (T) > 0
\] (5)
of the tilt angle which is strictly positive at finite temperatures \(T\). Thus the interface is always locally tilted, so that one may observe relevant thermal fluctuation features already in the mean value \(\langle \theta \rangle (T)\), in contrast to the mean interface position \(\langle f \rangle (R) = 0\) which always vanishes. A vanishing mean value of \(\theta\) would imply the complete absence of capillary wavelike fluctuations. Thus, the 'structure' of the interface reveals itself via the interface position \(f(R)\) only through its variance, i.e., the mean squared deviation
\[
\sigma^2(T) = \langle (f(R))^2 \rangle = \int_{\mathbb{R}^2} \frac{d^2 q}{(2\pi)^2} \sigma^2(q)
\] (6)
from its vanishing mean value, where \(\sigma^2(q)\) denotes the fluctuation contributions stemming from interfacial modes with lateral wavevector \(q\) with \(q = |q|\) (see, c.f., Eq. (27)).

Recent progress in grazing incidence X-ray scattering experiments \(^{10,11,12}\) enables an almost complete determination of \(\sigma^2(q)\) and therefore of the structure and the fluctuations of the interfacial position \(f(R)\). In particular, as predicted theoretically \(^{24,25}\), it has been demonstrated by X-ray scattering experiments that for wavevectors above a few \(nm^{-1}\) there is a decrease of up to 75% of the surface energy due to the attractive dispersion forces. But for some fluids the fluctuation spectrum at large wavevectors \(q\) could not be resolved close to the physical limit \(q_{\text{max}} = \frac{2\pi}{a}\) of a few \(\text{Å}^{-1}\) where \(a\) denotes the microscopic size of the molecules. As we shall show in the following the fluctuations of the local tilt angle \(\theta(R)\), i.e., its mean value \(\langle \theta \rangle\) and its mean squared deviation \(\langle (\delta \theta)^2 \rangle\) with \(\delta \theta = \theta - \langle \theta \rangle\) are much more sensitive to the structure of the interface at large wavevectors, so that the analysis of them promises a significant improvement of the understanding of fluid interfaces.

### III. CAPILLARY WAVE THEORY

The cost in free energy to generate an undulation of a flat interface, i.e., to generate a non-flat interface configuration depends on the amplitude \(f(R)\) of the undulation but also on physical parameters such as temperature \(T\), the gravitational constant \(G\), the surface tension \(\gamma_0\), and the bending rigidity \(\kappa_0\) or ultimately the interaction potential between the fluid particles. The usual approach to describe this cost in free energy assumes that the amplitudes are small so that the Hamiltonian may be expanded into powers of \(f(R)\) and its derivatives \(\nabla f(R)\) and \(\Delta f(R)\) yielding (\(m\) denotes the mass of the particles and \(\Delta \rho = \rho_l - \rho_g\) the difference in number densities of the coexisting liquid and vapor phase)
\[
\mathcal{H}^{(H)}[f(R)] = \frac{1}{2} \int_{\mathbb{R}^2} d^2 R \left[ mG\Delta \rho (f(R))^2 + \gamma_0 (\nabla f(R))^2 + \kappa_0 (\Delta f(R))^2 \right]
\] (7)
This gradient expansion is known also as the Helfrich Hamiltonian for fluctuating membranes \(^{23,24,25}\).

It is transparent to study \(\mathcal{H}^{(H)}\) in Fourier space in which the bending modes decouple. To this end we introduce the Fourier transformed functions
\[
\hat{f}(q) = \int_{\mathbb{R}^2} d^2 R e^{-iq \cdot R} f(R) , \\
f(R) = \int_{\mathbb{R}^2} \frac{d^2 q}{(2\pi)^2} e^{iq \cdot R} \hat{f}(q)
\] (8)
yielding the Fourier transformed Hamiltonian
\[
\mathcal{H}^{(H)}[\hat{f}(q)] = \frac{1}{2} \int_{\mathbb{R}^2} \frac{d^2 q}{(2\pi)^2} |\hat{f}(q)|^2 \left( mG\Delta \rho + \gamma^{(H)}(q)q^2 \right)
\] (9)
with the momentum dependent surface tension
\[
\gamma^{(H)}(q) = \gamma_0 + \kappa_0 q^2 .
\] (10)

We note that the use of an upper cut-off \(q < q_{\text{max}} = 2\pi/a\) for the wavevectors is indispensable because the concept of capillary wave fluctuations becomes meaningless on length scales smaller than the microscopic size \(a\) of the molecules.
Instead of starting from the \textit{ansatz} in Eq. (7) an alternative strategy (see Ref. [9]) to derive $\mathcal{H}[f(R)]$ is based on a microscopic density functional theory for inhomogeneous simple fluids, which is a successful approach for the description of nonuniform fluids [26, 27]. The different kinds of occurring density fluctuations - bulk bubbles and interface undulations - are separated by determining the intrinsic density profile $\rho_f(r)$ via minimizing the grand canonical density functional $\Omega[\rho(r)]$ under the constraint of a locally prescribed interface position $f(R)$, i.e., the location of the isodensity contour of the mean density is fixed as function of the lateral coordinates $R$. Due to the long-ranged character of the underlying van der Waals interparticle potential $W(r)$ between the fluid particles nonanalytic contributions occur and therefore a gradient expansion of the Hamiltonian breaks down. Instead, in Fourier space one obtains in terms of the amplitudes $\tilde{f}(q)$ describing the interface position the Hamiltonian

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

where the superscript $(G)$ indicates that this expression refers to a Gaussian approximation bilinear in the amplitudes $f(q)$ of the bending modes. The momentum dependent energy (per (length)$^4$)

$$E(q) = E_0 + \gamma(q) q^2$$

with $E_0 = m G \Delta \rho$ can be written in terms of a momentum dependent surface tension $\gamma(q)$, which is not simply given by the Helfrich expression [10] but by an explicit functional of the molecular interaction potential $W(r)$. Based on the simple functional [27]

$$\Omega[\rho(r)] = \int_V d^3r (f_h(\rho(r)) + \mu \rho(r) + \rho(r) V(r))$$

$$+ \frac{1}{2} \int_V d^3r \int_V d^3r' w(|r-r'|) \rho(r) \rho(r')$$

where $V$ is the volume of the sample, $\rho(r)$ is the number density of the fluid particles at $r = (x,y,z)$, $r = |r|$, $f_h(\rho)$ is the reference bulk free energy of a system determined by the short-ranged, repulsive contribution $w_\rho(r)$ to the interaction potential $W(r)$, and $w(r)$ is the attractive part of $W(r)$, one finds within the reliable so-called product approximation [9]

$$\gamma(q) \simeq \left( \gamma_0 + \kappa_0^{(H)} q^2 \right) \frac{\tilde{w}(q) - \tilde{w}(0)}{\tilde{w}''(0) q^2}$$

$$+ \left( \kappa_0 - \kappa_0^{(HH)} \frac{\tilde{w}(q)}{\tilde{w}(0)} \right) q^2 + \mathcal{O}(q^4)$$

with the surface tension and bending rigidities

$$\gamma_0 = \frac{1}{12} \tilde{w}''(0) \frac{(\Delta \rho)^2}{\xi} > 0$$

$$\kappa_0^{(H)} = \frac{1}{24} \tilde{w}''(0) (\Delta \rho)^2 \xi C_H > 0$$

$$\kappa_0^{(HH)} = -\frac{4}{65} \tilde{w}(0) (\Delta \rho)^2 \xi^3 C_H^2 > 0$$

$$\kappa_0 = \frac{4}{65} (\Delta \rho)^2 \xi^3 C_H^2 \left\{ \frac{\partial^2 f_h(\rho)}{\partial \rho^2} \right\} > 0$$

For the bulk free energy density $f_h(\rho)$ one may use the Carnahan-Starling expression [27]

$$f_h(\rho) = k_B T \rho \left\{ \ln(\rho \lambda^3) - 1 + \frac{4\eta - 3\eta^2}{(1-\eta)^2} \right\}$$

where $\lambda$ is the thermal de Broglie wavelength and $\eta = \frac{\pi}{6} \rho \sigma^3$ the packing fraction. (For the definition of $r_0$ see, c.f., Eq. (18)). Within this product approximation the momentum dependence of $\gamma(q)$ in Eq. (14) is determined by the three-dimensional Fourier transform

$$\tilde{w}(Q) = \int_{\mathbb{R}^3} d^3r e^{-iQ \cdot r} w(|r|)$$
of the interparticle potential $w(r)$ evaluated for the absolute value $q$ of the lateral momentum $q$ with $\ddot{w}(0) > 0$ and $\ddot{w}(0) < 0$.

Considering particles which interact via van der Waals forces one may adopt for the attractive part of the interaction potential $w(r)$ the form

$$w(r) = -\frac{w_0 r_0^6}{(r_0^2 + r^2)^3} \quad \rightarrow \quad -Ar^{-(d+\tau)}$$

which exhibits the correct large distance behavior $w(r \rightarrow \infty) \rightarrow -Ar^{-(d+\tau)}$ with $A = w_0 r_0^6$ for $d = 3$, $\tau = 3$. The length $r_0$ corresponds to the diameter of the particles and thus serves as a lower limit for the length scale of the density fluctuations and of the capillary waves considered below. Then, Eq. (14) reduces to the explicit expression

$$\gamma(q) \approx \frac{(1 + 3\gamma_0) e^{-q r_0}}{(q r_0)^2} + 0.74 C_H^2 (\xi r_0)^2 \left( \frac{\xi}{r_0} \right)^2 (q r_0)^2 + O((q r_0)^3)$$

depending solely on the bulk correlation length $\xi$, the diameter $r_0$ of the molecules, and the dimensionless parameter $C_H \approx 0.25$ describing the distortion of the intrinsic density profile due to the bending of the interface. Upon increasing $q$, $\gamma(q)/\gamma_0$ decreases below 1, reaches a minimum and increases again (for more details see Ref. [9]). This decrease of $\gamma(q)$ is in accordance with recent simulation data [29, 30] which, however, have not yet confirmed the predicted and experimentally observed reincrease of $\gamma(q)$ at large $q$.

For the density functional theory given in Eq. (13) and the interaction potential in Eq. (18) one has $\ddot{w}(q) = w(0)(1 + qr_0) e^{-qr_0}$ with $\ddot{w}(0) = -\pi^2 r_0^6 w_0/4$, so that one finally finds the temperature dependences

$$\gamma_0 = \frac{\pi^2}{48} \frac{w_0 r_0^5}{\xi} (\Delta \rho)^2,$$

$$\bar{\kappa}_0^{(H)} = \frac{\xi^2 C_H^2 \gamma_0}{2},$$

$$\bar{\kappa}_0^{(HH)} = \frac{48 \xi^4}{65 r_0^6} C_H^2 \gamma_0,$$

$$\kappa_0 = \frac{\bar{\kappa}_0^{(HH)}}{1 + \frac{1}{2} \frac{r_0^2}{\xi^2}} \xi$$

and close to the critical point at $T_c$:

$$\Delta \rho = \frac{1.23}{r_0^3} \left( 1 - \frac{T}{T_c} \right)^{\frac{1}{2}},$$

$$\xi = \frac{r_0}{2 T_c} \left( 1 - \frac{T}{T_c} \right)^{-\frac{1}{2}}.$$

Although it is straightforward to determine $\xi$ and $\Delta \rho$ numerically we found that these approximate but analytic expressions are quite accurate for temperatures between the triple point $T_{tr} \approx (2/3)T_c$ and the critical point (apart from the critical region in which deviations from the above mean-field behavior occur), so that they can be used in the following. For temperatures below $T_{tr}$ - where no fluid interface exists - the model defined by Eq. (13) ceases to be applicable because it does not capture the freezing transition, which would require a more sophisticated version of the density functional.

