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On the failure of certain integral equation theories to account for complete wetting at solid–fluid interfaces

by R. EVANS, P. TARAZONA and U. MARINI BETTOLO MARCONI
H. H. Wills Physics Laboratory, University of Bristol,
Bristol BS8 1TL, England

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We examine the usefulness of the integral equations derived from the HNC and PY closures of the wall-particle Ornstein–Zernike equation for describing the density profile and pairwise distribution function of models of the solid–fluid interface. It is shown that these, and closely related closure approximations, cannot account for complete wetting of a solid–gas interface by liquid or complete wetting by gas of a purely repulsive substrate at a solid–liquid interface. The closure approximation to the first YBG equation which sets the total pairwise correlation function equal to that of the bulk fluid exhibits the same failings. Since none of these approaches can describe liquid–gas coexistence, they cannot be used as a basis for a self consistent theory of contact angle and wetting phenomena. Moreover, they cannot account for the growth of thick, liquid-like, adsorbed films which develop at solid–gas interfaces at temperatures T above the wetting transition temperature T_{w}.

Such approaches also give an inadequate description of pairwise correlations in the interface. This is illustrated by the introduction of a ' surface ' compressibility sum rule which relates an integral over the interfacial part of the pairwise distribution function to $(\partial\Gamma/\partial\mu)_T$, the derivative with respect to chemical potential μ of the coverage Γ. For $T > T_{\mathrm{w}}$ Γ and, hence, $(\partial\Gamma/\partial\mu)_T$ diverge as μ approaches its value at saturation with exponents that reflect the asymptotic behaviour of the attractive part of the solid–gas potential. The sum rule shows that the range of transverse (parallel to the surface) pairwise correlations must diverge in an equivalent fashion. Divergences of this kind are not predicted by the integral equation approaches. The growth of long-ranged transverse correlations has important repercussions for computer simulations of thick adsorbed films.

1. INTRODUCTION

It is the purpose of this paper to point out the limitations of several widely used theories of solid–fluid interfaces. In particular we show that these theories cannot account for the phenomenon of complete wetting by liquid or by gas.

There are three main theoretical approaches employed in calculations of the microscopic structure of simple fluids near model solid substrates. The first of these makes use of closure approximations to the wall-particle Ornstein–Zernike equation. This approach was pioneered by Perram and White [1] and Henderson *et al.* [2] and has been applied to a variety of model systems—see, for example, [3, 4] and references therein. Two of the simplest and most commonly used closures are the hypernetted-chain (HNC) and Percus–Yevick

(PY) approximations. In the former the density profile of the fluid $\rho(z)$ satisfies the non-linear integral equation

$$\rho(z)=\rho_0 \exp\left(-\beta V(z)+\int d\mathbf{r}'\, c_0(|\mathbf{r}-\mathbf{r}'|)(\rho(z')-\rho_0)\right), \tag{1}$$

where $\beta=1/k_{\mathrm{B}}T$, ρ_0 is the density of the bulk fluid far away from the substrate and $V(z)$ is the solid–fluid potential which is assumed to depend only on the direction z perpendicular to the substrate. $c_0(r)$ is the direct correlation function of the *homogeneous* bulk fluid of density ρ_0. The corresponding result for the PY closure is a linearized version of (1), i.e.

$$\rho(z)=\rho_0 \exp(-\beta V(z))\left(1+\int d\mathbf{r}'\, c_0(|\mathbf{r}-\mathbf{r}'|)(\rho(z')-\rho_0)\right). \tag{2}$$

Given a model for $V(z)$ and some prescription for calculating $c_0(r)$ these equations can be solved numerically for the density profile and are known to yield results in good agreement with computer simulations for *certain* cases [5, 6, 3, 4].

The second approach is based on the use of approximate density functional theories. This was introduced by Ebner *et al.* [7, 8]. It consists, in essence, of constructing an approximate free energy functional for the inhomogeneous fluid and minimizing this to determine the equilibrium density profile. Alternatively it can be regarded as a procedure which approximates the direct correlation function of the *inhomogeneous* fluid [8, 9, 4]. Considerable controversy concerning the relative merits and failings of these two approaches has arisen since Saam and Ebner [8] published the results of their calculations for a Lennard-Jones 12–6 fluid near an integrated Lennard-Jones 9–3 substrate. For a gas whose density was close to the saturated vapour density at the temperature T in question, the density profiles calculated from their density functional approach showed that thick, liquid-like, films were adsorbed at the substrate and that the thickness of the film increased as the bulk gas density approached its value at saturation. Such behaviour is associated with complete wetting by liquid and will occur if $T_{\mathrm{w}}<T<T_{\mathrm{c}}$. Here T_{c} is the bulk critical temperature and T_{w} is the temperature of the wetting transition [10–14]. By contrast the results obtained from (2) with $c_0(r)$ calculated in the (bulk) PY approximation, did not show any thick films. Saam and Ebner [8] concluded that the PY theory (2) was markedly inferior to the density functional approach because of the former's failure to predict the growth of thick liquid films above T_{w}. Their conclusion was challenged by Lane *et al.* [5] who performed Monte Carlo simulations for the same model. For the same temperature they found no thick liquid films even for the case when the bulk gas was very close to saturation. Lane *et al.* concluded that the density functional approach used by Saam and Ebner must be defective, and since their Monte Carlo profiles were rather close to those obtained [8] from the PY theory they argued that PY and related theories should be preferred. Subsequently other authors [14–16] have criticized Saam and Ebner's approach.

