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Does the Three-Dimensional Capillary Wave Model Lead to a Universally Valid and Pathology-Free Description of the Liquid–Vapor Interface Near $g = 0$? A Controversial Point of View

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Since the predictions of the capillary wave model (CWM) are often claimed to be universally valid, we scrutinize its microscopic foundations and discuss the legitimacy of the necessary approximations. We show that there may very well be regimes where the CWM is inadequate and demonstrate how to treat such scenarios. As the CWM—despite of its lack of microscopic foundation—seems to be supported by its appealing scaling properties (in $d < 3$), we examine the scaling behavior also for $d = 3$. It turns out that the CWM in $d = 3$—especially the corresponding direct correlation function and several of its descendants—is plagued by various pathologies which exclude a proper scaling limit in the usual sense. In connection with these features we critically comment upon recent work of Weeks *et al.*, presenting a markedly deviating interpretation of the phenomena which emerge when g goes to zero.

KEY WORDS: Capillary wave model; scaling picture; interface Hamiltonians.

1. INTRODUCTION

The behavior and internal structure (both macroscopic and microscopic) of the liquid–vapor interface (after the thermodynamic limit has been taken) when the gravitational constant g approaches zero has been the focus of interest for quite some time. This has its origin both in fundamental and in practical considerations (e.g., Goldstone excitations, correct definition of surface tension γ as an "intrinsic" quantity, etc.) and in various quite intricate mathematical features and subtleties which invariably enter the

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stage when the above limit $g \to 0$ is taken *properly* and *carefully* (which has not always been the case!).

That something peculiar is happening (e.g., poor clustering of the pair correlation H) in the interface was already observed by Wertheim.[1] The degree of power-law decay of H in this limit was then quantitatively specified by one of the authors.[2] In contrast to other papers about this point, the approach developed in ref. 2 started from the true microscopic level of statistical point mechanics and made no model assumption such as, e.g., the capillary wave ansatz. It was *a fortiori* stressed in the paper that the poor decay is a completely normal feature within the Goldstone picture proper of spontaneous symmetry breaking. Further consequences for the direct correlation function C were then drawn in ref. 3.

Another line of reasoning originated with the capillary wave model (CWM) of Buff *et al.*,[4] which has been substantially developed further by Weeks and co-workers (cf., e.g., refs. 5–7 or the review in ref. 8). This model gave the screw another turn due to its prediction of a washing out of the density profile $\rho(z)$ in dimensions $d \leqslant 3$ as $g \to 0$ and its strikingly elegant scaling properties for $d < 3$ as well as $d > 3$.[6,7] However, there remains a discussion of whether the nonexistence of a stable self-maintained ($g = 0$) interface also for $d = 3$ is an inescapable fact of any description of liquid–vapor systems whatsoever or whether it is on the contrary just an artificiality of the CWM which is then surmised to be an oversimplification of the underlying truly microscopic theory.[9,10] To scrutinize this question several distinct strategies have been developed. The first one we mention is due to Robert.[3,11] Starting with his result that in a self-maintained interface in $d = 3$ the direct correlation function C has to display an extremely poor algebraic decay, he then adds the *a priori* assumption that the Triezenberg–Zwanzig expression γ_{TZ} for the surface tension (see refs. 12 and 13 or for a more complete list of references about the whole field the beautiful book of Rowlinson and Widom[14]) is also in the limit $V = \infty$, $g = 0$ the correct expression for the macroscopic "mechanical" surface tension γ, which can in any case be safely identified with the older Kirkwood–Buff version γ_{KB}.[15] It is essentially this assumption that leads to the requirement that γ_{TZ} is a finite quantity even in this limit, and Robert then concludes that, in order to compensate the in principle too long-ranged tails emerging in the integral expression for γ_{TZ}, $d\rho/dz$ has to be zero for $g = 0$. The identification of γ_{TZ} and γ_{KB} was supported by a paper by Schofield.[16] However, we closely inspected—among other things—the validity of this observation in ref. 17 and showed that γ_{TZ}, γ_{KB} could—at least in the limit $V = \infty$, $g = 0$—as well differ by even an infinite amount (with γ_{KB}, however, being always finite). This is just a consequence of the peculiar long-range character of H, C in this limit, which leads inescapably to various boundary corrections, thus rendering the above conclusion $\rho'(z) \equiv 0$ somewhat obscure.