In order to study the dependences on the numerous physical parameters we define two length scales: the capillary length $L_c$ and the stiffness length $L_\kappa$, respectively,

$$L_c = \sqrt{\frac{\gamma_0}{E_0}}, \quad L_\kappa = \sqrt{\frac{\bar{\kappa}_0}{\gamma_0}},$$

(22)
which in addition to the microscopic cut-off lengths \( r_0 \) (range of the hard-core repulsion potential) and \( a = \frac{2\pi}{q_{max}} \) (size of the molecules), and the bulk correlation length \( \xi \) are relevant for the cost in free energy for bending an interface with wave vector \( \mathbf{q} \) (see Eqs. (11) and (12)). For simple liquids the values for \( r_0, a, \) and \( L_\kappa \) are of the same order of magnitude and may be identified in a first approximation. But since the distributions of the local orientations of the interface turn out to depend sensitively on these microscopic length scales we prefer to keep them distinguished until their influence has been elucidated. Moreover, colloidal suspensions (see, e.g., Ref. [22]) might offer the possibility to keep these length scales well separated and to vary them to large extent independently.

IV. GAUSSIAN INTERFACIAL FLUCTUATIONS

Before we study in detail the dependence of the interfacial structure on physical parameters such as the surface tension \( \gamma_0 \) or the interparticle potential \( w(\mathbf{r}) \) in this section we discuss those properties of an interface which follow from the Gaussian approximation given by Eq. (11).

Since within the Gaussian approximation \( P[f] \sim \exp(-\beta H^{(G)}) \), see Eq. (11), the bending modes are decoupled one finds for the probability of a surface wave \( \tilde{f}(q) \) of wavevector \( q \) the explicit expression (see Eq. (11))

$$ P[\tilde{f}(q)] = \frac{E(q)}{\pi k_B T} e^{-\frac{E(q)}{k_B T} |\tilde{f}(q)|^2} $$

so that mean values \( \langle f \rangle \) for functionals \( A[f(\mathbf{R})] \) of the interface position can straightforwardly be calculated by

$$ \langle f \rangle = \int Df \ A[f(\mathbf{R})] $$

where

$$ \int Df \ldots = \prod_{\mathbf{q} \in \mathbb{R}^2} \int_{-\infty}^{\infty} d \left( \Re e \tilde{f}(\mathbf{q}) \right) \int_{-\infty}^{\infty} d \left( \Im m \tilde{f}(\mathbf{q}) \right) \ldots \frac{E(q)}{\pi k_B T} e^{-\frac{E(q)}{k_B T} \left( (\Re e \tilde{f}(\mathbf{q}))^2 + (\Im m \tilde{f}(\mathbf{q}))^2 \right)} $$

(25)

denotes the integration measure for the interfacial degrees of freedom which solely depends on \( \beta E(q) \) as the inverse thermal energy. Because of the relation \( \tilde{f}(-\mathbf{q}) = \tilde{f}^*(\mathbf{q}) \), the product in Eq. (25) runs only over suitably discretized vectors \( \mathbf{q} \) in the half space \( \mathbb{R}^2/2 \). Details on the Wiener measure in terms of Fourier coefficients can be found in Ref. [31].

In a first step we consider local second order moments \( \sigma_{2n,2m}^2 \) (see, c.f., Eq. (25)) characterizing the distribution functions of lateral derivatives of \( f(\mathbf{R}) \) at one and the same lateral position \( \mathbf{R} \), whereas Subsec. IV.B focuses on correlations of \( f(\mathbf{R}) \) at points \( \mathbf{R} = \mathbf{R}_1, \mathbf{R}_2 \) with non-vanishing distance vector \( \mathbf{a} = \mathbf{R}_2 - \mathbf{R}_1 \).

A. Local variances

The probability \( P[f_0] \) to find the interface at the lateral coordinate \( \mathbf{R} \) at a specified position \( f_0 = f(\mathbf{R} = 0) \) is given by (see Eq. (8))

$$ P[f_0; \sigma] = \int Df \ \delta \left( f_0 - \int_{\mathbb{R}^2} \frac{d^2 \mathbf{q}}{(2\pi)^2} \tilde{f}(\mathbf{q}) \right) $$

$$ = \int \frac{dp}{2\pi} e^{ipf_0} \prod_{\mathbf{q} \in \mathbb{R}^2/2} \int_{-\infty}^{\infty} d \left( \Re e \tilde{f}(\mathbf{q}) \right) \int_{-\infty}^{\infty} d \left( \Im m \tilde{f}(\mathbf{q}) \right) \ldots \frac{E(q)}{\pi k_B T} e^{-\frac{E(q)}{k_B T} \left( (\Re e \tilde{f}(\mathbf{q}))^2 + (\Im m \tilde{f}(\mathbf{q}))^2 \right)} $$

$$ \times \frac{1}{\sqrt{2\pi \sigma^2}} e^{-\frac{q^2}{2\sigma^2}} $$

(26)

with the fluctuation spectrum (see Eq. (8)), \( \sigma^2(q) = k_B T/E(q) \) and the variance

$$ \sigma^2 = \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \frac{k_B T}{E(q)} = \int dq \frac{k_B T}{E(q)} \frac{q}{2\pi} $$

(27)
Integrating over all wavevectors requires special care since modes may be constrained by physical boundary conditions. As stated after Eq. (10) \( q_{\text{max}} = 2\pi / a \) denotes the maximum possible wavevector because fluctuations on length scales smaller than the microscopic size \( a \) of the molecules are not compatible with the concept of capillary waves. Accordingly, one may introduce a lower cut-off \( q_{\text{min}} = 2\pi / L \) due to the finite lateral size \( L \) of the interface. If \( L \) is larger than the capillary length \( L_c \) (see Eq. (22)) one may safely set \( q_{\text{min}} = 0 \) so that fluctuations with long wavelengths are suppressed only by gravity.

Indeed, \( P[f_0; \sigma] \) is properly normalized so that \( \int_{-\infty}^{\infty} df_0 P[f_0; \sigma] = 1 \). Accordingly, the probability \( P[f_0^{(n,m)}; \sigma_{2n,2m}] \) to find a prescribed derivative

\[
f_0^{(n,m)} = \left. \frac{\partial^{n+m} f(R)}{\partial x^n \partial y^m} \right|_{R=0}
\]

at \( R \) is given analogously to Eq. (26) with \( f_0 \) replaced by \( f_0^{(n,m)} \) but with the variance

\[
\sigma_{2n,2m}^2 = \int \frac{d^2 q}{(2\pi)^2} q_x^{2n} q_y^{2m} \frac{k_B T}{E(q)} = I_{n,m} \sigma_{2n+2m+1}^2
\]

with

\[
\sigma_k^2 = \int \frac{dq}{2\pi} q^2 \frac{k_B T}{E(q)}
\]

and \( I_{n,m} = \int_0^{2\pi} \frac{d\phi}{\pi} \cos^{2n} \phi \sin^{2m} \phi = \frac{1}{m} (J_{n,m} + J_{m,n}) \) for integers \( n, m \in \mathbb{N} \) with \( J_{n,m} = 2 \int_0^{\pi/2} d\phi \cos^{2n} \phi \sin^{2m} \phi = B(m + \frac{1}{2}, n + \frac{1}{2}) \) (3.621.5 and 8.384.1 in Ref. 32) so that \( (n, m) \in \mathbb{N} \)

\[
I_{n,m} = \frac{1}{\pi} \frac{\Gamma(n + \frac{1}{2}) \Gamma(m + \frac{1}{2})}{\Gamma(n + m + 1)}
\]

In particular, one finds \( I_{0,0} = 1, I_{1,0} = I_{0,1} = \frac{1}{2}, I_{2,0} = I_{0,2} = \frac{3}{8}, I_{1,1} = \frac{1}{8} \). Therefore the probability \( P[f_0'; \sigma'] = P[f_0^{(1,0)}; \sigma'] P[f_0^{(0,1)}; \sigma'] \) for the slope (orientation) \( f_0' = \nabla f(R = 0) \) of the interface at \( R = 0 \) has the variance \( \sigma'^2 = \sigma_{2,0}^2 = \sigma_{1,1}^2 / 2 \). Note that \( \sigma', \sigma_3, \) and \( f_0' \) are dimensionless. The probability \( P[\Delta f; \sigma_H] \) of the Laplacian \( \Delta f(R) \), which in lowest order in \( f \) is twice the mean curvature

\[
H_0 = \frac{f_{xx}(1 + f_y^2) - 2f_{xy}f_{yx} + f_{yy}(1 + f_x^2)}{2(1 + f_x^2 + f_y^2)^2}
\]

has the variance \( \sigma_{\Delta}^2 = \sigma_0^2 \):

\[
\sigma_{\Delta}^2 = \int \frac{d^2 q}{(2\pi)^2} (q_x^2 + q_y^2)^2 \frac{k_B T}{E(q)} = \int \frac{dq}{2\pi} q^2 \frac{k_B T}{E(q)}
\]

**B. Finite distance variances**

An alternative to the local slope \( f_0' \) as a measure for the orientation of an interface is provided by finite differences \( \delta f := f(R + a) - f(R) \) of the interface position. Analogous to Eq. (26), the joint probability of finding the heights
$f_0$ and $f_a$ of the interface at the lateral positions $0$ and $\mathbf{a} \neq 0$, respectively, reads

$$
P[f_0, f_a] = \int \mathcal{D}f \delta \left( f_0 - \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \hat{f}(\mathbf{q}) \right) \delta \left( f_a - \int \frac{d^2 \mathbf{q}}{(2\pi)^2} \hat{f}(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{a}} \right)
$$

$$
= \frac{1}{2\pi \sqrt{\lambda_+ \lambda_-}} \exp \left\{ \frac{1}{2} \left( f_0, f_a \right) \mathbf{\Sigma}^{-2} \left( f_0, f_a \right) \right\}
$$

using the formula

$$
\int_{-\infty}^{\infty} \prod_{i=1}^{N} dx_i \exp \left\{ -\frac{1}{4} x_i A_{ij} x_j + s_i x_i \right\} = \frac{2^{N} \pi^{\frac{N}{2}}}{\sqrt{\det A}} \exp \left\{ s_i A^{-1} x_i \right\}
$$

for any symmetric and positive definite matrix $(A_{ij})$ with the matrices of the variances $(\mathbf{\Sigma}^2 \mathbf{\Sigma}^{-2} = \mathbf{I})$

$$
\mathbf{\Sigma}^2 = \begin{pmatrix} \sigma^2 & \sigma^2(\mathbf{a}) \\ \sigma^2(\mathbf{a}) & \sigma^2 \end{pmatrix}, \quad \mathbf{\Sigma}^{-2} = \begin{pmatrix} \sigma^2 & -\sigma^2(\mathbf{a}) \\ -\sigma^2(\mathbf{a}) & \sigma^2 \end{pmatrix}
$$

where $\sigma^2$ is given by Eq. (27). The eigenvalues

$$
\lambda_{\pm}(\mathbf{a}) = \sigma^2 \pm \sigma^2(\mathbf{a}) \geq 0
$$

of the matrices $\mathbf{\Sigma}^2$ and $\lambda_{+} \lambda_{-} \mathbf{\Sigma}^{-2}$ are determined by Eq. (27) and by the correlation function