Recently two of us [12] have suggested that the wetting transition for this model system may occur at a significantly higher temperature than that calculated by Ebner and Saam [10] so that the temperature at which the simulations were performed probably lies below T_{w} and that is why no thick liquid films were found in the Monte Carlo results. During the course of this study [12, 13] of wetting transitions at models of solid–fluid interfaces we also examined the usefulness of the HNC and PY theories as well as that of related theories for describing wetting behaviour. Here we show that the PY equation (2) is incapable of describing complete wetting by liquid at a solid–gas interface and cannot, therefore, account for the growth of the thick, liquid-like, films above T_w which are obtained from density functional calculations [8, 12, 13], and which are predicted on general grounds by Cahn [11] and Sullivan [14]. The HNC equation (1) is also shown to be inadequate in this respect. These theories also fail to account for the complete wetting by gas of a purely repulsive hard wall which must occur when the bulk liquid is close to coexistence. Several computer simulations [17–19] of Lennard-Jones liquids near infinitely repulsive walls have obtained structureless density profiles which resemble a part of the free liquid–gas interface. Such behaviour is characteristic of wetting by gas [14].

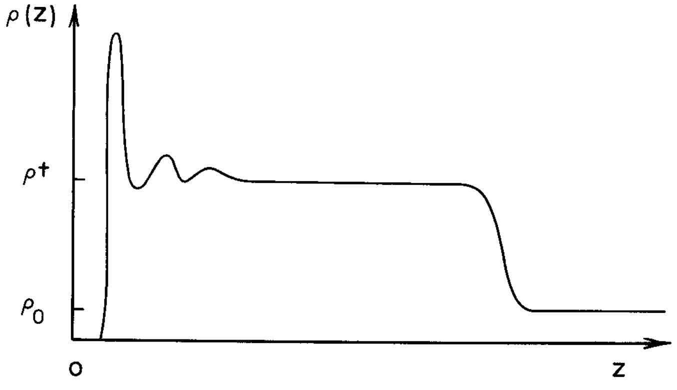
Whilst several authors, in particular [8, 17, 14, 19, 20], have anticipated the failings maintained above we were not aware of any explicit ‘ proof ’ that the PY, HNC and related integral equation theories could not account for complete wetting. (The important work of Sullivan *et al.* [19] certainly suggests that this is the case since the profiles which they calculate from integral equation theories are completely different from those obtained in their simulation of the same Lennard-Jones liquid near the hard wall and show no indication of wetting by gas.) The arguments we give here are, we believe, rather compelling and demonstrate quite clearly why integral equation theories of the PY or HNC type will often prove useless for studies of fluids in coexistence or near coexistence states.

A third approach often used to describe solid–fluid interfaces consists of finding approximate solutions of the first YBG equation [3, 4]. We show that a commonly applied closure approximation to this equation yields an integral equation for the density profile which exhibits the same failings as those described above. Moreover, this equation exhibits other fundamental shortcomings which limit severely its applicability and, therefore, its usefulness. We conclude that all these theories, unlike the density functional theories, cannot describe liquid–gas coexistence and are, therefore, incapable of accounting for wetting phenomena—a fact which does not appear to be widely recognized.

Our paper is arranged as follows: in § 2 we examine the various integral equations for near complete wetting situations and show how these fail to describe the growth of thick liquid or gas films. The physical explanation for these failings is discussed in § 3 where we analyse the grand potential densities which correspond to HNC and PY theories and show that these do not exhibit the two minima which are required for coexistence. The approximate YBG equation is shown to be inconsistent with linear response theory and we discuss the consequences of this in § 4, where we analyse the pairwise correlation functions resulting from different theories. This permits us to examine the status of each theory in some detail. The approximate YBG equation also fails to satisfy an important test of self consistency—the surface compressibility sum rule. This rules, which relates an integral over the pairwise distribution function in the interface to the derivative with respect to chemical potential of the coverage, is particularly revealing in the limit of complete wetting where it links the divergence of the coverage to that of the transverse structure factor, i.e. to the growth of long ranged transverse correlations. We discuss the importance of fluctuations near complete wetting and, by making an analogy with bulk critical phenomena, suggest that such fluctuations must be taken into consideration in attempts to simulate thick liquid films. We conclude in § 5 with a discussion of our results where we compare and contrast the density functional approach with the integral equation approaches. Implications for the theory of the liquid–gas interface are mentioned briefly.

