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Comment on the Capillary Wave Model in Three Dimensions

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We argue that the capillary wave model provides an accurate description of long wavelength fluctuations of the liquid-vapor interface in three dimensions, provided that effects of external fields are properly taken into account.

KEY WORDS: Liquid-vapor interface; fluctuations; scaling picture.

Since my co-workers and I have argued for the utility of the capillary wave model[1,2] (CWM) combined with scaling ideas for interface fluctuations,[3–7] it was suggested that I comment briefly on Requardt and Wagner's (RW) paper.[8] I will emphasize here three points, and refer to our published papers for more complete discussions.

(i) RW suggest that the effective interaction kernel U in their Eq. (3.3) can in some cases be sufficiently long-ranged to cause a breakdown of the capillary wave model and of the usual identification of γ_{TZ} with γ_{KB}. [Hereafter references to equations in their paper will be preceded by R, e.g., (R3.3).] This is certainly a logical possibility, and in fact, is known to happen in certain well-defined situations. For example, Weeks *et al.*[7] have solved exactly a model with long-ranged anisotropic interactions parallel to the interface. They pointed out that γ_{TZ} is a *surface stiffness* that in general need not equal the usual surface tension γ_{KB}. They found for this particular model exact results showing that the interface width W remains finite as $g \to 0^+$, but that $\gamma_{TZ} = \infty$ while γ_{KB} remains finite. This is precisely the scenario advocated by RW for the ordinary

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liquid–vapor interface in $d=3$. A generalized interface Hamiltonian H_{int} with similar behavior has been studied by Lipowsky,[(9),2] where

$$H_{\text{int}}=\frac{1}{2}\int dq\,\Sigma_{\text{eff}}(q)\,q^2\,|\hat{h}(q)|^2 \tag{1}$$

with

$$\Sigma_{\text{eff}}(q)\sim kq^{-\eta} \tag{2}$$

and k a constant. For $\eta=0$ the model reduces to the surface tension term of the usual capillary wave model, while for $\eta>0$ we arrive at a model satisfying condition (R3.12ii). This model with $\eta>0$ is believed to apply to an interface in a quasiperiodic potential, which can be thought of as exhibiting an increasing stiffness on large scales.[(9)] Such an interface is always smooth in $d=3$ (i.e., always has a finite width W).

However, I doubt very strongly that any such scenario could apply to the liquid–vapor interface in $d=3$ of an ordinary isotropic fluid with short-ranged intermolecular interactions! Here the surface stiffness tends to a constant on large length scales with $\gamma_{\text{TZ}}=\gamma_{\text{KB}}$.[(7)] I find compelling the original physical argument leading to the TZ formula[(11),3]: we know from thermodynamics that the free energy change for a long-wavelength distortion of the liquid–vapor interface is given by the macroscopic surface tension times the change in area (plus work against an external field, if present). On the other hand, we can use the standard density functional formalism[(12)] (which should be exact provided there is an invertible relationship between the external potential and the density profile) to calculate theoretically the same free energy change. The latter gives Eq. (R3.1). It is perhaps not *a priori* obvious that one can justify the further expansion of this result[(7)] to yield the usual TZ formula in Eq. (R3.9), but thermodynamics tells us that such a relation [i.e., a constant (the surface tension) times the change in area $(1/2\int ds\,|\nabla h(s)|^2)$ to lowest order] *must hold* if indeed (R3.1) is exact and correctly evaluated. Similarly, it is really thermodynamics that tells us that for the ordinary liquid–vapor interface we should have $\eta=0$ in the generalized interface Hamiltonian (1).

(ii) RW attempt to cast doubt on the CWM [i.e., Eq. (1) with $\eta=0$ plus a term describing work against an external gravitational field with strength g] because its predictions for $d=3$ in the limit $g\to 0^+$ and $V=\infty$ do not obey certain scaling relations given in (R2.4). They claim that these scaling relations for $d=3$ were widely believed to be true, and seem to argue in their Section 4 that a proper scaling theory must give relations of the form (R2.4) even for $d=3$.

[2] For a comprehensive general review see Forgas *et al.*[(10)]

[3] See, in particular, on this point Appendix C of ref. 7.

I agree with RW that the CWM for $d=3$ does not obey the scaling relations given in (R2.4), but I assert that there is absolutely no reason to believe it should! That is, it is these naive scaling relations that are incorrect in $d=3$, rather than the CWM.[4] Incidentally, I doubt there ever was a widespread acceptance of these (incorrect) scaling relations in $d=3$, though it is true that some careless statements about their validity have appeared in the literature.

In my original work on interface scaling and the CWM,[(3)] I showed that the CWM satisfied scaling relations of the form (R2.4) only in dimensions $d<3$, where the ultraviolet cutoff can be ignored. However, this is not the case for the crossover dimension $d=3$ (and for $d>3$). I explicitly mentioned[(3)] that the correlation function H in (R2.4ii) in $d=3$ takes on a "crossover logarithmic form" not consistent with the scaling in (R2.4ii). I also referred to an earlier calculation using the CWM in $d=3$ where the logarithm can be seen explicitly[(2)] and mentioned exact results for lattice (SOS) systems in $d=3$ (i.e., corresponding to an interface dimension $d'=2$) where logarithms again appear.[(13)] If despite this[5] there exists a widespread belief to the contrary, I trust the blame will not be placed at my doorstep!