$$
\sigma^2(\mathbf{a}) = \int \frac{d^2 q}{(2\pi)^2} \frac{k_B T}{E(q)} \cos(\mathbf{q} \cdot \mathbf{a})
$$

$$
= \int_{q_{min}}^{q_{max}} dq \frac{k_B T}{2\pi} E(q) J_0(qa),
$$

with $\sigma^2(a = 0) = \sigma^2$ and where $J_0(x)$ denotes the Bessel function with $J_0(x \to 0) = 1 - \frac{x^2}{2} + \mathcal{O}(x^4)$ and $J_0(x \to \infty) = (\sin x + \cos x) \frac{1}{\sqrt{\pi x}} + \mathcal{O}(x^{-1})$. Since $E(q)$ increases at least as $\sim q^2$ for large $q$ the latter property of $J_0(x)$ allows one to set $q_{max} = \infty$ for any finite $a$. For $q_{min} = 0$ and $q_{max} = \infty$ and $E(q)$ given by Eq. (10) one finds for the correlation function defined in Eq. (35)

$$
\sigma^2(\mathbf{a}) = \frac{k_B T}{2\pi \gamma_0} K_0 \left( \frac{a}{L_c} \right), \quad \kappa_0 = 0,
$$

$$
\rightarrow \frac{k_B T}{2\pi \gamma_0} \ln(L_c/a), \quad L_c >> a,
$$

where $K_0(x)$ denotes the modified Bessel function. One recovers the distribution of the interface position (Eq. (28))

$$
P[f_0; \sigma] = \int_{-\infty}^{\infty} df_a \ P[f_0, f_a; \mathbf{\Sigma}]
$$

by integrating over the positions at $\mathbf{a}$.
Note that the conditional probability

\[
P[f_0, f_a]/P[f_0] = \exp \left\{ \frac{-1/2 \left( f_0^2/\sigma^2(a) - 1 + f_0^2/\sigma^2 - 2 f_0 f_a \sigma^2(a)/\sigma^4 \right)}{\sqrt{2\pi\sigma^4(1 - \sigma^4(a)/\sigma^4)}} \right\}
\]

is not a function of \( \delta f = f_0 - f_a \) alone, but depends on \( f_0 \) and \( f_a \) separately. For the distribution of the difference \( \delta f(a) := f(\mathbf{R} + a) - f(\mathbf{R}) \), i.e., the probability that at given points \( \mathbf{R} \) and \( \mathbf{R} + a \) the height difference has a certain value \( \delta f(a) \), one finds not the conditional probability, Eq. (41), but the expression

\[
P[\delta f(a)] = \int df P[f_0 + f, f_a + f] \\
= \int_{-\infty}^{\infty} \frac{df}{2\pi \sqrt{\lambda_+ \lambda_-}} \exp \left\{ -\frac{\left( f + \frac{f_0 + f_a}{2} \right)^2}{\lambda_+} + \frac{(f_0 - f_a)^2}{4\lambda_+} - \frac{\sigma^2(f_0 - f_a)^2}{2\lambda_+ \lambda_-} \right\}
\]

with

\[
\sigma^2(a) = 2\lambda_- = 2(\sigma^2 - \sigma^2(a)) = \frac{1}{\pi} \int_{q_{\text{max}}}^{q_{\text{min}}} dq \frac{k_B T}{E(q)} q(1 - J_0(qa)) .
\]

Due to the translational invariance in lateral directions this distribution for \( f(\mathbf{R} + a) - f(\mathbf{R}) \) is independent of \( \mathbf{R} \) so that without loss of generality one can set \( \mathbf{R} = 0 \). The finite difference variance \( \sigma^2_\delta(a) \) is shown in Fig. 2 for the phenomenological capillary wave model with \( \frac{E(q)}{E_0} = 1 + \frac{L_\kappa^2 q^2}{1 + L_c^2 q^2} \) (see Eqs. (10) and (12)) and the effective length scales \( L_c = \sqrt{\gamma_0/E_0} \) and \( L_\kappa = \sqrt{\kappa_0/\gamma_0} \) given by Eq. (22).

![Figure 2: Finite difference variance \( \sigma^2_\delta(a) \) (Eq. (43)) normalized by the variance \( \sigma^2 \) of the interface position (Eq. (27)) as function of \( a/L_\kappa \) for various values of \( L_\kappa/L_c \) (Eq. (22)) for the phenomenological capillary wave model (Eqs. (10) and (12)). The quadratic increase of \( \sigma^2_\delta(a) \) in the limit \( a \to 0 \) (see Eq. (44)) is visible on the scale \( a/L_\kappa \) only for small values of \( L_\kappa/L_c \).](image-url)
In the limit $|a| \to \infty$ one recovers the variance $2\sigma^2$ corresponding to two independently fluctuating interfaces. In the limit $|a| \to 0$ one finds

$$\sigma_g^2(a) \to \sigma^2 a^2 + O((q_{\text{max}}a)^4)$$

(44)

in accordance with the expectation that for small distances $a$ the difference $f(R + a) - f(R)$ is determined by the slope of $f(R)$, so that its variance is given by the variance $\sigma' = \sigma_{2,0} = \sigma_3/\sqrt{2}$ of the slope (see Eq. (40)) times the distance $a$.

The comparison of Eqs. (43) and (30) allows one to express the variance $\sigma^2$ of the local slope in terms of the finite distance variance $\sigma_g^2(a)$ for the height distribution at an effective lateral distance $a(L_\kappa q_{\text{max}}, L_c q_{\text{max}})$:

$$\sigma^2 a_0^2 = \sigma_g^2(a(L_\kappa q_{\text{max}}, L_c q_{\text{max}}))$$

(45)

where $\sigma^2 a_0^2$ is a local estimate of the variance $\sigma_g^2(a_0)$ at a finite distance $a_0$. For small values of $a_0$ one may apply the expansion in Eq. (44) yielding $a(L_\kappa q_{\text{max}}, L_c q_{\text{max}}) = a_0$, but for finite distances the effective lateral distance $a(L_\kappa q_{\text{max}}, L_c q_{\text{max}})$ is determined implicitly by

$$0 = \int_0^1 dy \frac{1 - (a_0 q_{\text{max}} y)^2/4 - J_0(a(L_\kappa q_{\text{max}}, L_c q_{\text{max}}) q_{\text{max}} y)}{(L_c q_{\text{max}})^2 + y^2 + (L_\kappa q_{\text{max}})^2 y^4}.$$  

(46)

The solution of Eq. (46) is plotted in Fig. 3 for several values of the capillary length $L_c q_{\text{max}}$. For sufficiently small distances $a_0$ one finds $a(L_\kappa q_{\text{max}}, L_c q_{\text{max}}) \approx a_0$. In general, the numerical equivalence of the finite distance approach and the local slope estimate, i.e., of $a$ and $a_0$ becomes better for increasing length scales $L_c$ and $L_\kappa$.

In order to obtain a good agreement of the local slope estimate $\sigma^2 a_0^2$ and the finite distance variance $\sigma_g^2(a)$ the distance $a_0$ should be smaller than $L_c$ and also smaller than $2\pi/q_{\text{max}}$.

The finite distance approach may be used as an alternative to regularize the fluctuation spectrum, i.e., to suppress the infrared divergence caused by the large wavelength mode $q \to 0$ which leads to an infinite variance $\sigma$ for vanishing gravity, i.e., $E_0 = 0$. Instead of introducing a minimum value $q_{\text{min}}$ for the allowed wavevectors - which is necessary for local quantities such as the variance studied in Subsect. IV A (see Eq. (21)) - one can consider correlations at finite distances $a$ for which one can set $q_{\text{min}} = 0$.

Also the ultraviolet divergence, which is caused by the diverging number of large momenta modes and yields an infinite variance $\sigma' = \sigma_3/\sqrt{2}$ of the slope (see Eq. (30)) - even for a non-vanishing bending rigidity $\kappa_0$, may be regularized by the finite distance approach. Instead of introducing a maximum value $q_{\text{max}}$ for the allowed wavevectors - which is necessary for local quantities such as the variance studied in Subsect. IV A (see Eq. (24)) - one can consider differences $f(R + a) - f(R)$ at finite distances $a$ for which one can use $q_{\text{max}} = \infty$ if $\kappa_0 \neq 0$. The corresponding variance $\sigma_g^2(a)$ of the difference $\delta f(a)$ remains finite for $\kappa_0 > 0$ whereas even in this case the variance $\sigma^2$ of the local slope diverges.

But as one can see from Eq. (44) the finite difference variance $\sigma_g^2(a)$ is given by the variance $\sigma^2$ of the local slope for small values of $a$, so that both approaches are even almost quantitatively equivalent for distances $a \lesssim \frac{2\pi}{q_{\text{max}}}$ or for large $q_{\text{max}}$. At least for variances significant differences cannot be observed. Therefore in the following we apply the simpler and conceptually more straightforward approach of local orientations with wavevectors larger than $q_{\text{max}}$ being not permitted.

C. Distribution of metric $g$ and tilt angle $\theta$

The geometry of an interface can be described by the so-called ‘fundamental forms’ of the two-dimensional manifold $f(R)$. Thus we need to derive the probability distribution of the tangent vectors $t_i$ $(i = x, y)$, the normal vector $n$ (see Eq. (2)), and the metric tensor $g_{ij} = t_i \cdot t_j$. For the tangent vectors

$$t_x = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad t_y = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

(47)

it is sufficient to know the distribution $P[\partial_i f; \sigma']$ of the derivative given by Eq. (29). Notice that we do not normalize the tangent vectors because we want to keep the relation $g_{ij} = t_i \cdot t_j$ for the metric. Then the probability distribution for the metric tensor reads

$$P[g_{xx}] = P[g_{yy}] = \frac{1}{\sqrt{2\pi} \sigma_g} e^{-\frac{2\sigma_{\text{max}}}{\sqrt{2}}}$$

(48)
FIG. 3: Effective lateral distance $a(L_c q_{\text{max}}, L_c q_{\text{max}})$ at which the variance $\sigma^2$ of height differences equals the estimate $\sigma^{'2}$ from the local slope variance (see Eqs. (43) and (45)): (a) for $a_0 q_{\text{max}} = 1$; (b) for $L_c q_{\text{max}} = \infty$; (c) for $a_0 = L_\kappa$; and (d) for $a_0 q_{\text{max}} = 3$. The ratio $a/a_0$ decreases towards unity for increasing values of $L_\kappa$ and decreasing finite distances $a_0$.

with $g_{xx} = 1 + f_x^2(R) > 1$ and $\sigma_g = \sigma_3$ given by Eq. (31). The off-diagonal values $g_{xy} = g_{yx} = f_x(R)f_y(R)$ are more complicated but can nevertheless be derived explicitly ($f_x = f_0^{(1,0)}$ and $f_y = f_0^{(0,1)}$, Eq. (28))

$$
P[g_{xy}] = \int_{-\infty}^{\infty} df_x \int_{-\infty}^{\infty} df_y P[f_x]P[f_y] \delta(g_{xy} - f_x f_y)$$

$$ = \int_{-\infty}^{\infty} df_x P[f_x] \int_{-\infty}^{\infty} df_y P[f_y] \delta(g_{xy} - f_x f_y)$$

$$ = \frac{1}{2\pi\sigma^2} \int_0^{\infty} dy e^{-\frac{1}{\sigma^2}\left(1+\frac{y^2}{\sigma^2}\right)}$$

$$ = \frac{1}{\pi\sigma^2} K_0 \left( \frac{|g_{xy}|}{\sigma^2} \right)$$

(49)

with (see Eqs. (29) - (31)) $\sigma_{x,0} = I_{1,0}\sigma_3 = \frac{1}{2}\sigma_3^2 = \sigma^2 = \sigma_y^2/2$. Here, we have used the integral expressions

$$
\int_0^{\infty} dx e^{-\gamma x - \beta/(4x)} = \sqrt{\frac{\beta}{\gamma}} K_1(\sqrt{\beta\gamma})
$$

