Critical Analysis of the Density Functional Theory Prediction of Enhanced Capillary Waves

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We present a critical analysis of the density functional description for capillary wave fluctuations on free liquid surfaces. The proposal made by Mecke and Dietrich, [Phys. Rev. E **59**, 6766 (1999)], to obtain the effective wave vector dependent surface tension, and their prediction of an enhanced regime of capillary waves at mesoscopic scales, has had a large impact including claims of experimental observation [Fradin *et al.*, Nature (London) **403**, 871 (2000); Mora *et al.*, Phys. Rev. Lett. **90**, 216101 (2003)]. Our analysis shows that there is a qualitative problem in the convergence of the low q expansion used for that prediction, and that the assumed link between the equilibrium density functional description of the liquid surface and its capillary wave fluctuations leads always to the unphysical decrease of the surface tension for large wave vectors.

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The capillary wave (CW) thermal fluctuations on the interface between two fluid phases were described by Smoluchowski and Mandelstam as a qualitative aspect missing in van der Waals (vdW) theory of liquid surfaces [1]. A century later, the density functional (DF) formalism has generalized vdW theory, and provided valuable information on the dependence of the surface structure with temperature, intermolecular forces, or the chemical composition of fluid mixtures [2]. The accuracy of these predictions has been systematically improved with the use of better DF approximations, but still all the density profiles $\rho_{\rm DF}(z)$ share the same fundamental flaw of vdW theory: their lack of dependence on the surface area, in contrast with the expected smoothening of $\rho(z, A)$ for increasing surface area A, unless a (gravity) external potential damps the long wavelength CW fluctuations. The capillary wave theory (CWT) [3] provided the modern theoretical framework to include the effects of the CW fluctuations over an *intrinsic density profile* $\tilde{\rho}(z)$, strictly independent of A, which represents the equilibrium distributions of relative distance from the molecules to the *intrinsic surface*, a mathematical surface $z = f(\mathbf{R})$, with the vector $\mathbf{R} = (x, y)$ on the plane of the macroscopic interface, to represent the instantaneous boundary between the coexisting bulk phases. However, the CWT does not specify the shape of $f(\mathbf{R})$ associated to each molecular configuration, and its connection with the molecular structure is based on empirical assumptions for the shape of $\tilde{\rho}(z)$, and for the effective surface Hamiltonian $\mathcal{H}[f]$, which describes the fluctuations of the intrinsic surface. There are some specific proposals for operational definitions of $f(\mathbf{R})$ in computer simulations [4–6], but only recently they are becoming a regular tool for the analysis of liquid surfaces [7,8], and so far without firm connection with DF theory.

In 1999, Mecke and Dietrich [9] made a proposal to link the DF and the CWT descriptions of a liquid surface. They suggested that the density profile $\rho_{\rm DF}(z)$ should be regarded as the intrinsic density profile $\tilde{\rho}_0(z)$, associated to a flat intrinsic surface, and that the surface Hamiltonian $\mathcal{H}[f]$ could be obtained as

$$\mathcal{H}_{\rm DF}[f] \equiv \Omega[\rho_f(\mathbf{r})] - \Omega[\rho_{\rm DF}(z)]; \tag{1}$$

i.e., the grand potential increases when the DF equilibrium density profile is deformed into a distribution $\rho_f(\mathbf{r})$ which follows the shape of the intrinsic surface $z = f(\mathbf{R})$, with $\mathbf{r} = (\mathbf{R}, z)$. The expansion at quadratic (Gaussian) order on the intrinsic surface Fourier components, $\hat{f}_q$, gives

$$\mathcal{H}[f] = \frac{A}{2}\sum_q q^2\sigma(q)|\hat{f}_q|^2 + \mathcal{O}[\hat{f}^4], \tag{2}$$

with a q-dependent *bare* surface tension $\sigma(q)$, extending the original CWT assumption $\mathcal{H}[f] = (\mathcal{A}[f] - A)\sigma$ with a constant σ times the increment from the nominal (macroscopic) area A, to that of the intrinsic surface,

$$\mathcal{A}[f] = A + \frac{A}{2}\sum_q q^2|\hat{f}_q|^2 + \mathcal{O}[\hat{f}^4]. \tag{3}$$

The functional form (2) leads to independent Gaussian probabilities for $\hat{f}_q$, with mean squared values $\langle|\hat{f}_q|^2\rangle = k_BT/[A\sigma(q)q^2]$, so that the DF predictions for $\sigma(q)$ could be compared with the observed CW amplitude distributions in experiments or computer simulations.