2. ANALYSIS OF THE PY, HNC AND RELATED INTEGRAL EQUATIONS FOR A COMPLETE WETTING SITUATION

In figure 1 (*a*) we sketch the density profile $\rho(z)$ of a simple (argon-like) fluid for a solid–gas interface corresponding to a temperature above the wetting transition temperature T_w. We assume that the solid–fluid potential $V(z)$ is sufficiently attractive (for $z > 0$) that T_w lies well-below T_c and that the bulk



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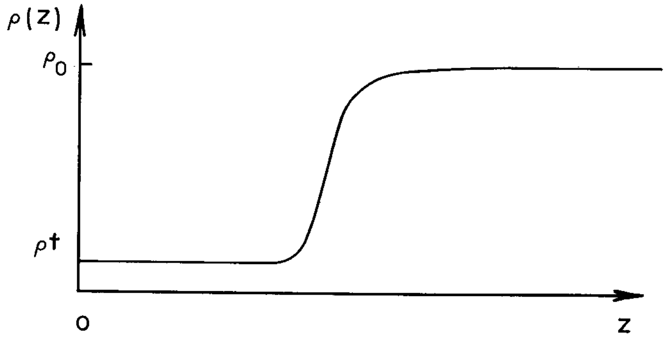

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Figure 1. (*a*) The density profile $\rho(z)$ (schematic) at a solid–gas interface for $T > T_W$. A thick liquid-like film of nearly constant density $\rho^\dagger$ develops at the substrate. The oscillations in the profile extend over two or three molecular diameters only. The bulk gas density ρ_0 is slightly below its value at saturation. (*b*) The density profile (schematic) at a solid–liquid interface for which the substrate is purely repulsive. A thick film of gas of nearly constant density $\rho^\dagger$ develops at the substrate. The bulk liquid density ρ_0 is slightly above its value at saturation.

gas is slightly undersaturated so that $\rho_0 \lesssim \rho_g$, the saturated vapour density. Under these circumstances a thick, liquid-like, film is adsorbed at the substrate and the density is constant with a value $\rho^\dagger \approx \rho_l$, the density of the coexisting liquid at the temperature in question, over a distance corresponding to several molecular diameters. In the limit $\rho_0 \to \rho_g$ the film becomes macroscopically thick and the substrate is wet completely by liquid.

We now ask whether (1) and (2) can describe such a situation. The integral in both equations can be written as

$$I(z) = 2\pi \int_0^\infty dr'\, r' c_0(r') \int_{-r'}^{r'} dz' (\rho(z+z') - \rho_0). \tag{3}$$

Assuming that $c_0(r)$ is short ranged† we Taylor expand $\rho(z+z')$ and integrate with respect to z' to obtain

$$I(z) = a(\rho_0)(\rho(z) - \rho_0) + b(\rho_0) d^2 \rho(z)/dz^2 + \ldots, \tag{4}$$

where

$$\left.\begin{aligned} a(\rho_0) &= \int d\mathbf{r}\, c_0(r), \\ b(\rho_0) &= \frac{2\pi}{3} \int_0^\infty dr\, r^4 c_0(r) \end{aligned}\right\} \tag{5}$$

are quantities which refer to the bulk fluid, in this case, gas. Substituting (4) into the HNC equation (1) we have

$$\ln\left(\frac{\rho(z)}{\rho_0}\right) = -\beta V(z) + a(\rho_0)(\rho(z) - \rho_0) + b(\rho_0) d^2 \rho(z)/dz^2 + \ldots, \tag{6}$$

whereas the corresponding expansion of the PY equation (2) is

$$\ln\left(\frac{\rho(z)}{\rho_0}\right) = -\beta V(z) + \ln(1 + a(\rho_0)(\rho(z) - \rho_0) + b(\rho_0) d^2 \rho(z)/dz^2 + \ldots). \tag{7}$$

These expansions should provide a realistic description of the 'tail' of the density profile where $\rho(z) \to \rho_0$ (see e.g. [9]). They should also be applicable to the region of constant density in figure 1 (*a*)—provided the 'plateau' exists and its extent is larger than the range of $c_0(r)$. Setting $\rho = \rho^\dagger$ and assuming that $V(z) \approx 0$ in the plateau it is clear that (6) and (7) imply, respectively,

$$\ln(\rho^\dagger/\rho_0) \sim a(\rho_0)(\rho^\dagger - \rho_0) \quad \text{(HNC)} \tag{8}$$

and

$$\rho_0 a(\rho_0) \sim 1 \quad \text{(PY)}. \tag{9}$$

The last equation, which must become an equality in the limit of complete wetting, is then equivalent to requiring that the isothermal compressibility κ_T of the bulk fluid be infinite since from the definition (5) it follows that

$$1 - \rho_0 a(\rho_0) = (\kappa_T \rho_0 k_B T)^{-1}. \tag{10}$$

Thus (9) is only valid if the fluid is at its critical point. This argument indicates that the PY theory is incapable of describing wetting by liquid at the solid–gas interface. The HNC theory, on the other hand, implies a relationship

