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Wall and Gravitational Effects on the Fine Structure of Interface Layers at Two-Phase Coexistence: Some Rigorous Results

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A rigorous inequality is derived relating density gradient, interface thickness, transverse correlation length, and distance of the interface from the wall in the presence of an explicit gravitational (resp. wall potential). The results are relevant to various possible scenarios, e.g. (critical) wetting, drying, roughening, free interfaces (i.e., far away from a wall). Attention is concentrated on the structure of the liquid–gas interface in a gravitational field. Results seem to indicate that the usual intuition concerning the fine structure of the liquid–gas interface (e.g., the capillary wave picture) cannot be entirely correct. The predictions are particularly puzzling in space dimension two. The results are physically interpreted, giving a more refined picture of the interface layer.

KEY WORDS: Interface structure; wall effects; wetting; roughening; transverse correlation length.

1. INTRODUCTION

There has been much interest in the nature of the transition zone between a liquid and its vapor in equilibrium (or, more generally, the interfaces between the various components of, e.g., a multicomponent fluid), in particular when it became clearer in the mid-1970s (see e.g., Refs. 1 and 2) that a flat liquid–gas interface seems to exhibit quite delicate properties in the limit of a vanishing exterior gravitational field. According to the so-called "capillary wave picture," a flat fluid–fluid interface cannot be maintained in zero gravity; the interface starts to oscillate with the log of the area of the interface. These questions have been considered in, e.g., Refs. 1–6 and 14.

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A little later these and related problems were approached from a different direction, concentrating on the derivation of rigorous bounds of various quantities of physical interest, e.g., the two-particle correlation function, $\rho^{(2)}(r_1, r_2) - \rho(r_1) \cdot \rho(r_2)$, in inhomogeneous fluids (see, e.g., Refs. 7–9 and, more recently, Ref. 10). The main tool in Ref. 7 was a special version of the Bogoliubov inequality,

$$|\langle \{A, B\} \rangle|^2 \leqslant \beta \langle A^2 \rangle \cdot \langle \{B, \{B, \mathscr{H}\}\} \rangle \tag{1.1}$$

where A, B are real, localized observables, $\mathscr{H}$ is the Hamiltonian, β is the inverse temperature, and the Poisson bracket on phase space is given by

$$\{A, B\} := \sum_i (\partial_{r_i} A \, \partial_{p_i} B - \partial_{r_i} B \, \partial_{p_i} A) \tag{1.2}$$

With A and B suitably chosen, we were able to supply a rigorous lower bound for the density–density correlation function.

In the above papers we studied self-maintained inhomogeneities, namely in the absence of an exterior field. Since, as already mentioned, gravity seems to play a key role in stabilizing, e.g., the liquid–gas interface, we treat in this paper explicitly the case of a fluid at two-phase coexistence in an exterior field, which contains as special situations both the linear gravitational field plus an explicit container bottom and various kinds of extra wall potentials.

The bulk of the paper consists of the derivation of a seemingly powerful inequality (given in Section 5). In one of its formulations it relates the density difference of the two phases in coexistence, the interfacial thickness, the distance of the interface from the wall, the transverse correlation length (i.e., parallel to the wall), and the wall (gravitational) potential with one another and holds in all dimensons $d \geqslant 2$. It enables us to study various scenarios, e.g. (critical) wetting, drying, roughening, and free interfaces.

In this paper we concentrate on the liquid–gas interface in a gravitational field, treating the cases where wall effects are dominant elsewhere. Since our (as far as we can see) rigorous results seem to indicate that the usual intuition stemming from models like the caillary wave picture cannot be entirely correct, we try to interpret our findings physically in Section 6, developing a different picture of the interface region. We furthermore touch upon the particularly puzzling situation in space dimension two.

2. TERMINOLOGY AND NOTATION

The Hamiltonian is given by

$$\mathscr{H} := \sum_i [p_i^2/2m + v(r_i)] + \frac{1}{2} \sum_{i \neq j} u(r_i - r_j) \tag{2.1}$$

where we restrict ourselves for simplicity to a one-component fluid. $v(r)$ is the exterior potential $u(r_{ij})$, $r_{ij} = r_i - r_j$, with $u(r) = u(-r)$ a pair potential. While our approach can possibly be extended (after some modifications) to the Coulomb, i.e., plasma case, we develop in this paper only the short-range case, i.e., we assume

$$\int_{|r| \geqslant a} |(\partial_\alpha)^2 u(r)| \cdot |r|^2 \, d^\nu r < \infty \tag{2.2}$$

$\alpha = 1, \ldots, \nu$, with ν the space dimension, and for some $a > 0$, that is, we give a condition at infinity, making, however, no restriction on the strength of the possible singularity at $r = 0$; even potentials having an additional hard core are admitted. For simplicity we assume the exterior potential $v(r)$ to depend only on one of the coordinates, which we denote by z. Furthermore, $v(z)$ has to fulfill some lower boundedness condition in an infinitely extended system with respect to the z direction (which we do not openly specify at the moment) in order for the system to be stable. Further conditions on $v(z)$ will be imposed as needed.