The self-consistent use of any DF approximation [1,2] guarantees that the $q = 0$ limit of $\sigma(q)$, defined in (1) and (2) is exactly equal to the grand potential surface excess $\sigma_{\rm DF}$. Previous results based on a step function $\tilde{\rho}_0(z)$ [10] gave an always decreasing function $\sigma(q)$, which would

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imply unphysically large CW fluctuations at molecular scale, while the use of a smooth $\tilde{\rho}_0(z)$ in [9] provided the expected growth, $\sigma(q) \approx \kappa q^2/2$, with positive κ for large q, but still keeping $\sigma(q) < \sigma_{\rm DF}$ for a finite range at small q, as shown in Fig. 1. That implies mesoscopic *enhanced capillary waves* with amplitude larger than the macroscopic CWT prediction. Such peculiar result has had a large impact [11], including claims of experimental observations [12]; however, the interpretation of the experimental data presents technical difficulties [13]. Here we address the original theoretical prediction in two aspects: we first show that the consistent use of (1) and (2) leads to an always decreasing $\sigma(q)$, and then we analyze the origin for such unphysical decay at large q.

$\mathcal{H}[f]$ in (1) requires us to specify the corrugated density profile $\rho_f(\mathbf{r})$ associated to each intrinsic surface shape $z = f(\mathbf{R})$. The simplest choice would be

$$\rho_f(\mathbf{r}) = \rho_{\rm DF}(z - f(\mathbf{R})) \equiv \tilde{\rho}_0(z - f(\mathbf{R})), \qquad (4)$$

which corresponds to a shift of the molecular positions, following the corrugations of the intrinsic surface, as in the classical CW assumption that the intrinsic profile is uncorrelated with the shape of $f(\mathbf{R})$. We refer to this density distribution as the *unrelaxed* one, to distinguish it from the generic prescription [9] in which $\rho_f(\mathbf{r})$ results from the minimization of $\Omega[\rho_f]$ over the restricted functional subspace assumed to be compatible with the shape of $f(\mathbf{R})$. Different choices for that subspace could be regarded as variant implicit definitions of $f(\mathbf{R})$. In a remarkable analytical effort, Mecke and Dietrich worked out the leading order terms in the low q expansion for the relaxation of $\rho_f(\mathbf{r})$, which emanate from the local curvatures of $f(\mathbf{R})$. The functional form was then expanded in the Gaussian approximation (2), and evaluated within a simple DF approximation, made of a mean field description of the attractive interactions, plus a local density approximation for the molecular hard cores. The negative second derivative of $\sigma(q)$ at low q appears as a generic result of the attractive interactions, including anomalies for power-law decaying interactions. The minimum of $\sigma(q)$ comes from the balance between that contribution and the $\kappa q^2/2$ term from the hard cores.

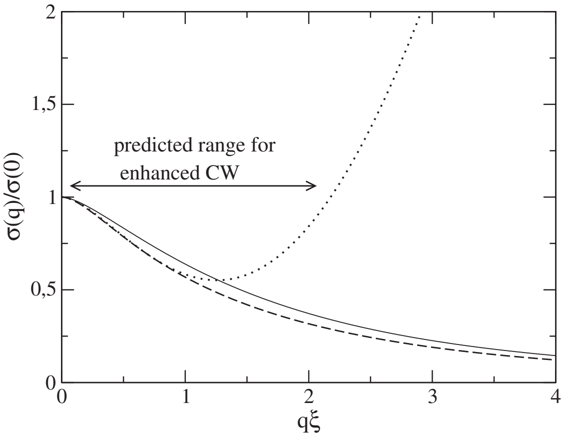

FIG. 1. The dotted line represents $\sigma(q)/\sigma_{\rm DF}$ from Ref. [9], with the parameters $C_H = 0.5$ and $\xi r_o = 1$ defined in that work. The full line gives the result from the unrelaxed density distribution (4), which is an upper bound for the DF prescription (1) and (2). The dashed line shows the relaxation effects when $C_H(q)$ is used as a free variational parameter.