A second strategy has been developed by ourselves[18] and discusses the implications for models which are described by interface Hamiltonians $\mathscr{H}[h]$ being functionals of an elongation field $h(s)$ of the interface. Our main result was that in $d=3$ such model systems do very well admit the description of self-maintained interfaces, provided that the "interaction kernel" $\delta^2 \mathscr{H}/\delta h(s)\, \delta h(s')$ is sufficiently long-ranged in the difference variable $s-s'$. This immediately makes clear why the CWM by its very definition does imply the washing out of the interface as $g \to 0$: Its interaction kernel is extremely short-ranged; it has in fact delta-function character! This observation leads naturally to the question of where and by which approximation the short-rangedness of the CWM Hamiltonian emerges, since, as we have shown, it is neither a necessary ingredient of models defined via interface Hamiltonians nor is it a consequence of the truly microscopic theory.

A partial answer was given somewhat incidentally already in ref. 19 after formula (C12), where the authors require—in order to establish the soundness of the CWM approximation—the direct correlation function C_{micro} of the underlying microscopic theory to be sufficiently short-ranged for any finite nonzero g. This is a physically reasonable—although nowhere proven—assumption, but it is not enough, as we will show, to guarantee the universal validity of such implications as the diverging interface thickness as $g \to 0$ for $d=3$. As to this, one needs in addition the crucial assumption that a certain integral expression containing C_{micro}, namely

$$U(s) = \frac{1}{\beta} \int dz_1\, dz_2\, \rho'(z_1)\, \rho'(z_2)\, C_{\text{micro}}(s, z_1, z_2) \tag{1.1}$$

is *uniformly* (!) short-ranged as $g \to 0$. This is—in our view—by no means obvious. A good example for the lack of such a behavior is the correlation function H of the CWM in $d>3$, which decays exponentially for every fixed $g>0$, but is not uniformly short-ranged, since $H_{g=0}$ decays only algebraically (more specifically: $\sim |s|^{-(d-3)}$). This lack of uniformity is in fact a standard feature of critical point and other nonanalytic behavior.

To put it in a nutshell, one has—as we think—two alternatives:

(i) $\gamma_{\text{TZ}} = \gamma_{\text{KB}} = \gamma$ remains valid also in the limiting state $V=\infty$, $g=0$ which is connected with uniform short-rangedness of $U(s)$ (the commonly accepted picture).

(ii) $\gamma_{\text{KB}} = \gamma < \infty$, but $\gamma_{\text{TZ}} = \infty$ in the limiting state $V=\infty$, $g=0$ (the possibility we would like to dwell upon, at least as a working hypothesis and which does not deserve to be completely ignored).

As a conclusion, if one has already some suspicion about the universal correctness of γ_{TZ}—at least for $V=\infty$, $g=0$—then by the same token the universality claimed for the implications of the CWM as $g \to 0$ becomes also necessarily suspicious. (This suspicion was, however, already raised by quantitative checks based on rigorous estimates carried through by one of the authors in ref. 20. In Section 6 of that paper a development of a different picture of the internal structure of the interface was initiated which we hope to expound in more detail elsewhere.)

While the CWM is, on the one side, free of logical contradictions (as, e.g., ref. 7 has shown), it suffers on the other side from the lack of a universally valid microscopic foundation. Therefore it is often attempted to suport the CWM by referring to its already mentioned appealing scaling properties (see, e.g., the reviews in refs. 8 and 21). The necessity of such scaling properties in order to be able to construct "intrinsic" theories, resp. properties of interfaces in the limit $V=\infty$, $g=0$, has been stressed e.g., in ref. 22. However, while the original papers on scaling[6,7] were cautious enough to exclude the dimension $d=3$ (at least implicitly) from the investigation, one became more cavalier as to this point later on (see, e.g., refs. 8 and 23). This latent tendency is, as we will show, by no means justified, since the case $d=3$ is full of traps and snares.

To subsume the implications of the above discussion: In order to test the value of the CWM, one must, on the one hand, go back to the microscopic regime from which the CWM sprang as a certain approximation and, on the other hand, drive the CWM to its extremes by choosing $d=3$ (the problematic and at the same time physically most interesting dimension) and then performing the limits $V \to \infty$, $g \to 0$ with extreme care, in order to test whether all the consequences and properties commonly attributed to such models (and models of statistical fluid mechanics in general) really survive under these conditions.