(50)
FIG. 4: (a) The probability distribution $P[\theta]$ of the tilt angle $\theta$ is given by Eq. (55). (b) The position $\theta_{\text{max}}$ of the maximum increases with increasing variance $\sigma_g^2 = 2\sigma_y^2 = \sigma_3^2$ (Eq. (30)), and approaches the limiting value $\pi/2$ for an infinitely rough interface. The maximum value $P(\theta_{\text{max}})$ depends non-monotonically on $\sigma_g^2$. The width $\Delta \theta$ at $P(\theta_{\text{max}})/2$ reaches its maximum value 0.69 for $\sigma_g^2 = 0.89$. and

$$\int_0^\infty \frac{dx}{x} e^{-\gamma x - \beta/(4x)} = 2K_0(\sqrt{\beta\gamma}) = -2(K_1'(\sqrt{\beta\gamma}) + \frac{K_1(\sqrt{\beta\gamma})}{\sqrt{\beta\gamma}})$$

(51)

yielding the modified Bessel functions $K_0(z)$ and $K_1(z)$. Then, for the determinant $g = \det(g_{ij}) = 1 + (\nabla f(R))^2$ it follows straightforwardly the exponential distribution

$$P[g] = \int_{-\infty}^{\infty} df_x \int_{-\infty}^{\infty} df_y \ P[f_x]P[f_y] \delta(g - f_x^2 - f_y^2)$$

$$= \frac{1}{\pi \sigma_{g,0}^2} \int_{0}^{\sqrt{g-1}} df_x \frac{df_x}{\sqrt{g-1 - f_x^2}} e^{-\frac{g-1}{2\sigma_{g,0}^2}}$$

$$= \frac{1}{\sigma_g^2} e^{-\frac{g-1}{2\sigma_g^2}} \ (52)$$

with $g > 1$ and the mean value and variance

$$<g> = 1 + \sigma_g^2 \ , \quad <g^2> - <g>^2 = \sigma_g^4 \ ,$$

(53)

respectively. Since $P[g_{xy}] = P[-g_{xy}]$ the mean values of the off-diagonal elements vanish, so that the mean value of the metric reads

$$<g_{ij}> = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 + \sigma^2 & 0 \\ 0 & 1 + \sigma^2 \end{pmatrix} \ .$$

(54)

Using Eqs. (1), (2), and (52) one can deduce the probability distribution $P[\theta]$ for the tilt angle $\theta$ between the normal $n$ of the interface and the vertical axes $e_z$. With $\theta = \arccos \left( \frac{1}{\sqrt{g}} \right)$ and noting that due to $g \in [1, \infty)$ one has $\theta \in [0, \pi/2)$, which excludes overhangs, we find ($\sigma_g^2 = 2\sigma^2 = \sigma_3^2$, Eq. (30))

$$P[\theta] = \frac{2}{\sigma_g^2 \cos^3 \theta} e^{-\frac{\theta_{\text{max}}^2}{\sigma_g^2}} \ , \quad \sigma_g^2 = \int_{q_{\text{min}}}^{q_{\text{max}}} dq q^3 k_B T \ ,$$

(55)
which is shown in Fig. 4 for various values of $\sigma_g^2$. Notice that the maximum of $P[\theta]$ at

$$\theta_{\text{max}} = \arctan \left( \frac{1}{2} \sqrt{3\sigma_g^2 - 2 + \sqrt{9\sigma_g^4 - 4\sigma_g^2 + 4}} \right)$$  \hspace{0.5cm} (56)$$

approaches the limiting values $\theta_{\text{max}} = 0$ for $\sigma_g \to 0$ and $\theta_{\text{max}} = \pi/2$ for $\sigma_g \to \infty$. Close to the vertical direction the tilt angle of the normal vector $\mathbf{n}$ is distributed linearly in $\theta$

$$P[\theta \to 0] = \frac{2\theta}{\sigma_g} \left( 1 + \left( \frac{4}{3} - \frac{1}{\sigma_g^2} \right) \theta^2 + \mathcal{O}(\theta^4) \right)$$  \hspace{0.5cm} (57)$$

whereas one finds an exponentially vanishing distribution towards the horizontal limit

$$P[\theta \to \pi/2] = \frac{2}{\sigma_g^2} \frac{1}{(\pi - \theta)^3} e^{-\frac{\pi - \theta}{\sqrt{\sigma_g}} \theta}.$$  \hspace{0.5cm} (58)$$

With the probability distribution given by Eq. (55) one finds straightforwardly the mean value of the tilt angle $\theta$ (using partial integration and 3.383.10 in Ref. [32]):

$$< \theta > = \int_0^\infty dx \ e^{-x} \arctan \sqrt{x\sigma_g^2} = \frac{1}{2\sigma_g} \int_0^\infty dx \ x^{-\frac{1}{2}} e^{-\frac{x}{x + \sigma_g^2}}$$

$$= \frac{\pi}{2} e^{\sigma_g^2} \left( 1 - \Phi(\sigma_g^{-1}) \right)$$

$$= \left\{ \begin{array}{ll}
\sqrt{\pi} \sum_{k=0}^\infty (-1)^k 2^{-k-1} (2k - 1)!! \sigma_g^{2k+1}, & \sigma_g < 1 \\
\frac{\pi}{2} e^{\sigma_g^2} - \sqrt{\pi} \sum_{k=0}^\infty \frac{2^k}{(2k+1)!!} \sigma_g^{2k-1}, & \sigma_g > 1
\end{array} \right.$$  \hspace{0.5cm} (59)$$

$$= \left\{ \begin{array}{ll}
\frac{\sqrt{\pi}}{\sigma_g} \left( \sigma_g - \frac{1}{2} \sigma_g^3 + \mathcal{O}(\sigma_g^5) \right)
\frac{\pi}{2} - \frac{\sqrt{\pi}}{\sigma_g} + \frac{\sigma_g^3}{2\sigma_g} - \frac{\pi}{3} + \mathcal{O}(\sigma_g^6), & \sigma_g \geq 1
\end{array} \right.$$  \hspace{0.5cm} (59)$$

Here, $\Phi(x)$ denotes the error function

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2} \, dt$$  \hspace{0.5cm} (60)$$

with its series representations

$$\Phi(x) = \frac{2}{\sqrt{\pi}} \sum_{k=1}^\infty \frac{(-1)^{k+1}}{(2k-1)!!} \frac{x^{2k-1}}{(2k-1)(k-1)!}$$

$$= \frac{2}{\sqrt{\pi}} e^{-x^2} \sum_{k=0}^\infty \frac{2^k x^{2k+1}}{(2k+1)!!}$$  \hspace{0.5cm} (61)$$

and

$$1 - \Phi(x) = \frac{1}{\pi} e^{-x^2} \sum_{k=0}^\infty \frac{(-1)^k \Gamma(k + \frac{1}{2})}{x^{2k+1}}$$  \hspace{0.5cm} (62)$$

with $\Gamma(k + \frac{1}{2}) = 2^{-k}(2k - 1)!!\sqrt{\pi}$, i.e., $\Gamma(1/2) = \sqrt{\pi}$, $\Gamma(3/2) = \sqrt{\pi}/2$, $\Gamma(5/2) = 3\sqrt{\pi}/4$, and $\Gamma(7/2) = 15\sqrt{\pi}/8$. Accordingly one finds for the mean squared deviation $< (\delta \theta)^2 > = < \theta^2 > - < \theta >^2$

$$< (\delta \theta)^2 > = \int_0^\infty dx \ e^{-x} \left( \arctan \sqrt{x\sigma_g^2} \right)^2 - < \theta >^2$$

$$= \left\{ \begin{array}{ll}
\frac{4\pi \sigma_g^2}{\sigma_g^2} - \frac{16 - 3\pi}{12} \sigma_g^4 + \mathcal{O}(\sigma_g^6)
\frac{2 \ln \sigma_g}{\sigma_g} + \mathcal{O} \left( \frac{1}{\sigma_g} \right)
\end{array} \right.$$  \hspace{0.5cm} (63)$$
These structural features $<\theta>$ and $(\delta\theta)^2$ of a fluctuating interface are shown in Fig. 5 as function of the variance $\sigma_g^2 = 2\sigma'^2$. Notice that even in the limit $\sigma_g \to \infty$, i.e., for a soft interface at high temperatures (Eq. (55)), one does not obtain the mean value and mean squared deviation

$$
<\theta>_0 = \frac{\pi}{2} = \int_0^{2\pi} d\phi \frac{2\pi}{2\pi} \theta = 1
$$

and

$$
(\delta\theta)^2_0 = \frac{\pi}{2} = \int_0^{2\pi} d\phi \theta^2 - <\theta>_0^2 = \pi - 3
$$

of directions $n$ uniformly distributed on the unit semi-sphere. Thus in the limit of a tensionless (i.e., $\beta E(q) = 0$) fluctuating interface the average defined in Eqs. (23)-(25) is not reduced to the 'random-direction' average $<A>_0$ due to a geometric coherence induced by the manifold.

![Graph](image-url)

**FIG. 5:** Mean value $<\theta>$ and mean squared deviation $(\delta\theta)^2$ of the tilt angle between the interface normal $n$ and the axis $e_z$ orthogonal to the mean interface (see Fig. 1 and Eqs. (1), (2), (59), and (63)) as function of the variance of the height fluctuations $\sigma_g^2 = 2\sigma'^2$ (see Eqs. (30), (52), (53), and (55)). The mean squared deviation obtains its maximum value $(\delta\theta)^2_{max} = 0.072$ for $\sigma_g^2 = 2.66$.

### D. Infrared and ultraviolet limit

The fluctuation spectrum (see Eqs. (27) and (6))

$$
\tilde{\sigma}^2(q) = \frac{k_B T}{E(q)}
$$

of the interface position $f(R)$ diverges in the limit of large wavelengths, $q \to 0$, and vanishing gravitation constant $G$, i.e., $E_0 \to 0$ (see Eq. (12)). This infrared divergence is a direct consequence of the occurrence of a so-called Goldstone mode with vanishing excitation energy (or effective mass). This mode exists because of the spontaneous symmetry
breaking of the translational invariance of the system due to the formation of an interface at \( f(\mathbf{R}) \) and due to the fact that the mean interface position can be shifted without any cost of free energy if \( G = 0 \) and without pinning lateral boundary conditions.

In contrast to \( \tilde{\sigma}^2(q) \), the fluctuation spectrum

\[
\tilde{\sigma}^2(q) = \frac{k_B T}{E(q) q^2} \frac{k_B T}{\gamma_0}
\]

(66)
of the metric (\( \sigma_\theta = \sigma_3 \); see Eqs. (30) and (55), i.e., of the orientations and of the tilt angle, remains finite in the limit of a vanishing gravitational constant \( G \) (see Eq. (12)). It does not diverge because the Goldstone mode at \( q = 0 \) is flat (corresponding to a rigid shift \( f = \text{const} \)) and does not contribute to an increase of the fluctuations of the local orientations, i.e., fluctuations of the tilt angle \( \theta \). In other words, modes with wavevector \( q \) contribute only proportional to \( q^2 \) to the distortion of a flat metric which finally suppress the spectrum in Eq. (66) in the long-wavelength limit \( q \to 0 \), i.e., \( \tilde{\sigma}^2(q \to 0) \) is a constant.