We have to point that, despite its formal definition, the restricted minimization of $\Omega[\rho_f]$, over the functional subspace compatible with $f(\mathbf{R})$, was not performed in [9]. Instead, the result of such optimization was obtained in terms of the local curvatures of $f(\mathbf{R})$; the amplitude of the only relevant term for the Gaussian approximation (2) was noted by C_H, and estimated from at its low-q limit. That fixed value of C_H was then used to obtain the large-q positive bending coefficient κ, and the full shape of $\sigma(q)$, in Eqs. (2.32) and (3.11) of [9]. The *unrelaxed* result for $\mathcal{H}[f]$, from the direct use of (4) into (1), corresponds to the choice $C_H = 0$, and it leads to the full line in Fig. 1. This unrelaxed $\sigma(q)$ has a qualitative difference with the (dotted line) results of Ref. [9], since it gives a monotonically decreasing $\sigma(q)$, going like q^{-2} for large wave vectors. That decay comes from the fact that the large-q bending coefficient is quadratic in C_H, so that it fully disappears in the *unrelaxed* estimation of $\mathcal{H}[f]$. It is clear that any restricted minimization of $\Omega[\rho_f(\mathbf{r})]$ over the corrugated density distributions compatible with $f(\mathbf{R})$ should be below the unrelaxed estimation, so that the rise of $\sigma(q)$ at large q implies an inconsistent use of the curvature relaxation. We may keep the functional form for $\rho_f(\mathbf{r})$ as in [9], but use $C_H(q)$ as an independent variational parameter used to minimize $\mathcal{H}[f]$. This variational result for $\sigma(q)$ is the broken line in Fig. 1, which is always below the unrelaxed result, but fairly close to the original prediction for low q. The macroscopic limit for the curvature relaxation of the density distribution estimated in [9] is fairly accurate up to $q\xi = 1$, so that it gives directly (without explicit minimization) a result for $\sigma(q)$ very close to the variational minimum within the free-$C_H(q)$ functional subspace. However, for $q\xi > 1$, plugging the macroscopic relaxation, with fixed C_H, into the low q expansion for $\sigma(q)$ leads to the (spurious) increase of $\sigma(q)$ over its unrelaxed value. The apparent safeguard of the $\kappa q^2/2$, to keep the physically expected increase of $\sigma(q)$ at large q, is destroyed by the q^{-2} decay in the amplitude of the curvature correction, which was assumed to be constant in [9]. Thus, for large q the curvature modulus goes like $\kappa \sim q^{-4}$, and the optimal $\sigma(q)$ follows closely the unrelaxed q^{-2} decay.

There is a generic explanation for the unphysical decay of the DF $\sigma(q)$ at large q. The ideal gas free energy, and the $\mu N[\rho]$ contributions to $\Omega[\rho]$ are unaffected by the unrelaxed corrugation of $\rho_{\rm DF}(z)$, since they are local DFs, and (4) is a mere shuffling of the relative positions. The whole

$\mathcal{H}[f]$ defined in (1) comes from the excess free energy $\mathcal{F}_{\rm ex}[\rho]$, with nonlocal measures based on the molecular size and interaction range, which we denote by r_o. Any intrinsic surface corrugated only with Fourier components $\hat{f}_q$ for $qr_o \gg 1$, would give a value of $\mathcal{F}_{\rm ex}[\rho_f]$ similar to that for a smoothed planar $\langle \rho_f(\mathbf{r})\rangle_{\mathbf{R}}$, defined as the transverse average of $\rho_f(\mathbf{r})$. From (4) that profile is the convolution of $\rho_{\rm DF}(z)$ with a Gaussian of square width $\sum_q |\hat{f}_q|^2$, and within the quadratic approximation (2) it becomes $\langle \rho_f(\mathbf{r})\rangle_{\mathbf{R}} \approx \rho_{\rm DF}(z) + \frac{1}{2}\rho''_{\rm DF}(z)\sum|\hat{f}_q|^2 + \ldots$, with the second derivative of the density profile.