This was recently done in a lengthy and technically rather intricate paper by ourselves.[24] However, as there is the risk that the red thread might perhaps be difficult to follow within the highly facetted and subtle reasoning, we decided to prepare a somewhat trimmed down version which may be easier to comprehend and refer to the original version for technical details.

2. SCALING HYPOTHESIS AND INTRINSIC INTERFACE STRUCTURE

The (at least as far as we can see) presently commonly accepted conventional wisdom (mostly based upon the CWM) can be summed up in the following sketchy statements:

(i) In dimensions $d \leqslant 3$ one has in the limit $g \to 0$ both a diverging interface thickness W and capillary length L (more properly: correlation length).

(ii) On the other hand, one wants to reconcile these features (for whatsoever reasons) with at least one aspect of the older (and presumably locally correct) van der Waals theory, i.e., the prediction of a finite surface tension γ in this limit. That is:

$$\text{(a)} \quad W \to \infty, L \to \infty; \qquad \text{(b)} \quad \gamma < \infty \tag{2.1}$$

as $g \to 0$ are the two (in some sense conflicting) constraints which make the study of this field both highly interesting and subtle.

This couple of demands leads immediately to the idea that these phenomena might hint at a situation being (at least qualitatively) similar to the behavior of (near) critical bulk systems in $d-1$ dimensions. In case of the CWM proper one, e.g., hopes that by a clever rescaling via W and L (as functions of g) one may tame the large fluctuations and manage to arrive at a "fixed-point" theory, resp. Hamiltonian displaying the "intrinsic" quantities and properties one is ultimately after, i.e., a stable *intrinsic* interface of *finite* thickness with a *nonvanishing* and finite surface tension. In a, however, different approach the same goal is invoked, e.g., in ref. 22, where the method of conditional correlations is exploited. The former picture, to which we will stick in the following, was to some extent advocated and expounded by Weeks[6] and has been shown to work very well in dimensions $d < 3$.[7]

On the other side, and somewhat suspiciously, remarks and observations have been, to say the least, extremely scarce and cloudy as far as the dimension $d = 3$ is concerned (for a few, however incomplete, results see ref. 5). This is quite nasty, since, evidently, the topic is of great practical and fundamental importance most notably for $d = 3$ (both for "free" interfaces and "wetting").

Unfortunately, the case $d = 3$ seems to be, in the language of critical point behavior, a "crossover dimension" with, e.g., logarithmic contributions, and calculational traps abound. This had the effect that, typically, results for $d < 3$, most notably for lattice systems, have been invoked to support the view that an analogous behavior prevails also in $d = 3$, while for $d > 3$ a drastic change is to emerge.

As to the use of lattice models, we would like to remark that we developed in Section 6 of ref. 20 an (at the moment still sketchy) picture of interface behavior which seems to indicate that exchange mechanisms parallel to the interface and kinetic effects may be important which are necessarily absent in lattice systems (in particular in column or SOS models).

Furthermore, the widespread attitude that the rigorous results, obtained for lattice systems (mostly for $d<3$), do support the universal validity of the CWM is in some respect self-referential, since, evidently, both model systems care only about the one-dimensional up and down motion of the interface as such assuming *a fortiori* only an extremely short-ranged interaction. (We shall discuss below that it is just this assumption of a too short-ranged interaction in interface models which may be problematic at least in $d=3$.)

It should be stressed that—despite of this sort of circular and in some sense "self-supporting" reasoning—there is no doubt that the CWM is *internally* consistent. That there exists, however, another chain of reasoning was expounded by us in Sections 4 and 5 of ref. 24, the red thread of which will be given in the next section. On the other hand, one can try to drive the CWM itself, in particular its scaling properties, to its extremes in order to test whether its predictions remain the physically expected ones also in the limiting region $g \to 0$. This was the concern of Sections 2 and 3 of ref. 24.