The following quantities of statistical mechanics will be of relevance below:

The one-particle density

$$\rho(r) := \langle n(r) \rangle, \qquad n(r) := \sum_i \delta(r - r_i) \tag{2.3}$$

the microscopic momentum density

$$p(r) := \sum_i p_i \, \delta(r - r_i) \tag{2.3}$$

the total momentum

$$P := \int d^\nu r \; p(r) = \sum_i p_i$$

and the density–density correlation functions

$$\begin{aligned} &\langle n(r) \cdot n(r') \rangle - \langle n(r) \rangle \cdot \langle n(r') \rangle \\ &\quad = \langle \delta n(r) \cdot \delta n(r') \rangle \\ &\quad = \rho^{(2)}(r, r') - \rho(r) \, \rho(r') + \rho(r) \cdot \delta(r - r') \\ &\quad = \rho_T^{(2)}(r, r') + \rho(r) \, \delta(r - r') =: H(r, r') \end{aligned} \tag{2.4}$$

It will turn out in the next section that as an object standing within

Poisson brackets, the overall momentum P is not really well-defined. So we introduce a localized version:

$$P_R := \int d^\nu r\, p(r)\, f_R(r) = \sum p_i f_R(r_i)$$

$$f_R(r) := f(|r|/R) \tag{2.5}$$

$$f(s) = \begin{cases} 1 & \text{for} \quad s \leqslant 1 \\ 0 & \text{for} \quad s \geqslant 2 \\ \text{smooth in between} \\ \text{and monotone decreasing} \end{cases}$$

3. A GENERAL RELATION BETWEEN DENSITY PROFILE, TRANSVERSE PAIR CORRELATION, AND EXTERIOR FIELD

Since the general strategy has already been exhibited in Refs. 7 and 10, we make only some short comments as to the approach in general and concentrate on the additional terms showing up in the calculations in the presence of an exterior field. We have in a first step

$$-\partial_z \rho(r) = \langle \{n(r), P^z\} \rangle = \langle \{\delta n(r), P^z\} \rangle \tag{3.1}$$

For various reasons (the Bogoliubov inequality holds in general only for *local* quantities A, B) we replace the overall momentum in the z direction P^z by its localized version:

$$-\partial_z \rho(r) = \langle \{\delta n(r), P_R^z\} \rangle \tag{3.2}$$

provided that $|r| < R$.

We now exploit the assumed translation invariance in the $\nu - 1$ directions transverse to the applied exterior field by substituting $\delta n(r)$ by a certain average with respect to the transverse directions. That is, we integrate $\delta n(r)$ over a $(\nu - 1)$-dimensional sphere of radius R centered (for simplicity) at the origin, while in the z direction we smear the density with an (in principle) arbitrary test function $g(z)$ with compact support, which in the end we will choose to be localized around any z value we want. We divide this quantity by the volume of the sphere, i.e.

$$n_R(g) := |V_R|^{-1} \int dz\, g(z) \int_{V_R} ds^{\nu-1}\, \delta n(s, z) \tag{3.3}$$

where s denotes the $\nu - 1$ transverse coordinates. [The reason for the smearing with respect to the z coordinate will become apparent below. It serves to avoid artificial singularities of the type $\delta(z-z)$, δ now being the δ-function.]

Due to translation invariance with respect to s we have, provided that $\operatorname{supp} g \subset \{|z| \leqslant R\}$,

$$-\partial_z \rho(g) := -\int dz\, g(z)\, \partial_z \rho(r) = \langle \{n_R(g), P_R^z\} \rangle \tag{3.4}$$

to which we can now safely apply the Bogoliubov inequality (1.1), yielding

$$[\partial_z \rho(g)]^2 \leqslant \beta \langle n_R(g) \cdot n_R(g) \rangle \cdot \langle \{P_R^z, \{P_R^z, \mathscr{H}\}\} \rangle \tag{3.5}$$

The main computational task consists in estimating the two terms on the rhs, in particular their R dependence for $R \to \infty$. The first term, i.e., $\langle n_R(g) \cdot n_R(g) \rangle$ can be estimated as in Ref. 7 (to which the reader is referred):

$$\begin{aligned} \langle n_R(g) \cdot n_R(g) \rangle &= V_R^{-2} \iint dz\, dz'\, g(z)\, g(z') \\ &\quad \times \int_{|s|<R} ds \int_{|s'|<R} ds'\, H(z, z', |s-s'|) \\ &\leqslant V_R^{-1} \iint dz\, dz'\, g(z)\, g(z') \\ &\quad \times \int_{|s-s'|<2R} d(s-s')\, |H(z, z', |s-s'|)| \end{aligned} \tag{3.6}$$

With

$$H(r, r') = \rho_T^{(2)}(r, r') + \rho^{(1)}(r) \cdot \delta(r-r')$$

$s_{12} := |s-s'|$, and 0_ν, Ω_ν the area and volume of the ν-dimensional unit sphere, we get

$$\begin{aligned} &\langle n_R(g) \cdot n_R(g) \rangle \\ &\quad \leqslant (0_{\nu-1}/\Omega_{\nu-1}) \iint dz\, dz'\, g(z)\, g(z') \\ &\qquad \times \int_0^2 ds_{12}\, |\rho_T^{(2)}(z, z', Rs_{12})|\, s_{12}^{(\nu-2)} + \Omega_{\nu-1}^{-1} R^{-(\nu-1)} \rho(g) \end{aligned} \tag{3.7}$$

This estimate will be made more quantitative in the following by inserting explicit expressions for, e.g., $H(r, r')$. But before doing so, we estimate the second term, which is a much more tedious task, but since most of the calculation has already been done in Ref. 7 for the zero-gravity case, we will only make comments as to the additional terms showing up in the presence of an exterior potential.