At linear order in a DF expansion from $\rho_{\rm DF}(z)$, we evaluate $\mathcal{F}_{\rm ex}[\rho_f]$ from its first functional derivative, and use the equilibrium DF condition to get

$$\mathcal{H}_{\rm DF}[f] \approx \frac{A}{2}\int dz \frac{k_B T}{\rho_{\rm DF}(z)}[\rho'_{\rm DF}(z)]^2 \sum_q |\hat{f}_q|^2, \qquad (5)$$

valid for any $f(\mathbf{R})$ made only of large q Fourier components. The comparison of this expression with (2) makes clear the problem: for CW with large q the DF prescription (1) for $\mathcal{H}[f]$ depends on the width of the intrinsic surface corrugations, $\sum|\hat{f}_q|^2$, and not on their area (3), which grows like $\sum q^2|\hat{f}_q|^2$. Casting this $\mathcal{H}_{\rm DF}[f]$ in terms of area increments leads to the unphysical result of vanishing surface tension for large q,

$$\frac{\sigma(q)}{\sigma(0)}\bigg|_{\rm DF} \approx \frac{k_B T}{q^2}\int dz \frac{[\rho'_{\rm DF}(z)]^2}{\rho_{\rm DF}(z)} \sim \frac{k_B T}{\rho_{\rm liq} q^2}\frac{(\rho_{\rm liq}-\rho_{\rm vap})^2}{\xi \sigma_{\rm DF}}.$$

With DF classical exponents $q^2\sigma(q)/\sigma(0)$ would be a smooth function of T up to the critical point. The local density approximation used for the molecular hard cores in [9] changes $k_B T/\rho_{\rm DF}(z)$ into the (larger) second derivative of the hard sphere free energy density, $f''_{\rm hs}(\rho)$. As shown in Fig. 3, improved DF approximations with nonlocal description of the molecular cores, produce a further decrease on the estimation for $\sigma_{\rm DF}(q)$ for large q, with respect to that in [9].

The bad convergence of the q expansion in [9], leading to spurious results already for $q\xi \approx 1.2$, comes from the lack of separation between those fluctuations which are already included in any $\rho_{\rm DF}(z)$ [14], and those which have to be added as corrugations of the intrinsic profile. The sketch in Fig. 2 gives a pictorial view of the problem, showing that the shift of the molecular positions along a nominal CW deformation $z = f(\mathbf{R})$ would only be identified as a physical surface modulation for very long wavelengths. The CW length in the lower frame is still much larger that the molecular size, but its amplitude could not be inferred from the molecular positions. Without the labeling of the molecules at the surface, the snapshot would be interpreted as that of a distorted planar surface, representing a deviation from the equilibrium configuration of the top frame, and associated to a grand potential energy excess (1) proportional to the macroscopic area A, without any dependence on the intrinsic surface area (3). In the middle frame the wavelength is large enough to keep the modulation at molecular level, but still the amplitude of $\hat{f}_q$ from the molecular positions would probably underestimate its nominal value.

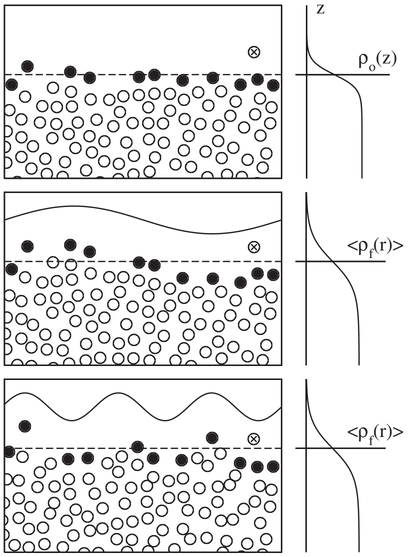

FIG. 2. The top panel sketches a molecular configuration of the surface, and its equilibrium density profile $\rho_0(z)$, associated to a flat intrinsic surface (dashed line). The molecules at the surface could be identified as the filled circles, with a (crossed) overhang. The two lower frames show the configurations obtained by the translation of the molecules along the z direction, following the nominal corrugation of the intrinsic surface given by the (displaced) wavy lines. The density profiles on the right of the lower frames represent the smoothed version of $\rho_0(z)$, produced by such corrugation.