In contrast to the infrared case, the ultraviolet limit \( q \to \infty \) becomes more violent for local orientations as compared to the case of positional fluctuations of an interface. Heuristically one may argue that small-scale undulations (ripples) do not alter the position considerably but accentuate the more horizontal local orientations due to the many 'steep hills' or descents with numerous sharply rising or falling slopes.

As a consequence the local orientations are very sensitive to the dependence of surface energies at large wavevectors—a regime which has been studied recently by grazing incident X-ray scattering [10,11,12]. This kind of experiment provides only access to \( \tilde{\sigma}^2(q) \) which makes it difficult to resolve the details of \( E(q) \) at large \( q \). These features are enhanced by monitoring the fluctuations of the tilt angle which are governed by \( \tilde{\sigma}^2(q) = q^2 \tilde{\sigma}^2(q) \).

E. Correlation function \( < \theta(0) \theta(a) > \) of tilt angles

The standard characterization of a fluid interface is given in terms of its surface tension, its mean position, the local height fluctuations, and the lateral height-height two-point correlation function. The latter one determines the diffuse scattering intensities of X-rays or neutrons from such an interface. In the present study we have put forward the mean tilt angle (and its variance) as an alternative characterization of a fluid (see Fig. 5). The temperature dependence of the scattering intensities of X-rays or neutrons from such an interface. In the present study we have put forward the mean is a more complex function. However, the analytic derivation of the distribution \( \Phi(n,m) \) (compare Eq. (28)) at the lateral positions \( a = (n,a) \). From that the joint distribution \( P[\theta(0),\theta(a)] \) of the metrics can be derived and finally \( \Phi(n,m) \) at a finite distance.

The concept of orientational fluctuations is frequently used in the context of microemulsions, membranes, and macromolecules. There a persistence length is defined which characterizes the correlation \( < \mathbf{n}(0) \cdot \mathbf{n}(a) > \) of two normal vectors at finite but not too large distances [38]. Although related the correlation \( < \theta(0) \theta(a) > = < \arccos(\mathbf{n}(0) \cdot \mathbf{e}_z) \arccos(\mathbf{n}(a) \cdot \mathbf{e}_z) > \) is a more complex function. However, the analytic derivation of the distribution \( \Phi[\theta(0),\theta(a)] \) allows us to determine the correlations exactly for arbitrary distances \( a \).

Following the same procedure as in Eqs. (20) and (44) one finds the joint probability of the \( N \) values \( f_i := f^{(n_i,m_i)}(a_i) \) (compare Eq. (25)) at the lateral positions \( a_i \) \( (i = 1, \ldots, N) \),

\[
P\left\{ f^{(n_i,m_i)}(a_i) \right\}_{i=1}^N = \frac{1}{(2\pi)^N \det(\Sigma^2)} \exp \left\{ -\frac{1}{2} \sum_{i,j=1}^N f_i \Sigma^{-1}_{ij} f_j \right\} \]

(67)

with the correlation matrix

\[
\Sigma^2_{ij} = \int \frac{d^2q}{(2\pi)^2} \frac{k_B T}{E(q)} q^{n_i+n_j} q^{m_i+m_j} S_{n_i+m_i,n_j+m_j} (\mathbf{q} \cdot (\mathbf{a}_i - \mathbf{a}_j)) = \Sigma^2_{ji}
\]

(68)

\[
= \pm \begin{cases} 
\tilde{\sigma}^2_{n_i+n_j,m_i+m_j} (\mathbf{a}_i - \mathbf{a}_j) , & \text{even} \\
\tilde{\sigma}^2_{n_i+n_j,m_i+m_j} (\mathbf{a}_i - \mathbf{a}_j) , & \text{odd}
\end{cases},
\]

\[
\tilde{\sigma}^2_{n_i+n_j,m_i+m_j} = \frac{k_B T}{E(q)} q^{n_i+n_j} q^{m_i+m_j} S_{n_i,m_i,n_j,m_j} \]

where \( E(q) \) is the energy of the wavevector \( q \). The correlation between the local orientations is given by the correlation function \( \Phi(n,m) \) at the lateral positions \( a = (n,a) \).
\[ S_{\nu,\mu}(x) = \frac{(-1)^{\frac{\nu-\mu}{2}} + (-1)^{\frac{\nu+m}{2}}}{2} \cos x + \frac{(-1)^{\frac{\nu-\mu}{2}} - (-1)^{\frac{\nu+m}{2}}}{2} \sin x , \quad (69) \]

and the correlation functions for \( n + m \) even (compare Eqs. (29) and (38))

\[
\sigma^2_{n,m}(a) = \int \frac{d^2q}{(2\pi)^2} \frac{k_BT}{E(q)} q^n_y q^m_y \cos(qa) , \quad n + m \text{ even} ,
\]

\[
= (-1)^{\frac{n+m}{2}} \frac{\partial^{n+m}}{\partial a_x^n \partial a_y^m} \sigma^2(a) 
\]

\[
= \sum_{i,j = 0}^{\infty} \frac{(-1)^{i+j}}{ij!} I_{n+m} \frac{m+j}{2} \sigma^2_{n+m+i+j+1} a^i_x a^j_y 
\]

as well as for \( n + m \) odd

\[
\tau^2_{n,m}(a) = \int \frac{d^2q}{(2\pi)^2} \frac{k_BT}{E(q)} q^n_y q^m_y \sin(qa) 
\]

\[
= (-1)^{\frac{n+m+1}{2}} \frac{\partial^{n+m}}{\partial a_x^n \partial a_y^m} \sigma^2(a) 
\]

\[
= \sum_{i,j = 0}^{\infty} \frac{(-1)^{i+j}}{ij!} I_{n+m} \frac{m+j}{2} \sigma^2_{n+m+i+j+1} a^i_x a^j_y . 
\]

For the calculation of the correlation function \(< \theta(0)\theta(a) > \) the joint probability distribution is needed only for the vector \( f = (f^{(1,0)}(0), f^{(0,1)}(0), f^{(1,0)}(a), f^{(0,1)}(a)) \) given by the matrices

\[
\Sigma_{ij} = \begin{pmatrix}
\sigma^2 & 0 & \sigma^2_{2,0}(a) & \sigma^2_{1,1}(a) \\
0 & \sigma^2 & \sigma^2_{1,1}(a) & \sigma^2_{0,2}(a) \\
\sigma^2_{2,0}(a) & \sigma^2_{1,1}(a) & \sigma^2 & 0 \\
\sigma^2_{1,1}(a) & \sigma^2_{0,2}(a) & 0 & \sigma^2 \\
\end{pmatrix} \quad \text{and} \quad \Sigma^{-2} = \begin{pmatrix} A_{ij} & B_{ij} \\
B_{ij} & A_{ij} \end{pmatrix} \quad (72) 
\]

with the matrix elements

\[
A_{11} = \frac{\sigma^4}{\det(\Sigma^2)} (\sigma^4 - \sigma^4_{0,2}(a) - \sigma^4_{1,1}(a)) \\
A_{12} = \frac{\sigma^4}{\det(\Sigma^2)} (\sigma^4_{1,1}(a)(\sigma^2_{2,0}(a) + \sigma^2_{0,2}(a))) \\
A_{22} = \frac{\sigma^4}{\det(\Sigma^2)} (\sigma^4 - \sigma^4_{2,0}(a) - \sigma^4_{1,1}(a)) \\
B_{11} = -\frac{\sigma^2}{\det(\Sigma^2)} (\sigma^4_{1,1}(a)\sigma^2_{0,2}(a) + \sigma^2_{2,0}(a)(\sigma^4 - \sigma^2_{0,2}(a))) \\
B_{12} = -\frac{\sigma^2}{\det(\Sigma^2)} (\sigma^4_{1,1}(a)(\sigma^4 + \sigma^2_{2,0}(a)\sigma^2_{0,2}(a) - \sigma^4_{1,1}(a))) \\
B_{22} = -\frac{\sigma^2}{\det(\Sigma^2)} (\sigma^4_{1,1}(a)\sigma^2_{2,0}(a) + \sigma^2_{0,2}(a)(\sigma^4 - \sigma^2_{2,0}(a))) 
\]

(73)

and the determinant

\[
\det(\Sigma^2) = \sigma^8 - \sigma^4(\sigma^4_{2,0}(a) + \sigma^4_{0,2}(a)) - 2\sigma^4_{1,1}(a)(\sigma^4 + \sigma^2_{2,0}(a)\sigma^2_{0,2}(a)) + \sigma^4_{1,1}(a) + \sigma^4_{2,0}(a)\sigma^2_{0,2}(a). \quad (74) 
\]
Repeating the derivation presented in Subsec. IV C, one finds the following explicit expression for the joint probability distribution

\[ P[\theta_0, \theta_a] = \frac{4\sin \theta_0 \sin \theta_a}{\cos^3 \theta_0 \cos^3 \theta_a} \frac{1}{\sqrt{\det(\Sigma^2)}} \int_0^\pi d\phi d\phi' e^{-\frac{1}{2}(\tan \theta_0, \tan \theta_a)^T C(\phi, \phi')(\tan \theta_0, \tan \theta_a)^T} \]

(75)

of the tilt angles at different positions of the random fluctuating interface. The elements of the matrix \( C(\phi, \phi') \) are given by

\[
C_{11}(\phi) = A_{11} \cos^2 \phi + A_{22} \sin^2 \phi + 2A_{12} \cos \phi \sin \phi \\
C_{22}(\phi') = A_{11} \cos^2 \phi' + A_{22} \sin^2 \phi' + 2A_{12} \cos \phi' \sin \phi' \\
C_{12}(\phi, \phi') = C_{21} = B_{11} \cos \phi \cos \phi' + B_{22} \sin \phi \sin \phi' + B_{12}(\cos \phi \sin \phi' + \sin \phi \cos \phi').
\]

(76)

FIG. 6: The correlation function \( < \theta(0)\theta(a) > \) for the tilt angles \( \theta \) depends effectively only on the variance \( \sigma_\theta^2 \) of the metric and on the functional form of the energy function \( \tilde{E}(y) = 1 + L_q q_{\max}^2 y^2 (1 + \tilde{\kappa}(y)^2) \), i.e., on the wavevector-dependent bending rigidity \( \tilde{\kappa}(y) \). Here, we have chosen (a) \( \tilde{\kappa}(y) = 0 \), for variances \( \sigma_\theta^2 = 0.2, 2.0, \) and \( 20 \) as well as (b) \( \sigma_\theta^2 = 20 \) and bending rigidities \( \tilde{\kappa}(y) = 1 + (L_q q_{\max})^2 y^2 \) with \( L_q q_{\max} = 0, 1, \) and \( 10 \) (see Eq. (74)). The dependence on the ratio \( L_q q_{\max} \) of the cut-off lengths is small, so that for physical relevant values \( L_q q_{\max} > 10 \) no significant change is observed. Here, we have chosen \( L_q q_{\max} = 10 \). The maximum at \( aq_{\max} \approx 0.0 \) does not reflect a minimum in the surface tension \( \gamma(q) \) but seems to be related to the sharp cut-off \( q_{\max} \) for capillary waves.