In these sections we found the CWM beset with irregularities and what we consider to be pathologies in the "critical region" around $g=0$ and which do not seem to have been universally known before. The most remarkable, in our view, is the nasty behavior of the direct correlation function C, which we will discuss below. But before going into the technical details, we would like to comment on what actually seemed to be surmised in $d=3$ when $g \to 0$ before (!) our paper[24] circulated. The scaling picture assumed the following equations (the prime denoting differentiation):

$$
\begin{aligned}
&\text{(i)} \quad \rho'(z_1) = -\beta \int dz_2\, ds\, H(z_1, z_2, s)\, v'(z_2) \\
&\text{(ii)} \quad \gamma_{\mathrm{TZ}}[v] = [2\beta(d-1)]^{-1} \int dz_1\, dz_2\, ds\, H(z_1, z_2, s)\, s^2 v'(z_1)\, v'(z_2) \\
&\text{(iii)} \quad \delta(z_1 - z_2)\, \delta(s_1 - s_2) = \int dz_3\, ds_3\, H(z_1, z_3, s_{13})\, C(z_3, z_2, s_{32}) \qquad (2.2) \\
&\text{(iv)} \quad \gamma_{\mathrm{TZ}}[\rho] = -[2\beta(d-1)]^{-1} \int dz_1\, dz_2\, ds\, C(z_1, z_2, s)\, s^2 \rho'(z_1)\, \rho'(z_2) \\
&\text{(v)} \quad v'(z_1) = -\frac{1}{\beta} \int dz_2\, ds\, C(z_1, z_2, s)\, \rho'(z_2)
\end{aligned}
$$

to go over into the limiting equations where z_1, z_2, s, H, C, ρ, and v are replaced by the corresponding rescaled quantities

$$
\begin{gathered}
\tau_{1,2} := z_{1,2}/W; \qquad x := s/L; \qquad H_s(\tau_1, \tau_2, x); \qquad C_s(\tau_1, \tau_2, x) \\
\rho_s(\tau); \qquad v_s(\tau); \qquad \gamma_{\mathrm{intr}} := \lim_{g \to 0} \gamma_{\mathrm{TZ}}(g) =: \gamma
\end{gathered} \qquad (2.3)
$$

(for more details see Section 2 of ref. 24).

As an illustrative example of what was usually surmised from the scaling picture (especially for the CWM), we would like to mention, e.g., some results of Chapter 1.3 of ref. 8 for $d \leqslant 3$, $g \to 0$:

$$\text{(i)} \quad W^2 \sim L^{3-d} \quad \text{for} \quad d<3; \qquad W^2 \sim \ln L \quad \text{for} \quad d=3 \tag{2.4}$$

(ii) $H(z_1, z_2, s)$ is asymptotically equal to $H_s(\tau_1, \tau_2, x)$ for $d<3$ *and* for $d=3$.

(iii) $C(z_1, z_2, s)$ is asymptotically equal to $L^{-(d+1)} C_s(\tau_1, \tau_2, x)$ for $d<3$ *and* for $d=3$.

(iv) $\int ds\, s^2 \cdot C(z_1, z_2, s) =: C_2(z_1, z_2)$ is asymptotically equal to $C_{2,s}(\tau_1, \tau_2)$ for $d<3$ *and* for $d=3$.

The scaling relation $H =_{\text{asympt}} H_s$ was independently taken for granted by, e.g., Ciach (both for $d<3$ and $d=3$) in ref. 23. Furthermore, we know from many discussions with various experts in the field that the above is not an unfair resumé of an at least widespread belief. In contrast to this, we want to emphasize that all these conclusions are true for $d<3$, but are *definitively wrong* with the exception of (i) in space dimension $d=3$! Contrary to widespread belief, for $d=3$ neither H nor C obeys the scaling relations. Even worse, as one of our main results we proved in ref. 24, Eq. (3.18)ff, that C_s does not even exist for $g=0$ and that its behavior for $g \to 0$ is catastrophic. That is, in contrast to (2.4), we actually have

$$C(z_1, z_2, s) =_{\text{asympt}} L^{-4} \cdot \left[C_0(\tau_1, \tau_2, x) + \sum_{n=1}^{\infty} W^{2n} \cdot C_n(\tau_1, \tau_2, x) \right] \tag{2.5}$$

In other words, only the zeroth order scales as expected by conventional wisdom. The remaining (and ultimately dominant) part is a term-by-term divergent series as $g \to 0$!

Summing up the content of Section 3 of ref. 24:

(i) H scales asymptotically as $W^{-2} \cdot H_s$ with H_s *degenerating* to a *one-dimensional projector*!

(ii) C splits into a "*regular*" and a "*singular*" contribution with *catastrophic* scaling behavior.