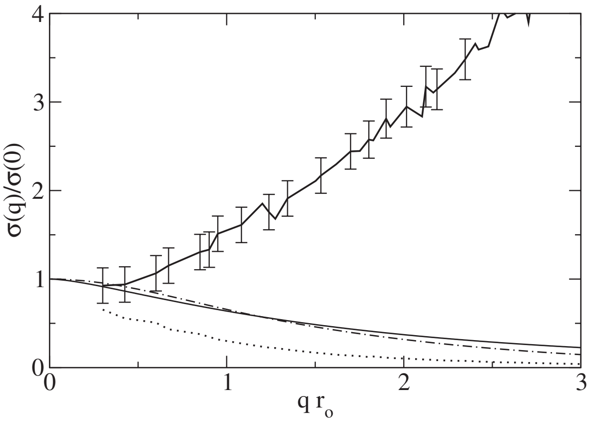

FIG. 3. Computer simulation results for $\sigma(q)$, in a Lennard-Jones liquid surface, with a local Gibbs dividing surface (dotted line), and a percolation-interpolation recipe (thick line with error bars). The thin full line reproduces the DF results from Fig. 1, and the dash-dotted line includes a nonlocal treatment of the hard cores.

Our main conclusion is that the proposed DFT-CWT link (1) gives unphysical $\sigma(q)$ for large q. The problem is not in the form (4) for the density distribution associated to a corrugated liquid surface, since any other choice for $\rho_f(\mathbf{r})$ would only enhance the spurious decay of $\sigma(q)$. A most valuable hint to the root of the problem comes from the mean square CW amplitudes averaged along computer simulations, $\langle|\hat{f}_q|^2\rangle$, which give direct access to $\sigma(q) = k_BT/(A\langle|\hat{f}_q|^2\rangle q^2)$, for $q \geq 2\pi/L_x$, in terms of the transverse size of the simulation box L_x. The shape of $\sigma(q)$ is strongly dependent on the definition used to get $f(\mathbf{R})$ from the molecular positions. It is computationally cheap to define $f(\mathbf{R})$ as a local Gibbs dividing surface [5], but that gives unphysical dependence of $\sigma(q)$ with the depth of the simulated liquid slab, and the same qualitatively problem than the DFT results from (1), i.e., the spurious decay for large q, as presented in Fig. 3 for a Lennard-Jones (LJ) liquid surface near its triple point [6]. Both problems come from the lack of separation between the bulk and surface fluctuations. Computationally, more demanding choices define the *first liquid layer*, by some kind of percolation analysis [4,6,8], and then $f(\mathbf{R})$ from a smooth interpolation between the molecular positions. Although the shape of $\sigma(q)$ still has some dependence on the details of the method, it is qualitatively correct at large q, since $\hat{f}_q$ becomes small [and hence $\sigma(q)$ large] for corrugations shorter than the molecular size, as shown in Fig. 3 for a *state of the art* recipe [15], applied to the same LJ liquid surface as the local Gibbs dividing surface. Notice that we cannot fully rule out the presence of a narrow low-q region with $\sigma(q) \lesssim \sigma(0)$, as it would correspond to the validity of the suggested DF link [9] for the first correction beyond the exact $\sigma(0) = \sigma_{\mathrm{DF}}$ identity, but even in that case, the rapid increase of $\sigma(q)$ would frustrate the appearance of any measurable enhancement of the capillary waves at mesoscopic wavelengths.

The crucial difference between the methods to define $f(\mathbf{R})$ in computer simulations is that (like in a DF treatment) the local Gibbs dividing surface uses only the one-particle distributions, while any percolation-interpolation method depends on many-particle correlations. The description of a corrugated liquid surface by a restricted one-particle distribution $\rho_f(\mathbf{r})$, cannot represent the full molecular constrains of a physical short wavelength corrugation. The molecular configurations compatible with a $f(\mathbf{R})$ have to be selected in terms of many-particle distributions, in a sharper selection which increases the free energy associated to each surface shape. Thus, $\mathcal{H}[f]$ and $\sigma(q)$ would be pushed up from the unphysically low DF value at large q corrugations. The open theoretical challenge is to find the method to include those many-particle constrains, and to evaluate the restricted free energy of the corrugated surface, with a good control on the threshold between the mesoscopic description of the liquid surface as $z = f(\mathbf{R})$ and its molecular discreteness, as done in the percolation-interpolation schemes for the intrinsic surface sampling in computer simulations.

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