The inner bracket $\{P_R^z, \mathscr{H}\}$ now reads

$$\left\{\sum p_i^z f_R(r_i), \mathscr{H}\right\}$$

$$= 1/m \cdot \sum \left[(p_i^z)^2 \, \partial_i^z f_R(r_i) + \sum_{\alpha=1}^{\nu-1} p_i^z \, p_i^\alpha \, \partial_i^\alpha f_R(r_i) \right]$$

$$- \sum_{i \neq k} f_R(r_i) \, \partial_i^z u(r_{ik}) - \sum f_R(r_i) \, \partial_i^z v(r_i) \tag{3.8}$$

where α runs over the $\nu - 1$ transverse directions. The double bracket yields

$$1/m \cdot \sum \text{[terms containing uneven powers of } p_i^z \text{ resp. } p_i^\alpha]$$

$$+ 1/m \cdot \sum \left\{ 3(p_i^z)^2 \, [\partial_i^z f_R(r_i)]^2 + \sum_\alpha (p_i^z)^2 \, [\partial_i^\alpha f_R(r_i)]^2 \right\}$$

$$- 1/m \cdot \sum (p_i^z)^2 \, f_R(r_i) (\partial_i^z)^2 \, f_R(r_i)$$

$$+ \sum_{i \neq k} \{ (\partial_i^z)^2 \, u(r_{ik}) [f_r^2(r_i) - f_R(r_i) \, f_R(r_k)]$$

$$+ \partial_i^z u(r_{ik}) \, f_R(r_i) \cdot \partial_i^z \, f_R(r_i) \}$$

$$+ \sum [\partial_i^z v(r_i) \cdot f_R(r_i) \cdot \partial_i^z f_R(r_i) + (\partial_i^z)^2 \, v(r_i) \, f_R^2(r_i)] \tag{3.9}$$

This lengthy expression becomes much simpler by taking its expectation value, whereupon the first term vanishes identically under the assumption that in equilibrium the momenta are distributed according to a Maxwellian. To eliminate some further nasty terms, we use the following trick (already employed in Ref. 7). For equilibrium states the following holds:

$$0 = \left\langle \left\{ \mathscr{H}, \sum p_i^z \, f_R(r_i) \cdot \partial_i^z \, f_R(r_i) \right\} \right\rangle$$

$$= \left\langle \sum_{i \neq k} \partial_i^z u(r_{ik}) \cdot f_R(r_i) \cdot \partial_i^z \, f_R(r_i) \right\rangle$$

$$- 1/m \cdot \left\langle \sum (p_i^z)^2 \, \{ f_R(r_i) (\partial_i^z)^2 \, f_R(r_i) + [\partial_i^z \, f_R(r_i)]^2 \} \right\rangle$$

$$+ \left\langle \sum \partial_i^z v(r_i) \cdot f_R(r_i) \cdot \partial_i^z \, f_R(r_i) \right\rangle \tag{3.10}$$

Inserting this into the expectation value of (3.9), we arrive at

$$\langle \{P_R^z, \{P_R^z, \mathscr{H}\}\}\rangle$$
$$= 1/m \cdot \left\langle \sum \left\{ 3(p_i^z)^2 \,[\partial_i^z f_R(r_i)]^2 + \sum_{\alpha=1}^{\nu-1} (p_i^z)^2 \,[\partial_i^\alpha f_R(r_i)]^2 \right\} \right.$$
$$+ \left\langle \sum_{i \neq k} (\partial_i^z)^2 \, u(r_{ik})[f_R^2(r_i) - f_R(r_i)\, f_R(r_k)] \right\rangle$$
$$+ \left\langle \sum (\partial_i^z)^2 \, v(r_i)\, f_R^2(r_i) \right\rangle \tag{3.11}$$

Integrating over momenta, inserting distribution functions, and exploiting the symmetry of $u(r_{ik})$ and the pair distribution function yields

LHS of (3.11)

$$= \beta^{-1} \int d^\nu r \left\{ 3[\partial_z f_R(r)]^2 + \sum_\alpha [\partial_\alpha f_R(r)]^2 \right\} \rho(r)$$
$$+ 1/2 \iint d_\nu r \, d_\nu r' \, (\partial_z)^2 \, u(r)[f_R(r+r') - f_R(r')]^2 \, \rho^{(2)}(r+r', r')$$
$$+ \int d_\nu r \, (\partial_z)^2 \, v(r) \cdot f_R^2(r) \, \rho(r) \tag{3.12}$$

Exploiting the special form of $f_R(r)$ [cf. (2.5)] and the assumption (2.2) about the pair potential $u(r)$, we can, as in Ref. 7, estimate the above expression in several steps:

(i) $[f_R(r+r') - f_R(r)]^2 \leqslant |r|^2/R^2 \cdot (\sup_r |\partial f|)^2$

(ii) $$1/2 \left| \iint d_\nu r \, d^\nu r' \, (\partial_z)^2 \, u(r)[f_R(r+r') - f_R(r')]^2 \, \rho^{(2)}(r+r', r') \right|$$
$$\leqslant 1/2 \int d_\nu r \, |(\partial_z)^2 \, u(r)| \cdot |r|^2/R^2 \cdot (\sup |\partial f|)^2$$
$$\times \int_K d_\nu r' \, \rho^{(2)}(r+r', r')$$
(with $K := \{|r'+r| < 2R\} \cup \{|r'| < 2R\}$)
$$\leqslant R^{\nu-2} \cdot 2^\nu \Omega_\nu (\sup |\partial f|)^2$$
$$\times \int d^\nu r \sup_{r'} \rho^{(2)}(r+r', r') \cdot |r|^2 \, |(\partial_z)^2 \, u(r)| \tag{3.13}$$

where the integral in the last line is finite due to assumption (2.2) provided that the integrand is locally integrable at coinciding points (i.e., for $r \to 0$), which is a natural assumption, since one expects $\rho^{(2)}$ to vanish very fast at $r = 0$ for highly repulsive pair potentials[2] s.t. the possible singularity of $u(r)$ at $r = 0$ will be balanced by the vanishing of $\rho^{(2)}$.

$$\text{(iii)}\quad \beta^{-1} \int d^\nu r \left\{ 3[\partial_z f_R(r)]^2 + \sum_\alpha [\partial_\alpha f_R(r)]^2 \right\} \rho(r)$$

$$\leqslant R^{\nu-2} \beta^{-1} \cdot 2^\nu \Omega_\nu \sup_r \rho(r) \int d^\nu r \left[3(\partial_z f)^2 + \sum_\alpha (\partial_\alpha f)^2 \right] \tag{3.14}$$

$$\text{(iv)}\quad \left| \int d^\nu r\, (\partial_z)^2 v(z)\, f_R(r)\, \rho(r) \right|$$

$$\leqslant R^{\nu-1} \cdot 2^{\nu-1} \Omega_{\nu-1} \sup \rho(r) \cdot \int_{-2R}^{+2R} |(\partial_z)^2 v(z)|\, dz$$

To make the expressions below more transparent, we make the following abreviations:

$$C_1 := 2^\nu \Omega_\nu (\sup |\partial f|)^2 \int d^\nu r \sup_{r'} \rho^{(2)}(r + r', r') \cdot |r|^2\, |(\partial_z)^2 u(r)|$$

$$C_2 := 2^\nu \Omega_\nu \int d^\nu r \left[3(\partial_z f)^2 + \sum_\alpha (\partial_\alpha f)^2 \right] \tag{3.15}$$

$$C_3 := 2^{\nu-1} \Omega_{\nu-1}$$

Putting now all the pieces together, we arrive at the following general but not yet particularly transparent estimate (supp $g \subset \{|z| \leqslant R\}$):

$$[\partial_z \rho(g)]^2 \leqslant \beta \Bigg[(0_{\nu-1}/\Omega_{\nu-1}) \iint dz\, dz'\, g(z)\, g(z')$$

$$\times \int_0^2 ds_{12}\, |\rho_T^{(2)}(z, z', Rs_{12})|\, s_{12}^{\nu-2}$$

$$+ R^{-(\nu-1)} \Omega_{\nu-1}^{-1} \rho(g) \Bigg] \Bigg[R^{\nu-2} C_1 + R^{\nu-2} \beta^{-1} \sup \rho(r) \cdot C_2$$

$$+ R^{\nu-1} \int_{-2R}^{+2R} |(\partial_z)^2 v(z)|\, dz \cdot C_3 \Bigg] \tag{3.16}$$

[2] We always tacitly assume that a possible hard core is shielded by a smoothly diverging potential in order that $\rho^2(r, r)\, u''(r)$ remains integrable at the singularity, i.e., $u(r) = \infty$ for $|r| \leqslant a$, $u(r)$ smoothly to $+\infty$ for $|r| \searrow a$ (e.g., of L-J type). For further remarks see the Appendix.

In the following section we will bring the expression within the first square bracket into such a form that a variety of quantitative results can be inferred from the above inequality. In doing this we will take advantage of the complete freedom of the smearing function $g(z)$ and the scaling parameter R, which we will usually take as large as possible.

4. THE TRANSVERSE PAIR CORRELATION FUNCTION

We now calculate the expression within the first square bracket of (3.16) in more detail. There are two typical modes of asymptotic behavior of $H(z, z', s_{12})$ for s_{12} large, i.e., exponential or polynomial decay. General folklore discriminates these two possibilities by the saying that in the former case the correlation length ξ_T is finite, while in the latter case it is infinite, and sets this statement in relation to whether the system is at the critical point or away from it. But real life is not as simple. So, since it is our impression that the above sketchy statement represents a widespread belief, we first dwell on this point a little.

The correctness of the above picture depends critically on the range of the pair potential. There are rigorous calculations showing that for potentials having roughly a power law decay at infinity (which can be arbitrarily fast!) the bulk correlation function $H(r-r')$ decays asymptotically exactly as the potential itself, namely as some inverse power. This has been proved for zero gravity (and in the single-phase region) in, e.g., Ref. 11. For lattice gases and *finite-range potentials* an exponential decay is, however, known to hold away from criticality, while for power law interactions, even in the presence of an exterior field, H decays again only like an inverse power (see Ref. 12). One can learn from these findings that an exponential clustering, suggested by heuristic arguments, is by no means a universal phenomenon away from the critical point.