Finally, the correlation function of the tilt angles \( \theta(0) \) and \( \theta(a) \) reads

\[
< \theta(0)\theta(a) > = \int_0^{\pi/2} d\theta(0)d\theta(a) < \theta(0)\theta(a) > P[\theta_0, \theta_a]
\]

\[ = \frac{\pi}{2} \frac{d\phi d\phi'}{\pi^2} \int_0^\infty dx_1 dx_2 x_1 x_2 \arctan(x_1) \arctan(x_2) e^{-\frac{1}{2}x^T C(\phi, \phi') x}, \]

(77)

which is shown in Fig. (a) for the phenomenological capillary wave theory with \( \gamma(q) = \gamma_0 \) and in Fig. (b) for finite bending rigidity \( \kappa_0 \) (see Eq. (10)). In general, one finds that the centered and normalized correlation function \( < \theta(0)\theta(a) > / < \theta >^2 \) does not depend sensitively on the particular functional form of the surface tension \( \gamma(q) \). In contrast to the one-point probability distribution \( P[\theta] \) given in Eq. (55), there is only a double-integral representation for the two-point probability distribution \( P[\theta_0, \theta_a] \) so that the determination of the correlation function \( < \theta(0)\theta(a) > \) involves a four-dimensional numerical integration, with the integrand depending parametrically on the distance \( a \) and functionally on the momentum dependent energy \( E(q) \). In order to be able to gain further insight into the expression given by Eq. (77) we study in the following section the dependence of the relevant variances \( \sigma_{\theta,n,m}^2(a) \) (Eq. (70)) on the physical parameters entering into \( E(q) \).


V. DEPENDENCE ON PHYSICAL PARAMETERS

Within the present Gaussian approach the observables $<\theta>$ and $(\delta\theta)^2$ are determined by the variance $\sigma_g$ (see Fig. 5). In this section we study the dependence of $\sigma_g^2 = \sigma_k^2$ on the physical parameters introduced in Sect. III. Since we do not consider systems with finite lateral extensions we set $q_{min} = 0$ and keep $G > 0$. Expressing the momentum dependent surface tension $\gamma(q)$ in terms of a momentum dependent bending rigidity (see Eqs. (12), (14), and (19)),

$$\gamma(q) = \gamma_0 + \kappa(q)q^2$$

one has in general

$$\sigma_k^2 = \frac{k_B T}{2\pi \gamma_0} q_{max}^{k-1} S_k(L_c q_{max}; [\kappa(q)])$$

with the normalized and dimensionless variances

$$S_k(x; [\bar{\kappa}(q)]) = \int_0^1 dy \frac{y^k}{x^2 + y^2 + y^4 \bar{\kappa}(y)}$$

where $\bar{\kappa}(y) = q_{max}^2 \kappa(q = q_{max})/\gamma_0$ is dimensionless and

$$S_k>1(x \rightarrow \infty; [\bar{\kappa} = 0]) = \frac{1}{k-1}.$$  

A. Phenomenological capillary wave theory

The phenomenological capillary wave theory is defined by Eqs. (7)-(10) with $\kappa_0 = const$. For the special case $\kappa_0 = 0$ the normalized variances $S_k(x, \bar{\kappa})$ (Eqs. (79) and (80)) for $k = 1, 2, \text{and} 3$ read:

$$S_1(x; 0) = \frac{1}{2} \ln(1 + x^2),$$

$$S_2(x; 0) = 1 - \frac{\arctan x}{x},$$

$$S_3(x; 0) = \frac{1}{2} \left( 1 - \frac{\ln(1 + x^2)}{x} \right).$$  

(82)

For large capillary lengths $x = q_{max} L_c >>> 1$ (Eq. (22)), which corresponds to the typical physical situation, one has (3.194.5 in Ref. [32])

$$T_{k>1}(\bar{\kappa}_0) \equiv S_{k>1}(x = \infty, \bar{\kappa}_0) = \frac{1}{k-1} _2F_1(1, \frac{k-1}{2}; \frac{k+1}{2}; -\bar{\kappa}_0)$$

where (Eq. (22))

$$\bar{\kappa}_0 = q_{max}^2 \kappa_0/\gamma_0 = (q_{max} L_c)^2.$$  

(84)

For $k = 2$ and $k = 3$ one has

$$T_2(\bar{\kappa}_0) = S_2(x = \infty, \bar{\kappa}_0) = \frac{1}{\sqrt{\bar{\kappa}_0}} \arctan \sqrt{\bar{\kappa}_0}$$

and

$$T_3(\bar{\kappa}_0) = S_3(x = \infty, \bar{\kappa}_0) = \frac{1}{2\bar{\kappa}_0} \ln(1 + \bar{\kappa}_0),$$

(86)
respectively. For \( k = 1 \), \( S_k \) diverges in the limit \( L_c \to \infty \):

\[
S_1(x; \bar{\kappa}_0) = \frac{1}{2\sqrt{\Delta}} \ln \frac{2\bar{\kappa}_0(1 + \sqrt{\Delta}) + 1 - \Delta}{2\bar{\kappa}_0(1 - \sqrt{\Delta}) + 1 - \Delta}, \quad \Delta = 1 - \frac{4\bar{\kappa}_0}{x^2},
\]

\[
\lim_{x \to \infty} x - \frac{1}{2} \ln(1 + \bar{\kappa}_0) + O(x^{-2}) = \ln \frac{L_c}{L_\kappa} - \frac{1}{2} \ln \left(1 + \frac{\gamma_0}{\kappa_0 q_{\max}^2}\right) + O \left(\left(\frac{L_\kappa}{L_c}\right)^2\right)
\]

with \( \Delta > 0 \), i.e., \( L_\kappa < \frac{1}{2} L_c \). The function \( S_1(x, \bar{\kappa}_0) \) is shown in Fig. 7.

![Graph showing the dependence of \( S_1(x; \bar{\kappa}_0) \) on \( x = L_c q_{\max} \) for different values of \( L_\kappa q_{\max} \).](image)

**FIG. 7:** Dependence of the normalized variance \( \sigma^2/(k_B T/(2\pi \gamma_0)) = S_1(x; \bar{\kappa}_0 = (L_\kappa q_{\max})^2) \) (Eqs. (27), (87), and (88)) on the capillary length \( x = L_c q_{\max} \) in units of the minimum wavelength \( 2\pi/q_{\max} \).

The functions \( S_1(x; \bar{\kappa}_0) \) and \( S_3(x; \bar{\kappa}_0) \) determine the variances \( \sigma^2 = \sigma_1^2 \) and \( \sigma_g^2 = \sigma_3^2 = 2\sigma^2 \), respectively:

\[
\sigma^2 = \frac{k_B T}{2\pi \gamma_0} S_1(L_c q_{\max}; \bar{\kappa}_0)
\]

and

\[
\sigma_g^2 = \frac{k_B T}{2\pi \gamma_0} q_{\max}^2 S_3(L_c q_{\max}; \bar{\kappa}_0)
\]

with

\[
S_3(x; \bar{\kappa}_0) = \frac{1}{2\bar{\kappa}_0} \left(\frac{1}{2} \ln \left[1 + (1 + \bar{\kappa}_0)x^2\right] - S_1(x; \bar{\kappa}_0)\right).
\]

The variance \( \sigma_g^2 \) characterizes the distribution function of the tilt angle \( \theta \) (see Eq. (55) and Figs. 4 and 5) and is shown in Fig. 8.
In the previous subsection we have discussed various variances as they are predicted by the phenomenological capillary wave theory which is characterized by a constant bending rigidity \(\gamma_0\) and which leads to a monotonically increasing wavelength depending surface tension \(\gamma(q) = \gamma_0 + \kappa_0 q^2\).

The actual microscopic capillary wave theory is defined by Eqs. (12), (14), and (19) and enters into the variances \(S_3\) of the phenomenological theory. \(S_3\) remains finite in the limit \(L_c \to \infty\) even for \(\kappa_0 = 0\). The variance \(\sigma_3^2\) characterizes the distribution of the tilt angle (Eq. 55) and Figs. 4 and 9.

### B. Microscopic capillary wave theory

In Fig. 9 we show the normalized variances \(S_1\) and \(S_3\) corresponding to \(\sigma_1^2 = \sigma^2\) and \(\sigma_3^2 = \sigma_3^2\), respectively, as function of \(x = L_c q_{\text{max}}\) (see Eqs. (15) and (60)). As in the phenomenological case (Figs. 7 and 8) \(S_1\) diverges \(\sim \ln x\) for \(x \to \infty\) whereas \(S_3\) reaches a finite limit \(T_3 = S_3(x = \infty)\) for \(L_c \to \infty\). For Fig. 9 the underlying \(\gamma(q)\) is given by Eq. (19) which is characterized by the bulk correlation \(\xi\), the molecular diameter \(r_0\), and the dimensionless parameter \(C_H\); the forms of the functions \(S_k\) are independent of \(\gamma_0 = \gamma(q = 0)\) which enters only via \(L_c\) (Eq. 22). Here and in the following we choose \(C_H = 0.25\) which has turned out to describe properly available experimental data of \(\gamma(q)\) [10, 11]. With this choice \(S_k\) depends on \(x = L_c q_{\text{max}}, \kappa_0 q_{\text{max}}, \xi q_{\text{max}},\) and \(\xi/r_0\) (Eqs. (19) and (60)). In Fig. 9 we choose \(r_0 = 2\pi/q_{\text{max}}\) so that, with \(\xi q_{\text{max}} = 2\pi\xi/r_0\), \(S_k(x)\) depends parametrically only on \(\xi/r_0\). By using Eq. (20) this parametric dependence on \(\xi/r_0\) can be expressed in terms of \(\kappa_0 = (2\pi/r_0)^2\kappa_0/\gamma_0 = (L_c q_{\text{max}})^2\) (see Eq. (60)) with \(\xi_0 = (12\pi^2/(\xi/r_0)^4 + 3(\xi/r_0)^2)\) which facilitates the direct comparison with Figs. 4 and 9. One finds similar functional forms but the variances as determined from the microscopic capillary wave theory are larger than their phenomenological counterparts. This increase of the variances indicates an increase of interfacial fluctuations due to the decrease of the actual surface tension \(\gamma(q)\) for small wavelengths.

In Fig. 10 we show the dependence of the limiting value \(T_3 = S_3(x = \infty)\) on various microscopic quantities. As stated above \(T_3\) depends on \(\kappa_0 q_{\text{max}}, \xi q_{\text{max}},\) and \(\xi/r_0\) where only two of these parameters are independent so that Figs. 10 (a) and 10 (b) exhaust the available parameter space. Note, that Fig. 9 explores the \(x\) dependence...
within the parameter subspace $r_0 q_{\text{max}} = 2\pi$. Figure 10(c) shows the dependence on $L_c q_{\text{max}}$ as introduced in Figs. 7, 8, and 9. Using Eq. (20) with $C_H = 1/4$ one has $\kappa_0 = 33\gamma_0 r_0^2 \left( \frac{\xi^2}{\kappa_0} + \frac{\xi^2}{r_0^2} \right)$ so that with Eq. (22) $L_c q_{\text{max}} = \sqrt{\frac{3}{65} r_0 q_{\text{max}} \xi^2} \sqrt{1 + \frac{1}{2} \xi^2}$. Figure 10 demonstrates that for $L_c \to \infty$ the variance for the tilt angle

$$\sigma_g^2 = \frac{k_B T}{2\gamma_0 q_{\text{max}}^2} T_3, \quad L_c q_{\text{max}} = \infty,$$

(91)

as determined from the microscopic capillary wave theory deviates strongly from the predictions of the simple capillary wave theory ($\gamma(q) = \gamma_0$) and of the phenomenological capillary wave theory ($\gamma(q) = \gamma_0 + \kappa_0 q^2$ with $\kappa_0$ as given above). Moreover, Fig. 11 shows that $\sigma_g^2$ depends strongly on the microscopic parameters $\xi$, $r_0$, and $q_{\text{max}}$. This means that the tilt angle distribution is a sensitive probe of the large-q behavior of $\gamma(q)$ and of molecular details.