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† The expansion described here is not strictly applicable to fluids for which $c_0(r)$ exhibits inverse power law decay (for example, [21]) but this is not important in the present argument.

between the densities of coexisting liquid and gas since taking the limit of complete wetting in (8) requires

$$\ln(\rho_l/\rho_g) = a(\rho_g)(\rho_l - \rho_g). \tag{11}$$

This result was obtained previously by Rowlinson and Widom [22] from an approximate analysis of the exact integrodifferential equation for the density profile of a free liquid–gas interface. At first sight (11) appears to be quite realistic. It has the solution $\rho_c a(\rho_c) = 1$ at the critical point, which is, of course, exact. Moreover for certain gaseous states it is possible to have $0 < \rho_g a(\rho_g) < 1$ so it seems that (11) might predict sensible values of ρ_l given ρ_g. What is not clear is whether the relation (11) has any fundamental significance as regards liquid–gas coexistence. We shall argue later that it does not and that having solutions to this equation does not guarantee the existence of the stable wetting film.

We turn now to wetting by gas (figure 1 (*b*)). The bulk fluid is a liquid with density $\rho_0 \gtrsim \rho_l$ and the substrate is purely repulsive so that a film of gas of nearly constant density $\rho^\dagger \approx \rho_g$ develops near the wall. This film will become macroscopically thick in the limit $\rho_0 \to \rho_l$. The analysis goes through as above. It is evident from (9) that the PY theory cannot describe wetting by gas. The HNC theory now requires

$$\ln(\rho_g/\rho_l) = a(\rho_l)(\rho_g - \rho_l) \tag{12}$$

in the limit of complete wetting. For this equation to have sensible solutions $(\rho_l > \rho_g)$ we require $\rho_l a(\rho_l) > 0$. However, dense liquids at temperatures well below the critical temperature are highly incompressible and we expect therefore that $1 - \rho_l a(\rho_l) \gg 1$, i.e. $\rho_l a(\rho_l) \ll 0$. This is completely inconsistent with (12) and we conclude that the HNC cannot account for complete wetting by gas at a solid–liquid interface.

Other integral equations, obtained from other closures of the wall-particle Ornstein–Zernike equation, have been applied to models of solid–fluid interfaces—see, for example, [19, 20, 3, 4]. The analysis of these (EXP, RHNC, MF–PY, MF–EXP) for complete wetting situations is more complicated than that given above because of the extra complexity introduced by the reference system. If the latter is chosen to be a hard sphere fluid, as is frequently the case, it is possible to demonstrate that these more sophisticated approximate theories suffer from the same type of difficulty as HNC and PY and are, therefore, also incapable of describing complete wetting by gas. The calculations of Sullivan *et al.* [19] substantiate this conclusion.

There is another class of approximate integral equations which have been used in studies of fluid interfaces. These are based on closure approximations to the first YBG equation. The simplest closure that has been employed sets the pairwise distribution function $\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho(z)\rho(z')g_0(|\mathbf{r} - \mathbf{r}'|)$ where $g_0(r)$ is the radial distribution function of the bulk fluid. The YBG equation can then be written, see, for example, [23], as

$$\rho(z) = C \exp\left[-\beta V(z) - \beta \int d\mathbf{r}'\, S(|\mathbf{r} - \mathbf{r}'|)\rho(z')\right] \tag{13}$$

where

$$S(r) \equiv - \int_r^\infty dR\, g_0(R)\, d\phi(R)/dR.$$

$\phi(r)$ is the pairwise potential between molecules in the fluid. Evidently (13) has a structure which is similar to that of the HNC equation (1). (For large $|\mathbf{r}-\mathbf{r}'|$, $g_0(|\mathbf{r}-\mathbf{r}'|)$ is close to unity so that $-\beta S(|\mathbf{r}-\mathbf{r}'|)\sim -\beta\phi(|\mathbf{r}-\mathbf{r}'|)$ which is the same as the asymptotic behaviour of $c_0(|\mathbf{r}-\mathbf{r}'|)$.) The constant C is determined by requiring $\rho(z)\to\rho_0$ as $z\to\infty$. It follows that

$$\ln(\rho_0/C) = -\beta\rho_0 \int d\mathbf{r}\, S(r) = \rho_0 K(\rho_0), \tag{14}$$

where

$$K(\rho_0) = \frac{4\pi}{3}\beta \int_0^\infty dr\, r^3 g_0(r)\, d\phi(r)/dr.$$

Thus $C=\rho_0 \exp(-\rho_0 K(\rho_0))$. It is instructive to apply (13) to complete wetting situations. Following the same procedure as that described above we find that (13) can only describe a ' plateau ' of nearly constant density $\rho^\dagger$, different from the bulk density ρ_0, if