(iii) This pathological behavior of C in the scaling limit is, however, shielded in γ_{TZ} (to some extent) thanks to the fact that all but the "regularly" scaling zeroth-order contribution is projected to zero.

Hence we come to the following:

Conclusion: A proper scaling limit of the CWM does not exist in $d=3$! Various expressions behave catastrophically in this limit. As a certain remnant the expression for γ_{TZ} stays finite as $g \to 0$ provided that the limit is performed *outside* (!) the z-integrals. Anyway, one building block of γ_{TZ}, namely C_s (or $C_{2,s}$) is ill-defined in this limit.

3. THE MICROSCOPIC (NON)FOUNDATION OF AND BEYOND THE CWM

In this section, which is partly an elucidation of Section 4 of ref. 24 (cf. also Appendix C of ref. 19), we briefly analyze how the CWM and the underlying microscopic theory may be related with each other, more properly, which preassumptions are actually needed to establish such a connection. Furthermore, we show a way beyond its limited range of applicability.

In a first step we evaluate the free energy of a given fixed fluctuation of the microscopic interface (in technical terms a partial trace) up to second order. We get [cf. (4.2), (4.5) of ref. 24]

$$\Delta F^{(2)} = 1/2\beta \int dr\, dr'\, C(r, r')\, \Delta\rho(r)\, \Delta\rho(r')$$

resp.

$$\Delta F^{(2)} = 1/2 \int ds_1\, ds_2 \left[1/\beta \int dz_1\, dz_2\, \rho'(z_1)\, \rho'(z_2) \times C(s_1 - s_2; z_1, z_2) \right] h(s_1)\, h(s_2) \tag{3.1}$$

where $\Delta\rho$ is substituted by a specific elongation $h(s)$.

Setting this in relation with a corresponding interface Hamiltonian, one has

$$\begin{aligned} \Delta\mathscr{H}[h] &:= \mathscr{H}[h] - \mathscr{H}[h \equiv 0] \\ &= 1/2 \int ds_1\, ds_2\, \delta^2\mathscr{H}/\delta h(s_1)\, \delta h(s_2) \restriction_{h\equiv 0} \cdot h(s_1)\, h(s_2) \end{aligned} \tag{3.2}$$

One can now identify the interaction kernel

$$U(s_1 - s_2) := \delta^2\mathscr{H}/\delta h(s_1)\, \delta h(s_2) \restriction_{h\equiv 0} \tag{3.3}$$

with

$$1/\beta \int dz_1\, dz_2\, \rho'(z_1)\, \rho'(z_2)\, C(s_1 - s_2; z_1, z_2)$$

Conclusion: From the above one sees that the interaction kernel $U(s_1 - s_2)$ of any effective interface Hamiltonian is uniquely determined by the microscopic theory via (3.2), (3.3)![3]

Evidently (3.2), (3.3) define already a completely satisfactory interface Hamiltonian, having the advantage of being both universally correct (up to second order!) and much more general than the CWM. In order to see under what special conditions one arrives in a further step at the CWM, one has to make a physically strong assumption, which is, via (3.3), a strong assumption about the underlying microscopic model.

Assuming that (i) the dominant contributions in the path integral originate from sufficiently smooth paths, and (ii) $U(s_1 - s_2)$ is sufficiently short-ranged for some fixed (!) exterior gravitational potential $v(z)$, a Taylor expansion may be justified in (3.2), (3.3):

$$h(s_2) = h(s_1) + (s_2 - s_1)\nabla h(s_1) + 1/2[(s_2 - s_1)\nabla_{s_1}]^2 h(s_1) + \cdots \tag{3.4}$$

leading (in second order) to

$$\Delta\mathscr{H}[h] = 1/2\int ds_1\, ds_2\, U(s_2 - s_1)\cdot h(s_1)^2$$
$$- 1/4(d-1)\int ds_1\, ds_2\, U(s_2 - s_1)\cdot(s_2 - s_1)^2\cdot|\nabla h(s_1)|^2 \tag{3.5}$$

With the identification (3.3) and using the well-known equation

$$\int dz_2\, ds\, \rho'(z_2)\, C(s; z_1, z_2) = -\beta v'(z_1) \tag{3.6}$$

the first term on the rhs reads

$$-1/2\int dz\, \rho'(z)\cdot v'(z)\cdot\int ds\, h(s)^2 \tag{3.7}$$

Replacing $v(z)$ by mgz [for measures of precaution as to this unbounded potential, see, e.g., (2.3)ff, resp. (4.13)ff, of ref. 24], we get finally

$$1/2\int ds\, U(s)\cdot\int ds'\, h(s')^2 = mg\,\Delta\rho/2\cdot\int ds\, h(s)^2 \tag{3.8}$$

i.e., the gravitational contribution in the CWM.