From the above it seems sufficient to discriminate among the following cases:

$$|\rho_T^{(2)}(z, z', s_{12})| \leqslant \text{const}_H \cdot \begin{cases} s_{12}^{-\alpha} \exp(-s_{12}/\xi_T), & \xi_T < \infty \\ (1+s_{12})^{-\alpha} \quad \text{(i)}\ \alpha > \nu - 1, \quad \text{(ii)}\ \alpha = \nu - 1, & \\ s_{12}^{-\alpha} \quad \text{(iii)}\ \alpha < \nu - 1, & \xi_T = \infty \end{cases} \tag{4.1}$$

Inserting this into the first square bracket of (3.16), denoted by I, we get:

$$
I \leqslant \begin{cases} R^{-(\nu-1)} \left\{ \mathrm{const}_H \cdot 0_{\nu-1}/\Omega_{\nu-1} \cdot \left[\int g(z) \right]^2 \right. \\ \quad \left. \times \int_0^\infty ds \, [s^{-\alpha} \exp(-s/\xi_T)] \, s^{\nu-2} + \Omega_{\nu-1}^{-1} \rho(g) \right\}, \qquad \xi_T < \infty \\ \left. \begin{array}{l} \text{(i)} \quad R^{-(\nu-1)} \int_0^\infty ds \, (1+s)^{-\alpha} s^{\nu-2} \\ \text{(ii)} \quad R^{-(\nu-1)} \ln(2R+1) \\ \text{(iii)} \quad R^{-\alpha} \int_0^2 ds \, s^{\nu-(\alpha+2)} \end{array} \right\} \begin{array}{l} \cdot \mathrm{const}_H \cdot 0_{\nu-1}/\Omega_{\nu-1} \cdot \left[\int g(z) \right]^2 \\ \\ + R^{-(\nu-1)} \Omega_{\nu-1}^{-1} \rho(g) \end{array} \end{cases} \tag{4.2}
$$

In a last step we introduce the following abbreviations:

$$
\begin{aligned} C_4(\xi_T) &:= \mathrm{const}_H \cdot 0_{\nu-1}/\Omega_{\nu-1} \cdot \int_0^\infty ds \exp(-s/\xi_T) \, s^{(\nu-2)-\alpha} \\ C_4(\infty) &:= \mathrm{const}_H \cdot 0_{\nu-1}/\Omega_{\nu-1} \\ C_5 &:= \Omega_{\nu-1}^{-1} \end{aligned} \tag{4.3}
$$

Remark. It is perhaps interesting to note that the scaling behavior in (4.2) is basically the same for exponential and polynomial decay of the pair correlation if $\alpha > \nu - 1$. The borderline case seems to be $\alpha = \nu - 1$.

5. ESTIMATES OF DENSITY GRADIENT AND TRANSVERSE PAIR CORRELATION

We now make use of our freedom in the choice of the smearing function $g(z)$. We choose it to be simply

$$
g(z) := \begin{cases} 1 & \text{for} \quad z_1 < z < z_2 \\ 0 & \text{elsewhere} \end{cases} \tag{5.1}
$$

which implies

$$
\begin{aligned} \partial_z \rho(g) &= \rho(z_2) - \rho(z_1) \\ \rho(g) &= \int_{z_1}^{z_2} \rho(z) \, dz \leqslant \sup_{z_1 < z < z_2} \rho(z) \cdot (z_2 - z_1) \\ \int g(z) \, dz &= z_2 - z_1 \end{aligned} \tag{5.2}
$$

With the abbreviations

$$\sup_r \rho(r) =: \rho_s, \qquad z_2 - z_1 =: z_{21}, \qquad \sup_{z_1 < z < z_2} \rho(z) =: \rho_{12} \tag{5.3}$$

we now give (3.16) its final form.

Central estimate:

$$\beta^{-1} \frac{[\rho(z_2) - \rho(z_1)]^2}{R^{\nu-2}(C_1 + \beta^{-1}\rho_s C_2) + R^{\nu-1} \int_{-2R}^{2R} |(\partial_z)^2 v(z)|\, dz \cdot C_3}$$
$$\leqslant \begin{cases} R^{-(\nu-1)}[z_{12}^2 C_4(\xi_T) + z_{12}\rho_{12} C_5], & \xi_T < \infty \\ \text{(i) } R^{-(\nu-1)}\left[z_{12}^2 C_4(\infty) \int_0^\infty ds\, (1+s)^{-\alpha} s^{\nu-2} + z_{12}\rho_{12} C_5 \right], & \alpha > \nu - 1 \\ \text{(ii) } R^{-(\nu-1)}[\ln(2R+1)\, z_{12}^2 C_4 + z_{12}\rho_{12} C_5], & \alpha = \nu - 1 \\ \text{(iii) } R^{-\alpha} z_{12}^2 \int_0^2 ds\, s^{\nu-(\alpha+2)} C_4 + R^{-(\nu-1)} z_{12}\rho_{12} C_5, & \alpha < \nu - 1 \end{cases} \tag{5.4}$$

provided that $R > \sup\{|z_2|, |z_1|\}$.

This is the central result we will exploit in the rest of the paper. All occurring constants can in principle be computed. We begin with the case $\xi_T < \infty$, $R \to \infty$.