$$\ln(\rho^\dagger/\rho_0) \sim K(\rho_0)(\rho^\dagger-\rho_0). \tag{15}$$

As expected this result has the same form as (8) obtained from the HNC theory. It implies another relationship between the densities of coexisting liquid and gas. If the bulk fluid is gas, (15) requires in the limit of complete wetting of substrate by liquid,

$$\ln(\rho_l/\rho_g) = K(\rho_g)(\rho_l-\rho_g). \tag{16}$$

We must now consider the sign and magnitude of $K(\rho_g)$. The pressure p of a bulk fluid is given by the virial equation

$$\beta p = \rho_0\left(1-\frac{\rho_0}{2}K(\rho_0)\right) \tag{17}$$

from which it emerges that K can be positive or negative. At the critical point (16) has the solution $\rho_c K(\rho_c)=1$ which implies $p_c/k_B T_c \rho_c = \frac{1}{2}$ [24]. The experimental values for this ratio are $\sim 0{\cdot}29$. For dilute gases at temperatures well below T_c we expect $0<\rho_g K(\rho_g)\ll 1$ and (16) to predict sensible values for ρ_l. (The argument is analogous to that discussed in connection with (11).)

When the bulk fluid is liquid complete wetting by gas requires

$$\ln(\rho_g/\rho_l) = K(\rho_l)(\rho_g-\rho_l). \tag{18}$$

This equation was derived earlier by Berry and Reznek [24] and used by them as a basis for a theory of coexistence. For dense liquids, however, $\rho_l K(\rho_l)$ can be of the order of unity and it is straightforward to show that (18) cannot then predict physically realistic values for ρ_g. Alternatively the pressure obtained by substituting (18) into (17) is negative when $\rho_l/\rho_g \gtrsim \exp(2)$ [24].

Finally, if we linearize the exponentials in (13) so that we have an equation which has the same form as the PY equation (2) it follows that complete wetting can only occur if

$$\rho_0 K(\rho_0) = 1$$

or $p\beta/\rho_0=\frac{1}{2}$. This linearized theory exhibits the same kind of failing as the PY theory.

The arguments given in this section indicate that the PY, HNC and related theories cannot give a proper account of liquid–gas coexistence and that this is the reason they cannot describe complete wetting situations. That the HNC and PY theories should fail to describe two coexisting fluid phases is not immediately apparent from the original presentation of the theory [2] in terms of the wall-particle Ornstein–Zernike equation. The failing becomes almost self-evident, however, when we view these theories as approximate density functional theories.

3. THE HNC AND PY THEORIES AS DENSITY FUNCTIONAL THEORIES

The equilibrium density $\rho(\mathbf{r})$ of an inhomogeneous fluid in an external potential $V(\mathbf{r})$ is given [25] by minimizing the grand potential functional

$$\begin{aligned}\Omega[\rho]=\Omega[\rho_0]+\int d\mathbf{r}\, V(\mathbf{r})(\rho(\mathbf{r})-\rho_0)+\frac{1}{\beta}\int d\mathbf{r}\,\rho(\mathbf{r})\ln(\rho(\mathbf{r})/\rho_0)\\ -\frac{1}{\beta}\int d\mathbf{r}\,(\rho(\mathbf{r})-\rho_0)-\frac{1}{\beta}\int_0^1 d\alpha\int_0^\alpha d\alpha'\int\int d\mathbf{r}\,d\mathbf{r}'\,c(\mathbf{r},\mathbf{r}'\,;\,\alpha')\\ \times(\rho(\mathbf{r})-\rho_0)(\rho(\mathbf{r}')-\rho_0), \qquad (19)\end{aligned}$$

where $c(\mathbf{r},\mathbf{r}'\,;\,\alpha)$ is the direct correlation function of an inhomogeneous fluid with density $\rho(\mathbf{r}\,;\,\alpha)=\rho_0+\alpha(\rho(\mathbf{r})-\rho_0)$. The parameter α characterizes the path in the space of density functions ; ρ_0 is the density of a uniform reference state having grand potential $\Omega[\rho_0]$. Equation (19) is exact. If one knew $c(\mathbf{r},\mathbf{r}'\,;\,\alpha)$ exactly then the minimum of $\Omega[\rho]$ would be the exact grand potential of the fluid. As pointed out by Grimson and Rickayzen [16], one can derive the HNC integral equation (1) by neglecting the dependence of $c(\mathbf{r},\mathbf{r}'\,;\,\alpha)$ on the parameter α and setting this function equal to the direct correlation function of the uniform (bulk) fluid of density ρ_0, i.e.

$$c(\mathbf{r},\mathbf{r}'\,;\,\alpha)\approx c(\mathbf{r},\mathbf{r}'\,;\,0)\equiv c_0(|\mathbf{r}-\mathbf{r}'|).$$