We note that for large correlation lengths the dependence of $T_3 = S_3(x = \infty)$ on $\xi/r_0$ differs qualitatively for the three theories under discussion, because of different functional forms of the bending rigidity function $\tilde{\kappa}(y)$ introduced in Eq. (80); whereas $\tilde{\kappa}(y) = 0$ and $T_3(\xi) = 1/2$ for the simple theory with $\gamma(q) = \gamma_0$, a constant bending rigidity $\tilde{\kappa}(y) = \kappa_0$ leads to $T_3(\xi) = \frac{1}{-\kappa_0} \ln(1 + \kappa_0)$ (see Eq. (80)) with $\kappa_0 = \frac{33}{65}(r_0 q_{\text{max}})^2 \left( \frac{\xi^2}{\kappa_0} + \frac{\xi^2}{r_0^2} \right)$ and therefore to the scaling behavior $T_3(\xi \gg r_0) \sim \xi^{-2} \ln(\xi/r_0)$ for the phenomenological capillary wave theory with $\gamma(q) = \gamma_0 + \kappa_0 q^2$. However, for the full microscopic theory given by Eq. (19) one finds for large correlation lengths

$$\tilde{\kappa}(y) \xrightarrow{\xi \to \infty} 0.74 C_H^2 \frac{\xi^4}{r_0^4} (r_0 q_{\text{max}})^2 (1 - (1 + r_0 q_{\text{max}}) y e^{-r_0 q_{\text{max}} y}) ,$$

(92)

i.e., $\tilde{\kappa}(y) \simeq \tilde{c}_0 y^2$ for $\frac{1}{q_{\text{max}}} \lesssim y \lesssim \frac{1}{r_0 q_{\text{max}}}$ with $\tilde{c}_0 = 0.37 C_H^2 (\xi q_{\text{max}})^4$. Thus $T_3 = \int_0^1 \frac{y dy}{1 + y^2} = \frac{1}{2\sqrt{\tilde{c}_0}} \arctan \sqrt{\tilde{c}_0}$ exhibits the scaling behavior $T_3(\xi \to \infty) \sim \xi^{-2}$ for the microscopic theory. These differences are important for the temperature dependence $T \to T_c$ which will be discussed in the following section.

### C. Temperature dependence

The temperature dependence of the local orientations of the liquid-vapor interface is of particular interest. The explicit results given above allow one to obtain a transparent view of the analytic structure of $< \theta > (T)$ and $< (\delta \theta)^2 > (T)$, as well as of its parametric dependence on various features of the intrinsic density profile (such as the correlation length $\xi$ and the stiffness parameter $C_H$) and of the interaction potential $w(r)$ (such as the molecular size $r_0$ and the range of the potential). This transparency follows from the product approximation for $\gamma(q)$ (see Eqs. (14)
the relations to the correlation length is needed. Moreover, it has the appealing property that at the triple point $r = \xi(r)$ values of $\nu$ exponent with using the analytic expression given in Eq. (21) with $\xi$ in Ref. [9].

Above so that we are able to assess the reliability of the product approximation compared to the full theory described and (19)). We have carried out a full numerical analysis of the temperature dependence for the model considered (a) entering the microscopic capillary wave theory (Eq. (19)); for simplicity the phenomenological capillary wave theory is shown only for $r_0q_{\text{max}} = 5$ in (a) and for $\xi/r_0 = 1$ in (b) since curves for other values of $r_0$ and $\xi$ can be obtained by rescaling the abscissa accordingly. Figure (2) corresponds to the parameter subspace $r_0q_{\text{max}} = 2\pi$. (c) Plotting $T_3$ as function of $L_\kappa q_{\text{max}} = \sqrt{r_0q_{\text{max}}^2/\kappa^2} \sqrt{1 + \frac{1}{r_0^2}}$ instead of $\xi/r_0$ or $r_0q_{\text{max}}$ allows a comparison of the microscopic theory with the phenomenological capillary wave theory for all bending rigidities $\kappa$ given by a single curve (circled solid line).

and (19)). We have carried out a full numerical analysis of the temperature dependence for the model considered above so that we are able to assess the reliability of the product approximation compared to the full theory described in Ref. [2].

For $T \to T_c$ the correlation length $\xi = \xi_0 t^{-\nu}$, $t = (T_c - T)/T_c$, diverges for $t \to 0$ where $\nu$ is a universal bulk exponent with $\nu = 0.5$ for the present mean field theory (Eqs. (13) and (16)). $\xi_0$ is a nonuniversal amplitude with $\xi_0 = r_0/2$ for the potential defined by Eq. (18). For temperatures well below $T_c$ the correlation lengths $\xi^{(i)}$ and $\xi^{(g)}$ in the liquid and in the vapor phase, respectively, differ from each other and from the limiting common form $\xi = \xi_0 t^{-\nu}$. Although it is straightforward to determine $\xi^{(i)}$ and $\xi^{(g)}$ numerically, we have opted for the advantage of using the analytic expression given in Eq. (21) with $\xi_0^{(i)} = r_0/2$. The expression in Eq. (21) has the virtue of fulfilling the relations $\xi^{(i)} > \xi(T) > \xi^{(g)}$ and will be used in the following whenever an explicit expression for the correlation length is needed. Moreover, it has the appealing property that at the triple point $T_{tr} \approx (2/3)T_c$ the correlation length $\xi(T_{tr}) \approx 0.58r_0$ is of the order of the microscopic cutoff length $r_0$, i.e., comparable to the diameter of the particles.

FIG. 10: Dependence of the normalized variance $T_3 = S(x = L_\kappa q_{\text{max}} = \infty)$ proportional to the variance $\sigma_\xi^2$ of the tilt angle (Eq. (21)) on $q_{\text{max}}$ and on the bulk correlation length $\xi$ (a) and the molecular diameter $r_0$ (b) entering the microscopic capillary wave theory (Eq. (19)); $C_H = \frac{1}{2}$. Comparison is made with the predictions of the simple capillary wave theory ($\gamma(q) = \gamma_0$) and the phenomenological capillary wave theory ($\gamma(q) = \gamma_0 + \kappa_0 q^2$ with $\kappa_0 = \frac{1}{4\pi} \nu r_0^2 (\xi_0^2 + \xi_0^2)$ (Eq. (20)); for simplicity the phenomenological capillary wave theory is shown only for $r_0q_{\text{max}} = 5$ in (a) and for $\xi/r_0 = 1$ in (b) since curves for other values of $r_0$ and $\xi$ can be obtained by rescaling the abscissa accordingly. Figure (2) corresponds to the parameter subspace $r_0q_{\text{max}} = 2\pi$. (c) Plotting $T_3$ as function of $L_\kappa q_{\text{max}} = \sqrt{r_0q_{\text{max}}}^2/\kappa^2} \sqrt{1 + \frac{1}{r_0^2}}$ instead of $\xi/r_0$ or $r_0q_{\text{max}}$ allows a comparison of the microscopic theory with the phenomenological capillary wave theory for all bending rigidities $\kappa$ given by a single curve (circled solid line).
Accordingly, one obtains for the temperature dependence of the variance \( \sigma^2 \) characterizing the tilt angle distribution (Eqs. (79), (20), and (21))

\[
\sigma_g^2 = 2 \lambda T^2 \left( 1 - \frac{T}{T_c} \right)^{-\frac{3}{2}} S_3(T)
\]

(93)

with

\[
\lambda = \frac{3.97 k_B T_c}{\pi^3} \left( \frac{q_{\text{max}} r_0}{w_0} \right)^2 .
\]

(94)

Within the density functional for fluids presented in Sec. III one has \( \frac{k_B T}{w_0} \approx 0.22 \) so that \( \lambda \approx 0.028 (q_{\text{max}} r_0)^2 \).

Whereas for the simple capillary wave theory \( \gamma(q) = \gamma_0 \) \( S_3(T) = \frac{1}{2} \) is constant, one finds for the microscopic theory with the bending rigidity \( \bar{\kappa}(y) \) given by Eq. (92) the temperature dependence \( S_3(T \rightarrow T_c) \sim t, \; t = 1 - \frac{T}{T_c} \), upon approaching the critical point at \( T_c \) so that with \( \gamma_0(t \rightarrow 0) \sim t^{3/2} \) within mean field theory \( \sigma_g^2(t \rightarrow 0) \sim t^{-1/2} \ln t \) diverges for \( T \rightarrow T_c \).

In contrast one finds \( S_3(T \rightarrow T_c) \sim t^2 \ln t \) for the phenomenological capillary wave theory with \( \gamma(q) = \gamma_0 + \kappa_0 q^2 \) and \( \kappa_0 = \frac{3}{35} \gamma_0 \gamma_0^2 \left( \frac{5 \pi^2}{2} + \frac{1}{2} \frac{\pi^2}{6} \right) \) (Eq. (20)), so that the variance \( \sigma_g^2 \) (Eq. (92)) does not diverge but vanishes as \( \sigma_g^2 \sim t^{1/2} \ln t \) for \( T \rightarrow T_c \). However, for the microscopic theory one finds \( S_3(T \rightarrow T_c) \sim t \) which implies \( \sigma_g^2 \sim t^{-1/2} \).

For the simple capillary wave theory (constant surface energy \( \gamma(q) = \gamma_0 \)) one has \( S_3(T) = \frac{1}{2} \) (Eq. (86) for \( \bar{\kappa}_0 = 0 \)) so that one finds the temperature dependences (Eqs. (53) and (13))

\[
< \theta > \underset{T \rightarrow T_c}{\sim} \frac{\pi}{2} - \sqrt{\frac{\pi^2}{2} + \frac{1}{2} t^\frac{2}{3}} - \sqrt{\frac{\pi^2}{2} - \sqrt{\frac{4\pi}{9\lambda^2} t^2 + \frac{\pi}{\lambda} t^\frac{2}{3}}} - \sqrt{\frac{\pi}{\lambda} t^\frac{1}{3}} + O(t^3)
\]

\[
< (\delta \theta)^2 > \underset{T \rightarrow T_c}{\sim} -\frac{3}{2} t^\frac{2}{3} \ln t, \; t = 1 - \frac{T}{T_c}, \; \gamma(q) = \gamma_0
\]

(95)

for the mean value \( < \theta > \) and the mean squared deviation \( < (\delta \theta)^2 > \) of the tilt angle \( \theta \), respectively (see Fig. 12).

The values for the mean tilt angle \( < \theta > \) and the mean squared deviations \( < (\delta \theta)^2 > \) depend strongly on the microscopic length scales \( r_0 q_{\text{max}} \), due to the sensitivity on the enhanced fluctuations of the interface on nanometer scales as predicted by the microscopic theory. In particular, the actual mean tilt angle is in general larger for the microscopic theory than the one predicted by the simple phenomenological capillary wave theory with a constant surface tension \( \gamma(q) = \gamma_0 \). Only close to the critical point where the increase of the surface energy \( \gamma(q) \) for large \( q \)
becomes dominant (Eq. (19)), the phenomenological capillary wave theory leads to larger values \( \langle \theta \rangle \) of the mean tilt angle, because it neglects bending energies. Due to the decrease in surface energy for wavevectors \( q \sim 2\pi/\xi \) (see Eq. (19)) and the increase \( \sim q^2 \) for larger wavevectors the asymptotic behavior in the microscopic theory is given by \( \pi/2 - \langle \theta \rangle \sim t^{1/4} \) and \( \langle (\delta\theta)^2 \rangle \sim t^{1/2} \ln t \) and not by the expressions given in Eq. (55) which hold for the simple capillary wave theory. The change of the asymptotic slopes is clearly visible in the double logarithmic plots in Figs. (c) and (d).