5.1. $\xi_T < \infty$, $R \to \infty$

Provided that

$$\lim \int_{-2R}^{2R} |(\partial_z)^2 v(z)|\, dz < \infty$$

we can neglect in the limit $R \to \infty$ the first term in the denominator on the lhs of (5.4) and have

$$[\rho(z_2) - \rho(z_1)]^2 \leqslant \beta \int_{-\infty}^{+\infty} |(\partial_z)^2 v(z)|\, dz \cdot C_3(z_{12}^2 C_4 + z_{12}\rho_{12} C_5) \tag{5.5}$$

This *a priori* inequality has to be fulfilled in the case of an exponential decay of the transverse pair correlation (where the main dependence on ξ_T is contained in the constant C_4). Furthermore, we see again that a density gradient is incompatible with exponential clustering in case of an everywhere vanishing exterior potential.

More interesting is the following situation, which leads immediately into one of the most exciting areas of present research efforts, connected with "wetting," wall effects, etc.

5.2. Interfaces in the Presence of a Linear Gravitational Potential, $v(z) = a \cdot z$, plus Wall Effects

The case $v(z) = a \cdot z$, i.e., the "usual" gravitational field, displays various remarkable aspects. First, it is a special merit of our approach that the exterior field enters only in the form of its second derivative (in contrast to the standard expressions of fluid physics, where it is the first derivative). Second, a linear field is not lower bounded s.t. statistical mechanics in a bottomless container becomes obscure. Hence we place a container bottom at $z = -L$, i.e., consider the fluid to be confined to the half-space $z > -L$. (Situations like these will be treated in more detail in a parallel paper about fluids near a wall.) Walls will be conventionally introduced into our scheme via extra exterior potentials being infinite for $z < -L$. In any case, as long as we keep the R of our formulas smaller than $\frac{1}{2}L$, our above estimates can be applied without any change, with $v(z)$ now completely dropping out (in the case of an ideal rigid hard wall). We have for $\xi_T < \infty$, $|z_{1,2}| < \frac{1}{2}L = R$,

$$[\rho(z_2) - \rho(z_1)]^2 \leqslant \beta \cdot 2L^{-1}(C_1 + \beta^{-1}\rho_s C_2)(z_{12}^2 C_4 + z_{12}\rho_{12} C_5) \quad (5.6)$$

This is a remarkable result. Assume, for example, that the exterior thermodynamic parameters are so chosen that, e.g., the liquid can coexist with its vapor. Then in the presence of the gravitational field and the container bottom a well-localised liquid–gas interface will form, say around $z = z_0$. Choosing now z_2, z_1 to be z positions where the system attains its bulk values (to a certain degree) for a liquid or a gas,[3] i.e., $z_2 = z_l$, $z_1 = z_g$, $\rho_2 = \rho_l$, and $\rho_1 = \rho_g$, (5.6) supplies us with an exact relation between $(\rho_l - \rho_g)^2$, L, and $|z_l - z_g|$!

With L representing a macroscopic distance, by adjusting the thermodynamic parameters we can choose it as large as we want while pinning the interface at a fixed z value z_0. With $(\rho_l - \rho_g)$ a fixed value, L^{-1} becoming arbitrarily small, we observe that the interface thickness $|z_l - z_g|$ has to become very large with increasing L in order that (5.6) remains true.[4] That is, in a linear gravitational field the interface becomes more and more diffuse with increasing distance from the bottom of the container. This does

[3] For example, the "10–90" thickness (cf. Ref. 5, p. 180).

[4] Provided that $C_4(\xi_T)$ is not singularly dependent on L (cf. Section 6) and that, e.g., C_1 can be chosen independent of L for a wide range of macroscopic L's (see Note added in Proof)!

not seem to be in accord with our usual intuition. Hence, if this situation does not prevail, the assumption $\xi_T < \infty$ must be wrong!

A way out is to abandon the assumption of an exponential decay parallel to the interface (resp. the wall). Inspecting again formula (5.4), we see that case (iii) with a polynomial clustering of the pair correlation, which goes in leading order with an exponent $-\alpha$, $\alpha \leqslant \nu - 2$, yields a result different from (5.6):

Observation. For $\xi_T = \infty$, $\alpha \leqslant \nu - 2$, we have

$$[\rho(z_2) - \rho(z_1)]^2 \leqslant \beta \left[z_{12}^2 \int_0^2 ds\, s^{\nu - (\alpha + 2)} C_4 + 2L^{-1} z_{12} \rho_{12} C_5 \right] [\cdots] \qquad (5.7)$$

5.3. Main Conclusion

The above observation indicates that in the case where the interface does not become more and more diffuse with increasing distance from the bottom of the container, which should be prevented by the presence of a linear gravitational field, the pair correlation function can only decay with a polynomial rate parallel to the interface, given by a power $-\alpha$, $\alpha \leqslant \nu - 2$!

Remarks. Similar observations can be made for other situations. A case in point is the wetting of a wall; for this case we refer to, e.g., Ref. 13, where arguments of a different kind are given, pointing, however, to perhaps related phenomena. Furthermore, our reasoning carries immediately over to crystals in coexistence with a vapor or liquid of the same species. By substituting the continuous symmetry parallel to the interface with a periodic one,[10] we get estimates that hold below (resp. above) the "roughening temperature." This will be studied in more detail elsewhere.