I cannot understand RW's insistence in their Section 4 that in a proper scaling theory "all (!)" distances have to be measured in terms of the "natural" length scale $x \equiv s/L_c$ as $L_c \to \infty$, with L_c the capillary length. My original interface scaling ansatz was patterned after that for the bulk pair correlation function H, where[(12)] $H(r) \sim r^{-(d-2+\eta)} H_s(r/\xi_B)$, with H_s a scaling function of order unity for small $x_B \equiv r/\xi_B$ which decays exponentially for large x_B. In addition to the "natural scale" x_B set by the bulk correlation length ξ_B, it is essential to allow for power-law decay on shorter length scales $r \ll \xi_B$. For the interface pair correlation function H, the analogous length scales $s \ll L_c$ again turn out to be important both in $d>3$ (where power-law decay is found) *and* in $d=3$, where the logarithm appears.[(2,4)] Only for $d<3$ is the scaling such that only the "natural" scale x is relevant.[(5)]

(iii) Finally, RW discuss several peculiar features of the CWM in $d=3$ for $g=0$ and $V=\infty$, particularly regarding its predictions for the direct correlation function. However, I believe these results of RW do not indicate any new and interesting physics, such as a nonzero η in Eq. (2); rather they arise from the fact that setting $g=0$ and $V=\infty$ in the CWM does not yield a well-characterized state of two-phase coexistence.[(2–7)]

[4] See ref. 5 for a detailed discussion of this point.

[5] Using Eqs. (A7) and (4.11) of ref. 4, one can see explicitly how the logarithm is generated as $d \to 3$.

A fundamental point, which I believe lies at the heart of the problems discussed by RW, is that in the grand canonical ensemble two-phase coexistence can be described only in the presence of appropriate *nonzero* external fields.[2–7] Examples of such fields for a system in a box with finite volume $V = L^3$ include short-ranged "wetting" and "nonwetting" wall potentials (the analogue of the familiar $+-$ boundary conditions for the Ising model) respectively located at the lower and upper parts of the box, or, as usually is considered in the CWM, an external gravitational field. Such fields can induce macroscopic phase separation, fixing both the average location of the interface and the relative volume fractions of the two bulk phases; indeed, in their absence no interface at all would be found in the grand ensemble, but rather only states of pure liquid or pure vapor.

In the CWM it is conventional[1] to consider an external (and strictly speaking, truncated[3]) gravitational field $v(z) = mgz$, which will induce the above "broken symmetry" state for any $g > 0$. With this bulk field present we do not need to consider the effects of any distant wall potentials to have a well-characterized state of two-phase coexistence, and the thermodynamic limit $V \to \infty$ can then be taken with no subtleties arising.

However, if we now set $g \equiv 0$ in the CWM we no longer have a well-characterized state with, e.g., fixed volume fractions for the bulk phases. The basic density functional formalism leading to Eqs. (R2.2) assumes an invertible relation between the external field and the density.[12] This is true for any $g > 0$, but breaks down in the degenerate case $g \equiv 0$. Thus it is no surprise that this limit seems very singular.

This singular behavior is only apparent and arises basically from the fact that one can ignore the effects of distant wall potentials on the interface for any $g > 0$ in the CWM, but must take them into account if the bulk field vanishes identically. There is no problem in principle with studying a state with $g \equiv 0$ in the CWM, but one must first specify for a finite volume $V = L^3$, say, the appropriate distant wall boundary conditions that will, e.g., fix the average location of the interface, etc. Then the limit $V \to \infty$ can be examined carefully. In such an analysis I would expect essentially the same behavior that one finds in the ordinary CWM as $g \to 0^+$ and $V = \infty$ with L playing the role of L_c.[6]

I ecourage RW to carry out a careful examination of the $g \equiv 0$ problem along the lines suggested here to see if this conjecture is correct. For my part, however, I am content to remain with the ordinary CWM with $g > 0$, where such subtleties do not arise. In the limit $g \to 0^+$, one can in a simple way establish scaling relations for correlation functions and show that the exact equations (R3.2) are satisfied in *all d* for the CWM.[3–6]

[6] A careful discussion of finite-size effects in the CWM is given by Gelfand and Fisher.[14]

Thus I see no reason to doubt the essential correctness of the CWM predictions for the usual liquid–vapor interface.

For a more technical discussion, including an approximate calculation of the direct correlation function in $d=3$, see ref. 5. In response to RW's remarks about this paper, I mention only that in our Section VI, we did try to examine in some detail the behavior of interface moments of the direct correlation function using the full expression (R4.1), and made no exclusion of the region $|q| \leqslant L_c^{-1}$.

Let me close by mentioning a basic area of agreement with RW. The CWM is very plausible, but to the best of my knowledge has never been derived rigorously from a realistic microscopic Hamiltonian. Such a calculation, including, in particular, a *proof* showing whether or not $\eta=0$ in the usual liquid–vapor case, could be quite instructive. If indeed against most expectations it turns out that $\eta>0$, then vast areas of interfacial physics,[10] including theories of wetting and roughening transitions, will have to be fundamentally reexamined. Some rigorous statistical mechanics is called for!

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