The grand potential functional (19) then simplifies to

$$\begin{aligned}\Omega_{\mathrm{HNC}}[\rho]=\Omega[\rho_0]+\int d\mathbf{r}\, V(\mathbf{r})(\rho(\mathbf{r})-\rho_0)+\frac{1}{\beta}\int d\mathbf{r}\,\rho(\mathbf{r})\ln(\rho(\mathbf{r})/\rho_0)\\ -\frac{1}{\beta}\int d\mathbf{r}\,(\rho(\mathbf{r})-\rho_0)-\frac{1}{2\beta}\int\int d\mathbf{r}\,d\mathbf{r}'\,c_0(|\mathbf{r}-\mathbf{r}'|)\\ \times(\rho(\mathbf{r})-\rho_0)(\rho(\mathbf{r}')-\rho_0). \qquad (20)\end{aligned}$$

The equation which results from setting $\delta\Omega_{\mathrm{HNC}}[\rho]/\delta\rho(\mathbf{r})=0$ is identical to (1) when $V(\mathbf{r})\equiv V(z)$ so that $\rho(\mathbf{r})\equiv\rho(z)$.

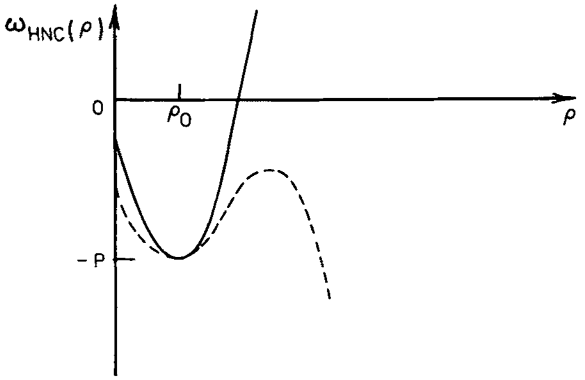
Equation (20) can also be derived by making a functional Taylor expansion of the non-ideal gas part of the intrinsic Helmholtz free energy functional about the bulk reference fluid. By making a further expansion in (20) it is possible to derive another grand potential functional which upon minimization yields the PY integral equation (2) [16].

From (20) we extract the grand potential density $\omega_{\mathrm{HNC}}(\rho)$ for a uniform fluid of density ρ :

$$\omega_{\mathrm{HNC}}(\rho)=\omega(\rho_0)+\frac{1}{\beta}(\rho\ln(\rho/\rho_0)-\rho+\rho_0)-\frac{1}{2\beta}(\rho-\rho_0)^2\,a(\rho_0), \qquad (21)$$

where we have ignored any contribution from an external potential and used (5). It is straightforward to prove that (21) corresponds to expanding the non-ideal gas contribution to $f(\rho)$, the Helmholtz free energy density, about ρ_0 in a Taylor expansion truncated at the quadratic term and treating the ideal gas contribution exactly. Note that $\omega(\rho)=f(\rho)-\mu\rho$, where $\mu=(df/d\rho)_{\rho_0}$ is the chemical potential of the bulk fluid.

We now enquire whether or not (21) can describe liquid–gas coexistence. The conventional treatment of the latter requires $\omega(\rho)$ to exhibit two minima separated by a maximum. The minimum with the lower value is at $\rho=\rho_0$ and $-\omega(\rho_0)=p$, the pressure. When the chemical potential is that appropriate to coexistence at the temperature in question the second minimum, at $\rho=\rho^{\dagger}$, is lowered and its value is then equal to $\omega(\rho_0)$. If $\omega(\rho)$ does not have this shape there is no van der Waals loop in the local chemical potential and, therefore, no coexistence. ω_{HNC}, as given by (21), does not have the required shape. Elementary analysis shows that (21) has only one minimum at $\rho=\rho_0$. Sketches



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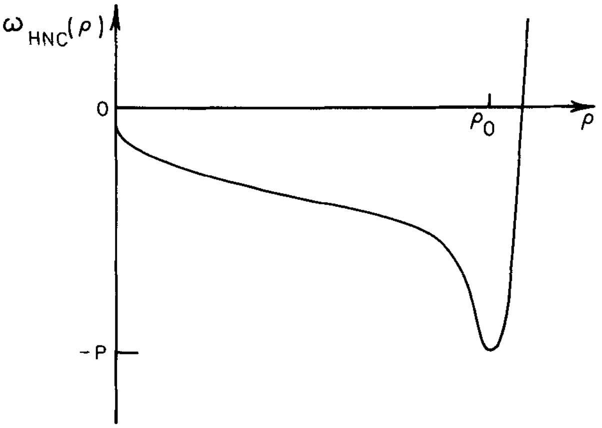

(*b*)

Figure 2. The grand potential density obtained from the HNC equation, ω_{HNC}, plotted as a function of density ρ (schematic). $p=-\omega_{\mathrm{HNC}}(\rho_0)$ is the pressure. (*a*) The density ρ_0 of the bulk phase corresponds to a gas. The solid line is the result for $\rho_0 a(\rho_0)<0$ and the dashed line for $0<\rho_0 a(\rho_0)<1$. (*b*) The density ρ_0 now refers to a bulk liquid for which $\rho_0 a(\rho_0)\ll 0$.