[3] As to some critical remarks concerning the range of applicability of interface models like the CWM, see the Appendix of this paper. In this connection we want to thank also one of the referees for criticism.

As to the second term on the rhs of (3.5), we have

$$1/2(d-1)\,\beta \int dz_1\, dz_2\, \rho'(z_1)\, \rho'(z_2) \cdot \int ds\, s^2 C(s; z_1, z_2)$$

$$\times 1/2 \int ds'\, |\nabla h(s')|^2$$

$$= \gamma_{\mathrm{TZ}}(g) \cdot 1/2 \int ds\, |\nabla h(s)|^2 \tag{3.9}$$

In order that the CWM approximation be meaningful also around $g = 0$, we have to assume that U, given by (3.3), is not only short-ranged for each nonzero g (i.e., pointwise), but moreover uniformly so as $g \to 0$!

Conclusion: (i) The CWM emerges for fixed $g > 0$ as a special approximation of the "rigorous" microscopic expression (3.5) under the proviso that a Taylor expansion up to second order of $h(s)$ be justified, in other words, that U be sufficiently short-ranged with respect to s.

(ii) As $g \to 0$ this *a priori* assumption may become problematical for $d = 3$, since we have severe doubts whether one can really consider U as being *uniformly* short-ranged with respect to s for $g \to 0$ to be self-evident.

From all this we infer that, at least as kind of a thought experiment, one should investigate the more fundamental expression (3.5) with some care and speculate, at least as a possibility, what might happen if matters do not behave as smoothly and universally as assumed by the CWM in reality.

Equation (3.5), resp. its Fourier transform

$$\Delta\mathscr{H}[h] = 1/2 \cdot (2\pi)^{2(d-1)} \cdot \int dq\, \hat{U}(q) \cdot \hat{h}(q)\, \hat{h}(-q) \tag{3.10}$$

leads via Gaussian integration to the height–height correlation

$$S(s) = 1/\beta(2\pi)^{2(d-1)} \cdot \int dq\, e^{iqs}/\hat{U}(q) \tag{3.11}$$

Assuming a suitable ultraviolet cutoff (as usual) being built into the theory [implying a sufficiently strong increase of $\hat{U}(q)$ for $q \to \infty$], the physically relevant situation is the limit $q \to 0$.

One has roughly two possibilities:

(i) If $\hat{U}(q, g) - \hat{U}(0, g) = O(q^2)$
uniformly in g, one arrives at the same situation
as in the CWM.

(ii) If $\hat{U}(q, g) - \hat{U}(0, g)$ can be uniformly bounded only by a function vanishing slower than $O(q^2)$ for g near 0, one may end up in a different regime! (3.12)

Typical cases in point of the asymptotic behavior of the bound are

$$O(|q|^{2-\eta}) \qquad \text{or} \qquad O(q^2 \cdot |\ln(a \cdot |q|)|^{1+\varepsilon}) \tag{3.13}$$

more specifically, for each $g > 0$ the asymptotic behavior of $\hat{U}(q, g) - \hat{U}(0, g)$ is analytic but *not uniformly* (!) so s.t. in the limit $g = 0$ a *nonanalyticity* (!) has emerged with, e.g., a $\eta > 0$ (and which can never be observed for $g > 0$!).

This is, by the way, a common feature both in mathematics proper and in critical point behavior s.t. the occurrence of this possibility should not come as a complete surprise. The various consequences of this phenomenon are compiled in the following observations [for more details see ref. 24, expression (4.20)ff.].

Observation. (i) If the *a priori* assumption of *uniform short-rangedness* of $U(s)$ as $g \to 0$ is not satisfied, one may arrive at a *nonanalytic* behavior of $\hat{U}(q, g = 0)$ at $q = 0$, which implies furthermore that $\hat{U}(q, g = 0)^{-1} \in L^1(R^2)$ becomes a possible feature.