6. A PHYSICAL INTERPRETATION OF THE RESULTS, SOME QUANTITATIVE ESTIMATES, AND THE SPECIAL CASE: SPACE DIMENSION $\nu = 2$

In order to judge the sensitivity of the above estimates, one first has to make some quantitative checks of the various constants occurring in, e.g., (5.4) [resp. (5.6)]. It is reasonable to take as appropriate unit of length the angstrom or a typical interatomic distance σ in the fluid. For argon, σ is 3.4 Å at 84 K; measured in σ units the particle density in the liquid is then ~ 0.76 (cf., e.g., Ref. 15).

With respect to this length scale, the constants $C_{1,2,3,5}$ (resp. their various combinations) (together with β) occurring in, e.g., (5.6) are all of order one, $O(1)$. More interesting behavior is seen in $C_4(\xi_T)$ [see (4.3)]. It is advantageous to extract the transverse correlation length ξ_T from this expression. One gets

$$C_4(\xi_T) = \text{const} \cdot \xi_T^{(\nu-1)-\alpha}, \qquad \text{const} = O(1) \tag{6.1}$$

with α stemming from $|H(z, z', s)| \lesssim \exp(-s/\xi_T)/s^\alpha$.

With (6.1) one can now give expression (5.6) a simple transparent form, which is most useful in studying all sorts of scaling properties (e.g., near T_c, T_w, approaching the bulk coexistence curve from the one-phase regime, etc.). We get

$$(\Delta\rho)^2 \leqslant \text{const} \cdot L^{-1} \xi_T^{(\nu-1)-\alpha} \Delta z^2 \qquad (\xi_T < \infty!) \tag{6.2}$$

where the constant is $O(1)$[5] and where we can safely drop the contribution linear in Δz. For large L this contribution becomes negligible, since only a diverging Δz or ξ_T can compensate the vanishing L^{-1} for L large. A rough quantitative check shows that (6.2) yields reasonable results. Inserting typical values for ρ_L, the constant, Δz, and L (e.g., away from criticality, Δz is usually a few angstroms), one sees that ξ_T is in the mm-regime, a value also predicted by capillary wave theory in the earth's gravitational field (in this picture ξ_T is expected to be of the order of the so-called caillary length; cf., e.g., Ref. 5).

Thus, the orders of magnitude predicted by both theories are more or less the same. But the discrepancies with respect to the physical content are nevertheless striking. As long as we have a finite transverse correlation length, (6.2) tells us that far from the container bottom, i.e., $L^{-1} \ll 1$, either ξ_T or Δz or both have to acquire a marked dependence on L, approaching ∞ with $L \to \infty$ (remember that a linear gravitational field is applied s.t. we should be always outside the regime of finite wetting). We do not know whether such a dependence on L has ever been experimentally investigated. In any case, as far as Δz is concerned, we think this dependence should have been observed anyway. All experimental data, however, seem to be in accord with an interfacial thickness of only a few angstroms. So, for the time being, we expect ξ_T to be the critical candidate for a singular dependence on L (provided it is finite at all!).

To clarify this point, we sketch briefly the picture underlying the capillary wave approach (as designed by Buff *et al.*[16] and extended by, e.g., Weeks.[2]) We think the crucial ingredient in this approach is the assumption that the interface behaves like a taut (basically simply connected) membrane similar to a drumhead, dividing unambiguously the liquid

[5] See Note added in Proof.

from the gas phase. This has the physically far-reaching effect that in the case in which one superimposes an arbitrary oscillation on the equilibrium position of the membrane, every element of liquid contributes with a *positive* potential energy, irrespective of whether it is moving up or down. One arrives at the following expression for the work done (cf., e.g., Ref. 5, p. 116):

$$W = \int d^{\nu}\bar{s}^{1} \left[\int_{0}^{\zeta(s)} (\rho_L - \rho_G)\, mgz\, dz + \sigma_b (1 + |\nabla_s \zeta|^2)^{1/2} \right] \qquad (6.3)$$

where for, e.g., $\zeta(s) < 0$ the corresponding fluid element has to be elevated at least to the height $z = 0$, which is the reference level of the potential energy, thus consuming a positive amount of potential energy. A further consequence of this model is that the gravitational constant g governs the range of transverse correlation (together with m and σ_b), making ξ_T finite and independent of L for large L.

Remark. One should, however, note that in the above situation, where one is not primarily interested in wetting and wall effects, the exterior gravitational field is usually only included in a cursory manner into the calculations, the whole treatment being restricted to an immediate neighborhood of the interface itself.

On the other hand, a *linear* gravitational field drops out completely from relation (6.2) if one stays away from the container walls (it may only have a small effect in altering the bulk densities a little). With Δz remaining microscopic for L becoming macroscopic, ξ_T *necessarily* has to diverge with increasing L (or is ∞ anyway).

Conclusion. The (exact) estimate (6.2) is not in accord with the predictions of the capillary wave model!

Particularly puzzling is the case of space dimension $\nu = 2$. Inspecting relations (5.4) and (5.7), we see that not even a polynomial clustering, be it arbitrarily week, can make the rhs of (5.4) and (5.7) nonvanishing for $L \to \infty$ unless Δz diverges also with L! Invoking some abstract machinery, one can show hat the same holds for the weakest form of transverse clustering one can think of (cf. Ref. 7, final section). Thus, we have the following:

Observation. For space dimension two a linear gravitational field seems unable to stabilize a finite interface thickness with increasing distance of the interface from the container bottom. If one assumes a polynomial clustering, i.e., $H(s) \sim s^{-\alpha}$ asymptotically, the interface thickness increases $\gtrsim L^{\alpha/2}$.