of this function are given in figure 2 (*a*) for bulk gas and in figure 2 (*b*) for bulk liquid. When ρ_0 corresponds to a dilute gas ω_{HNC} will exhibit a maximum at some value of $\rho > \rho_0$ provided $1 > \rho_0 a(\rho_0) > 0$. For larger values of ρ, however, ω_{HNC} decreases monotonically and there is no second minimum. This is obviously an unphysical situation since it favours an infinitely dense liquid. Note the requirement that $1 > \rho_0 a(\rho_0) > 0$ implies (see (10)) that the bulk gas is more compressible than an ideal gas at the same density and temperature. If $\rho_0 a(\rho_0) < 0$, which is expected for most bulk gases and all dense bulk liquids, ω_{HNC} exhibits only the minimum at $\rho = \rho_0$ and no maximum.

The same exercise can be carried out for the PY grand potential functional given in [16]. The grand potential density now has parabolic form

$$\omega_{\mathrm{PY}}(\rho) = \omega(\rho_0) + \frac{1}{2\rho_0\beta}(\rho - \rho_0)^2(1 - \rho_0 a(\rho_0)) \tag{22}$$

with the minimum at $\rho = \rho_0$.

We conclude from these analyses that neither of these theories yields a grand potential density of the form which is required to describe liquid–gas coexistence. It follows that relations (11) and (12), which were derived by assuming the integral equations could describe complete wetting, are spurious. Similar remarks apply to (16) and (18) obtained from the approximate YBG equation. The integral equations do not have stable solutions corresponding to a free liquid–gas interface.

4. PAIRWISE CORRELATIONS AND THE SURFACE COMPRESSIBILITY SUM RULE

Further insight into the limitations of the integral equation theories is provided by an examination of the pairwise correlation functions predicted by these theories. If we regard the latter as density functional theories the direct correlation function of the inhomogeneous fluid $c(\mathbf{r}, \mathbf{r}')$ can be calculated by functional differentiation since [9] :

$$c(\mathbf{r}, \mathbf{r}') = \frac{\delta(\mathbf{r} - \mathbf{r}')}{\rho(\mathbf{r})} - \beta \frac{\delta^2 \Omega[\rho]}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')}. \tag{23}$$

It follows from (20) and the corresponding equation [16] for the PY case that, for both theories

$$c(\mathbf{r}, \mathbf{r}') = c_0(|\mathbf{r} - \mathbf{r}'|). \tag{24}$$

Obviously this result is exact in the limit of the uniform bulk fluid and is consistent with the arguments used in the derivation of the approximate grand potential functionals. It is, moreover, consistent with linear response theory. Indeed, in the limit of an infinitesimal potential $\delta V(\mathbf{r})$ producing an infinitesimal change in density $\delta\rho(\mathbf{r}) = \rho(\mathbf{r}) - \rho_0$, it is straightforward to prove that (1) and (2) reduce to the linear response result

$$\delta\rho(\mathbf{r}) = -\beta \int d\mathbf{r}'\, G_0(|\mathbf{r} - \mathbf{r}'|)\delta V(\mathbf{r}'). \tag{25}$$

Here $G_0(r) = \rho_0^2(g_0(r) - 1) + \rho_0\delta(r)$ is the density–density correlation function of the uniform fluid and is related to $c_0(r)$ via the Ornstein–Zernike equation.

Given some prescription for calculating $c(\mathbf{r}, \mathbf{r}')$ the total pairwise correlation function $h(\mathbf{r}, \mathbf{r}')$ can be obtained from the Ornstein–Zernike equation for the inhomogeneous fluid :

$$h(\mathbf{r}, \mathbf{r}')=c(\mathbf{r}, \mathbf{r}')+\int d\mathbf{r}''\, h(\mathbf{r}, \mathbf{r}'')\rho(\mathbf{r}'')c(\mathbf{r}'', \mathbf{r}'). \tag{26}$$

It is related to the usual pairwise distribution function via

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}')=\rho(\mathbf{r})\rho(\mathbf{r}')(h(\mathbf{r}, \mathbf{r}')+1). \tag{27}$$