(ii) With the help of (3.9) and (3.11), this latter possibility yields

$$W := S(0)^{1/2} < \infty$$

and

$$\gamma_{TZ}(g = 0) = (2\pi)^{d-1}/2(d-1) \cdots (\nabla^2 U) \restriction_{q=0} = \infty \tag{3.14}$$

Remark. As to the last point, there is nothing really to worry about, since, as was shown by us in detail in ref. 7, γ_{TZ} is *not* necessarily the correct expression in the limit $g = 0$, as $\lim_{g \to 0} \gamma_{TZ}(g)$ and $\gamma_{TZ}(g = 0)$ are no longer equal for such a scenario.

Conclusion. As the (for $g \to 0$) diverging W was responsible for all the pathologies, accompanying the scaling assumptions [see, e.g., the expression for C in (2.4)], we arrive now at the following sequence of observations:

(i) Assuming that the CWM remains a valid approximation also for $g \to 0$ and that the physically intuitive scaling ansatz holds, one has to face a whole bunch of nasty features of the limit theory.

(ii) The applicability of the CWM requires U to be uniformly short-ranged with respect to s as $g \to 0$. If this assumption is not fulfilled, one has to expect a nontrivial interaction kernel $U(s_1 - s_2)$, resp. an $\hat{U}(q)$ which may become nonanalytic at $q = 0$ as $g \to 0$.

(iii) Such nonanalyticity, which is quite common in, e.g., critical point behavior, can, on the other hand, give rise to a *nondiverging* (!) W as $g \to 0$ and implies an ill-defined $\gamma_{TZ}(g = 0)$.

We think the model suggested by us is a valid alternative to the CWM in current use. We conjecture that there might be situations where our theory leads to more reliable results. This is the more so as there are already examples where a behavior as suggested by us prevails, such as, e.g., in harmonic crystals with long-ranged Couomb-like interactions [cf. (4.24)ff. of ref. 24). The counterpart of the ill-defined $\gamma_{TZ}(g = 0)$ in the interface model is an infinite longitudinal velocity of sound in such crystal models.

As a last point, we want to remark that we have introduced in Section 5 of ref. 24 an explicitly solvable interface model which displays all the features we have alluded to above. Furthermore, its detailed analysis, in particular the eigenfunction expansion of H and C, shows some fascinating side aspects as to the universal validity of the so called "Wertheim ansatz,"[1] i.e., the dominance and nondegeneracy of the eigenvalue zero, on which, more or less openly, quite a large part of microscopic interface physics has been built (cf. in particular Appendix 4 of the review in ref. 27).

In our conclusion to that section we show that the validity of this ansatz is extremely sensitive and highly unstable against any perturbation, which makes the "neighborhood" of the CWM extremely erratic. To give an example: for $\hat{U}(q, g = 0) \sim |q|^{2-\eta}$ the eigenvalue zero of $\hat{C}(q = 0)$ turns out to be $[2/\eta]$-fold degenerate in our model, in contrast to the above-mentioned hypothesis of nondegeneracy. We want to emphasize that we consider this feature to be quite typical and not to be an artifact of our model.

4. THE PATHOLOGICAL BEHAVIOR OF THE LIMIT-DIRECT CORRELATION FUNCTION. TWO CONFLICTING VIEWS

In this section we want both to dwell in slightly more detail on what we consider to be the main shortcoming of the currently prevailing scaling philosophy of the three-dimensional CWM in the limit $g \to 0$ and comment on some recent work of Weeks *et al.*[25,26] which, mainly as a reaction to our criticism of the present state of affairs in ref. 24, embarked on a closer and more careful inspection of various points raised by us.

While the breakdown of the (unmodified) scaling picture in $d = 3$ has, as far as we can see, also been acknowledged by Weeks *et al.*,[25] it still depends on one's personal philosophy what one is going to make of this observation. As to this, there seem to exist at the moment two conflicting views, the one held by us, the other by Weeks *et al.*

While, in contrast to various critical remarks of Weeks *et al.*,[25] our mathematical treatment of the delicate limit $g \to 0$ is perfectly sound and has been done with great care, it is worthwhile to scrutinize the (partly not openly stated) physical assumptions which lie at the core of these, at first glance, seemingly contradictory results.

It is in fact not particularly difficult to put one's finger on the point where Weeks' approach bifurcates from our treatment of the same subject: According to the philosophy of the original scaling picture we chose as "natural" length scale parallel to the interface the correlation length L. That is, we maintain that when adopting the scaling philosophy in the asymptotic regime $g \gtrsim 0$, all (!) distances have ultimately to be measured as multiples of L with $x := s/L$ the only (!) remaining natural length variable.