VI. RELATIONS WITH EXPERIMENTS

Spectroscopic determinations of molecular orientations at fluid interfaces provide valuable insights into the nature and structure of inhomogeneous fluid systems. These techniques render interfacial informations which are complementary to those which are obtained by X-ray and neutron scattering which give no direct access to orientational ordering at interfaces. Recently Simpson and Rowlen have discussed relationships between the capillary wave spectrum and the local tilt angle of the surface.

One finds in general two different types of approaches to measure local tilt angles of interfaces:

(i) The interface is decorated with anisotropic particles which keep either a fixed angle with the fluctuating interface or the thermal fluctuations of the molecule depend in a systematic way on the interface orientation. Assuming that
at low concentrations the decoration does not significantly modify the interfacial fluctuations, one can use the dipole moments of these macromolecules as a probe to measure surface specific properties such as the distribution of tilt angles (see, for instance, fluorescence and infrared spectroscopy, and Maxwell displacement current (MDC) measurements).

(ii) The fluctuating interface itself - albeit separating isotropic bulk phases of anisotropic fluid particles (e.g., carrying dipole moments) - can exhibit anisotropic features described by orientational profile (see, e.g., Ref. [34]). Assuming that such an orientational profile follows rigidly the fluctuations of the interface, one can probe selectively the interface, i.e., measure surface specific signals even without adding tracer macromolecules (see, for instance, second harmonic generation, AFM micrographs).

**Fluorescence Spectroscopy**

A standard way to measure molecular orientations at interfaces is using fluorescence spectroscopy. For such an excitation the polarization of the emitted light depends on the orientation \( \theta_e \) of the emitting dipole and the orientation \( \theta_a \) of the absorbing dipole which both are related to the orientation \( \theta \) of the molecule at the interface. The relations \( \theta_e(\theta) \) and \( \theta_a(\theta) \) depend on the chemical structure of the fluorescent molecule and are in general fixed and time-independent. The so-called time-dependent anisotropy decay is usually defined as

\[
\frac{r(t) = \frac{1}{2} \left( \frac{1}{2} < \cos^2 \theta_a(\theta) > - 1 \right. - \frac{1}{2} \cos^2 \theta_e(\theta) > }{\left. \frac{3}{2} < \cos^2 \theta_a(\theta) > - 1 \right)} , \quad (96)
\]

where \( < \cdot > \) denotes an average over the orientations \( \theta \) of the interface and thus probes the distribution function for the tilt angle \( \theta \) (Eq. [35]).

**Infrared Spectroscopy and linear dichroism**

A classical technique to measure directly the orientation of macromolecules at interfaces is infrared reflection-absorption spectroscopy (see, e.g., Ref. [38] and references therein). Molecular tilt angles of Langmuir-Blodgett films can be measured by the comparison of reflection and transmission intensities of infrared beams. The enhancement factor for the reflection-absorption to transmission-absorption intensities allows for a quantitative evaluation of molecular orientations [39]. However, the dependence on the orientation is rather complex.

Anisotropic mean orientations of molecules at interfaces give rise to dichroism, i.e., a polarization dependent absorption due to the associated orientation of the transition dipole moments. The intensity \( I \) of absorption is proportional to the mean squared cosine of the angle \( \theta_a \) between the transition moment axis and the electric field:

\[
I \sim \langle \cos^2 \theta_a \rangle . \quad (97)
\]

The angle \( \theta_a(\theta) \) is determined by the chemical structure of the absorbing molecule and by the orientation \( \theta \) of the interface normal. Because this relation is fixed, the orientational fluctuations of \( \theta_a \) are given by the probability distribution \( P[\theta] \) of the local orientation \( \theta \) of the supporting fluid interface (Eq. [36]). For applications see Ref. [14] and references therein.

**Generation of Maxwell displacement current (MDC)**

It is convenient to investigate, for instance, the electrical properties of monolayers of macromolecules floating on water surfaces (such as Langmuir-Blodgett films) by the surface potential method with which the Maxwell displacement current is measured [16, 17]. The induced charge \( Q \) at the electrode is directly proportional to the vertical component \( m_z \) of the dipole moment of the molecule, i.e., for uniaxial polar molecules

\[
Q \sim \langle \cos \theta \rangle = \int_0^{\pi/2} \sin \theta \cos \theta \, P[\theta] . \quad (98)
\]
Second harmonic generation (SHG)

As a second-order nonlinear optical process, the frequency doubling of light, i.e., the second harmonic generation, is forbidden in isotropic media and thus provides a signal exclusively from spatial regions exhibiting deviations from isotropy, such as interfaces. Therefore, it can be used to measure orientational order at interfaces. Such measurements have been primarily performed for films of dye molecules of reasonably high symmetry, so that the number of nonzero components of the second-order nonlinear optical tensor $\beta^{(2)}$ of the isolated molecule is small. In these cases, with one component often dominating the nonlinear response, the nonlinear susceptibility tensor $\chi^{(2)}$ of the film can be used to extract information on molecular orientation.

For an uniaxial system of rod-like molecules information about the molecular tilt angle can be inferred from the relation

$$\frac{2\chi_{zzz}^{(2)}}{\chi_{zzz}^{(2)} + 2\chi_{zxx}^{(2)}} = \frac{<\sin^3 \theta \cos \theta >}{< \cos \theta >}. \quad (99)$$

The value of each tensor component is proportional to the square root of the second harmonic intensity measured under the polarization conditions indicated by the indices. The first subscript denotes the direction of the generated polarization driven by polarized electric fields indicated by the second and the third index.

Direct Measurement of the tilt angle distribution

Finally, the tilt angle distribution $P[\theta]$ (see Eq. (55)) may be measured directly from an AFM micrograph provided that the tip diameter is smaller than the typical feature length of the interface. This experiment was done for solid interfaces such as silica surfaces (see Refs. [13, 14]) but may be achieved also for fluid interfaces when the capillary modes can be shock frozen quickly enough. For simple liquids the typical relaxations are too fast for any freezing technique to succeed in freezing the capillary waves. But for interfaces involving polymers such as polystyrene-air interfaces at temperatures close to the glass transition $T_g$, the tilt angle distribution may be measured by cooling fast below the critical temperature $T_g$ (see Ref. [46]).

Laser scanning confocal microscopy

Adding polymers to a colloidal suspension under suitable conditions induces a fluid-fluid demixing transition into a colloid-rich phase and a colloid-poor phase which are separated by a fluid interface. This phase separation is driven by entropic forces. The mesoscopic size of the colloidal particles leads to ultralow values of the surface tension which scales up the thermal interface roughness into the $\mu m$ regime. The corresponding interface fluctuations can be monitored directly in real space by laser scanning confocal microscopy and can be interpreted in terms of the capillary wave spectrum [22]. It seems to be possible to infer from such images also the local interface orientations and thus the full tilt angle distribution $P(\theta)$ as well as the lateral correlation function of tilt angles. This approach would be particular promising in that these systems allow one to tune the effective interaction between the colloidal particles within a wide range and thus generate designed forms of the wavelength dependent surface tension $\gamma(q)$ which governs the capillary waves. It might be possible to achieve a resolution down to the scale of the colloidal particles, which corresponds to short wavelengths on the atomic scale of simple fluids, and thus opens up the possibilities to study the influence of the large momentum cutoff.

VII. SUMMARY AND CONCLUSIONS

We have studied the local orientations of liquid-vapor interfaces with a particular emphasis on the thermal fluctuations of the polar tilt angle $\theta$ between the local surface normal and the vertical direction given by the normal of the flat mean interface (Fig. 1). Our analysis is based on describing the interface by an effective interface Hamiltonian $\mathcal{H}$ which provides the statistical weight for capillary wavelike fluctuations. $\mathcal{H}$ is expressed in terms of a wavelength dependent surface tension $\gamma(q = 2\pi/\lambda)$ and we have used three expressions for it: the simple capillary wave theory for which $\gamma(q) = \gamma_0$ is constant and equals the macroscopic surface tension $\gamma_0$ (Eq. (9) with $\kappa_0 = 0$), a phenomenological expression for $\gamma(q)$ which takes into account bending rigidities (Eq. (10) with $\kappa_0 \neq 0$), and a microscopic expression which is derived from density functional theory (Eqs. (14) and (19)). Within the Gaussian approximation we have calculated the ensuing variances for the local interface positions and for its derivatives (Eqs. (26) and (30)) as well
as the variance for the distribution of finite interfacial height differences (Eqs. \[31\], \[38\], and \[13\] as well as Figs. \[2\] and \[9\]). Based on these considerations we have derived the probability distribution function $P[\theta]$ for the tilt angle (Eq. \[151\]), which exhibits a nonmonotonic dependence on the variance (Fig. \[3\]) and allows us to determine the mean tilt angle $<\theta>$ and its mean squared deviation $<\theta^2> - <\theta>^2$ (Fig. \[5\]). In order to probe also non-local properties of the interface the correlation function $<\theta(0)\theta(a)>$ of the tilt angles at different lateral positions is calculated (see Eq. \[71\]) which offers an interesting future tool to analyze recent experimental data \[22\]. The mean tilt angle and its moments depend on the physical parameters of the system solely via the variance of the height fluctuations $\sigma = \sigma_{k=3}$ (Eq. \[39\] and Fig. \[5\]). Therefore, Sec. \[VI\] discusses the dependences of the variances (Eq. \[79\]) on the capillary length $L_c$ (Eq. \[23\]), the minimum wavelength $2\pi/\eta_{max}$, the stiffness length $L_\kappa$ (Eq. \[22\]), and temperature (Figs. \[7\]-\[11\]). These results demonstrate that these quantities discriminate clearly between the three types of wavelength dependent surface tensions mentioned above. This capacity of discrimination between different sophistications of effective interface Hamiltonians is transferred also to the temperature dependence of the tilt angle $<\theta>$ and its moments (Fig. \[6\]). Our choice in Eq. \[18\] reduces the resulting nonanalyticity of effective interface surface tensions and resembles closely the standard separation into $\eta_k$ and $\sigma_k$ (Eq. \[6\]), at $r < \eta$ and $\sigma_k$ (Eq. \[6\]), at $r > \eta$. The resulting nonanalyticity of effective interface surface tensions at short wavelengths which are difficult to reach with X-ray scattering. In Sec. \[VI\] we have discussed a variety of experimental techniques which allow one to measure the mean tilt angle by optical means. We conclude that the local orientations expressed in terms of the mean tilt angle and its moments offer an additional characterization of the thermal states of fluid interfaces on equal footing with the surface tension and density profiles and with a particular emphasis on the capillary wavellike fluctuations. This underscores the transferability of the concept of the wavelength dependent surface tension from describing interfacial structure factors to local orientations of fluid interfaces.

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furthermore $w(r)$ as given in Eq. [18] has the advantage that it is analytic and thus facilitates our following analysis. This advantage outweighs the fact that Eq. [18] deviates slightly from the standard WCA approach.

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