Provided the above conclusions are correct, one has to develop a picture of the interface region that deviates from the drumhead model at least with respect to the finer details. As a hint of where modifications are perhaps appropriate, we note the following observations:

(i) It is just the linearity of the gravitational field that was responsible for its completely dropping out from the above calculations far from the container walls.

(ii) It is just the assumed tautness of the membrane that has the effect that in (6.3) even a piece of liquid moving down contributes with a *positive* potential energy, since the only way to realize this motion within the capillary wave model is to transport the piece of liquid to the level $z=0$. This has the effect that one cannot have oscillations of the surface with negligible potential energy, thus making the transverse correlation finite.

We now invoke a slightly different picture of the fine structure of the interface region. Since this paper reports on rigorous results, we present only a rough outline of our ideas, which we plan to elaborate in more detail in a forthcoming paper. We assume the interface layer to be a statistical subsystem of finite thickness in contact with, so to say, two large reservoirs, i.e., the bulk liquid and the gaseous phase, and containing, as a typical transition zone, a sizable amount of (quasiliquid) clusters of atoms, which are permanently exchanged with the two bulk phases.

In a linear gravitational field the following (quasi) collective motion now suggests itself: There are liquid clusters moving up and down, i.e., reentering the liquid or diffusing into the gas phase (with an additional potential coming from the liquid phase, stabilizing the interface as a whole). A cluster moving up consumes a certain amount of potential energy, a cluster moving down sets a certain amount free. The linearity of the exterior gravitational field has the additional peculiar effect that these amounts are independent of the vertical location of the clusters. To put it in a nutshell, one can visualize a long-ranged horizontal collective motion with clusters moving up and down while the gains and losses of the respective potential energies nearly balance each other s.t. the overall potential energy of the excitation is almost zero.

In concluding this paper we briefly comment on investigations of the interface structure via computer simulation. There exist various reliable studies (e.g., Ref. 15). Unfortunately, the diameter of the simulated box remains microscopic (typically a few σ) s.t. the (large-L) behavior is beyond the reach of these investigations. But the asymptotic behavior of, e.g., $H(s)$ may be difficult to check anyway, since one has to be prepared for the possibility that the above nonexponential contribution is very small.

On the other hand, Fig. 12 of Ref. 15 displays the typical distribution of clusters we expect in the interface region s.t. the computer results of Ref. 15 may suport our picture as well as the caillary wave model.

APPENDIX

In this appendix we address the class of interparticle potentials admitted in expression (3.13) in more detail. For most of the results after the estimate (3.13) it is essential that, e.g., $\rho^{(2)}(r+r', r')\,|r|^2\,|u_{zz}(r)|$ remains locally integrable at coinciding points, i.e., $r \to 0$, resp. at the contact singularity in the case of a hard core.

By a standard procedure of statistical fluid mechanics one realizes that one can extract a factor from $\rho^{(2)}(r, r')$ s.t.

$$\rho^{(2)}(r, r') = e^{-\beta u(r-r')} f(r, r')$$

with f smooth to some degree across a singularity of u. Two classes of potentials are of relevance: (i) point interactions with a possible singularity at $r=0$; (ii) potentials containing a hard core part, i.e., $u(r)=\infty$ for $|r|<a$ for some a.

For class (i) the following natural condition suggests itself: Possible singularities of u at $r=0$ have to be of the form $u(r)$ to $+\infty$ smoothly for $r \to 0$ [e.g., $O(r^{-\alpha})$] s.t. $u''(r)$ is $O(r^{-\alpha-2})$. Under this proviso $u''(r)\,e^{-u(r)}$ is locally integrable in $r=0$. In particular, all sorts of L-J potentials are admitted.

In the case of a hard core the condition has to be slightly more restrictive. Take, e.g., an "unscreened" hard core, i.e., $u(r)=\infty$ for $|r|<a$, uniformly bounded for $|r|>a$. Jump discontinuities of this kind are nasty. While $u'(r)\,e^{-u(r)} = (-e^{-u(r)})'$ is still integrable across the contact singularity (developing a δ-contribution), this is no longer the case for, e.g., $u''e^{-u}$, which contains a nonintegrable distributional singularity.

The class of potentials we actually have in mind have hard cores always shielded by a smoothly diverging repulsive part, i.e., $u(r)=\infty$ for $|r|<a$, smoothly diverging to $+\infty$ for $|r| \searrow a$ as in (i).

Taking $u(r)$ from these two classes guarantees that the above expression is locally integrable at contact singularities of u. It is nevertheless interesting that (at least at first glance) our reasoning does not apply to unshielded hard core potentials (which, while being a little bit artificial, are an important tool for numerical calculations). Whether there is a deeper physical reason for this "defect" shall be discussed in a future paper.

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NOTE ADDED IN PROOF

Note that the gravitational field still has an indirect effect on the value of some of the "constants" as, e.g., C_1 (cf. its definition in (3.15)). C_1 is expected to increase a little with L as the molecules deep in the fluid come closer together under high pressure. For reasonable (not extremely large) macroscopic L's this effect should, however, be weak so that we are allowed to choose constant bounds for a wide range of L's.

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