This implies that in the scaling limit all s-values which remain constant, resp. grow significantly weaker than $\sim L$, are mapped into the point $x \equiv 0$ and lose their individual physical meaning (as is also the case at the critical point).

In contrast to this, Weeks *et al.* try to invoke something like a "floating length scale" picture; they, e.g., employ in their counterarguments against our conclusions s-values being constant resp. growing $\sim \sqrt{L}$, i.e., $s \ll L$ (with $L \to \infty$), thus hoping to escape the nasty consequences we brought to the fore in ref. 24. However, in doing this they leave their own scaling framework and make the whole philosophy of this model system rather fuzzy.

But what is actually worse in our view (and which will be shown below) is that by staying away from the regime $s = O(L)$ they lose entirely the control over the really crucial and significant pieces of the theory which, with $g \to 0$, become more and more concentrated in the region $s = O(L)$, resp. $q \approx 0$ (q is the Fourier transform of s).

To show this, it is advantageous to employ the Fourier transform of $C(z_1, z_2; s)$, i.e., $\hat{C}(z_1, z_2; q)$ which, with the help of (2.5), has the (exact) representation (irrespective of any *a priori* scaling assumption):

$$\hat{C}(z_1, z_2; q) =_{\text{asympt}} L^{-2} \cdot \left[\hat{C}_0(\tau_1, \tau_2; Q) + \sum_1^{\infty} W^{2n} \cdot \hat{C}_n(\tau_1, \tau_2; Q) \right] \tag{4.1}$$

with $Q := L \cdot q$ corresponding to $x := s/L$, $\hat{C}_n$ being proportional to the reciprocal of the Fourier transform of $[K_0(x)]^{n+1}$, K_0 the modified Bessel function of second kind. [For more details see (3.17) of ref. 24, and ref. 25, Section 5.]

From this exact relation one can infer that the singular and dominant contribution comes in the limit $g \to 0$ (implying $L \to \infty$, $W \to \infty$) from Q-values being more or less constant, i.e., from the infinitesimal neighborhood $\{|q| \lesssim L^{-1}\}$!

Weeks *et al.*, however, truncated this crucial region (almost from the outset) by confining themselves (for reasons we cannot really follow) to the regime $\{|q| \gg L^{-1}\}$, i.e., $s \ll L$. By this trick they pick up the entirely harmless part of C, resp. $\hat{C}$, while the physically most relevant and ultimately singular contribution gets out of their sight.

As a concluding remark, we would like to emphasize that, in our view, one has not really the physical freedom of excluding the critical region $\{|q| \lesssim L^{-1}\}$ in the limit $g \to 0$. As (4.1) is an exact relation, the singularities mentioned by us are already present in $C(z_1, z_2; q)$ around $q = 0$ for $g \to 0$. They are only brought to light by magnifying and unfolding this infinitesimal region with the help of the transition to the variable $Q = q \cdot L$.

To sum up what we have tried to say: Starting from the conventional wisdom, we showed rigorously that one will presumably run into all sorts of technical and physical difficulties due to the fact that the *degree* (!) of exponential clustering need not be uniform for $g \to 0$. As a consequence, one may arrive at two limiting scenarios: (i) Either the CWM is in some sense an oversimplification or (ii) the scaling picture is no picture at all, being then a mere technical "epiphenomenon," working well for $d < 3$, $d > 3$ (especially supplying us with well-defined $g = 0$ theories), but developing nasty features for $d = 3$ (!). In our view, these features escape the notice of Weeks *et al.*, as they never really attempt to explicitly perform the limit $g \to 0$.

5. APPENDIX TO SECTION 3

We would like to remark the following: Note that, in order to be logically consistent, one actually has to break off the expansion after the second order, as the CWM itself is only a second-order (!) theory, its physical reliability being restricted to sufficiently small elongations (if compared, e.g., with some "natural" length in the direction of the interface itself). This is, by the way, also the case for γ_{TZ}!

The procedure is comparable with the common approximation of the fully microscopic theory of a crystal lattice by a harmonic crystal model via expanding the microscopic Hamiltonian up to second order in the displacements of the particles from their equilibrium positions.

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