Using (24) in (26) it is clear that in the inhomogeneous fluid $h(\mathbf{r}, \mathbf{r}')\neq h_0(|\mathbf{r}-\mathbf{r}'|)$, the total correlation function of the bulk fluid. In order to proceed it is convenient to introduce [26] the transverse structure factor

$$H(z, Q)\equiv 1+\int dz'\, \rho(z')\int d\mathbf{R}\, \exp(i\mathbf{Q}\,.\,\mathbf{R})h(z, z', R), \tag{28}$$

where we have specialized to the fluid in a potential $V(z)$ so that $\rho(\mathbf{r})\equiv\rho(z)$ and $h(\mathbf{r}, \mathbf{r}')\equiv h(z, z', R)$ with $R^2=(x'-x)^2+(y'-y)^2$. $\mathbf{Q}$ is a wavevector parallel to the surface. It follows from Fourier transforming (26) that $H(z, Q)$ satisfies the integral equation

$$H(z, Q)=1+\int dz'\, H(z', Q)\rho(z')c(z', z, Q) \tag{29}$$

which can be regarded as an interfacial analogue of the bulk Ornstein–Zernike equation. When the direct correlation function is given by (24)

$$\begin{aligned} c(z, z', Q)&\equiv \int d\mathbf{R}\, \exp(i\mathbf{Q}\,.\,\mathbf{R})c(z, z', R)=c_0(|z-z'|, Q)\\ &=2\pi\int_0^\infty dR\, RJ_0(QR)c_0((R^2+(z'-z)^2)^{1/2}), \end{aligned} \tag{30}$$

where J_0 is the Bessel function of order zero, and the transverse structure factor satisfies

$$\int dz'\, H(z', Q)[\delta(z-z')-\rho(z')c_0(|z-z'|, Q)]=1. \tag{31}$$

In earlier papers [26, 13] we showed that the behaviour of $H(z, Q)$ afforded a signature of the approach to complete wetting. For a solid–gas interface at temperatures above the wetting transition temperature T_w this function exhibits Ornstein–Zernike behaviour at small Q when a thick, liquid-like, film develops at the interface and z is located in the edge of this film [26, 13]. This behaviour is associated with the growth of long ranged transverse correlations, i.e. $h(z, z', R)$ decreases slowly with R, in the edge of the film. As the pressure of the gas approaches the saturated vapour pressure and the liquid film becomes macroscopically thick, $H(z, 0)$ and hence the correlation length of the transverse fluctuations, diverges. The long ranged transverse correlations can be attributed to damped capillary-wave-like fluctuations occurring in that part of the density profile which resembles the profile of a liquid–gas interface ; as the liquid film thickens the damping due to the solid substrate decreases so that the capillary-wave-like fluctuations become more pronounced [26]. Analogous fluctuations develop at the edge of the gas film which occurs in the approach to complete wetting at a solid–liquid interface.

A necessary requirement for any theory of complete wetting is that it should predict the divergence of $H(z, 0)$. From the definition (28), it is clear that

$H(z, 0)$ is a measure of the 'local' compressibility. (In a bulk fluid $H(z, 0) = S(0)$, the long wavelength limit of the bulk structure factor, which is $\rho_0 k_B T \kappa_T$.) This interpretation also follows from the relation [27, 26]

$$H(z, 0) = \frac{1}{\beta \rho(z)} \left(\frac{\partial \rho(z)}{\partial \mu} \right)_T, \tag{32}$$

where the derivative is performed at fixed T and fixed potential $V(z)$. The proof of (32) follows straightforwardly from the well-known result for the pairwise distribution function as a functional derivative of the density—see, e.g. [9]. A divergence of $H(z, 0)$ implies a divergence in $\partial \rho(z)/\partial \mu$. Unlike the divergence of κ_T, which occurs only at the critical point of the bulk fluid, this divergence occurs at all temperatures for which there is complete wetting. In other words there is a line of critical points lying on the liquid–gas coexistence curve above T_w associated with the divergence of an interfacial quantity. In order to emphasize that we are dealing with interfacial properties and not bulk quantities, and to make contact with the thermodynamics of adsorption, it is useful to consider an integrated form of (32).

Defining the adsorption (or coverage) Γ, at the substrate, which is assumed to be impenetrable for $z < 0$, by

$$\Gamma = \int_0^\infty dz \, (\rho(z) - \rho_0) \tag{33}$$

it follows from (32) and the relation $(\partial \rho_0/\partial \mu)_T = \rho_0^2 \kappa_T$ that

$$\int_0^\infty dz \left(\rho(z) H(z, 0) - \frac{\rho_0^2}{\beta} \kappa_T \right) = \frac{1}{\beta} \left(\frac{\partial \Gamma}{\partial \mu} \right)_T. \tag{34}$$

The left and right hand sides of (34) now refer explicitly to interfacial quantities, i.e. surface excess functions. We refer to this result as the surface compressibility sum rule because of its analogy with the bulk compressibility sum rule. It relates an integral over the pairwise distribution function in the interface to a surface thermodynamic function. The analogy becomes stronger when we recall that the coverage is itself a derivative with respect to chemical potential, i.e. $\Gamma = -(\partial \gamma/\partial \mu)_T$ where γ is the solid–fluid interfacial tension.

We believe (34) to be an exact result. It can be generalized immediately to impenetrable substrates with less restrictive potential functions. We find

$$\int \int d\mathbf{r} \, d\mathbf{r}' \, \rho(\mathbf{r}) \rho(\mathbf{r}') h(\mathbf{r}, \mathbf{r}') + \langle N \rangle - \frac{V}{\beta} \left(\frac{\partial \rho_0}{\partial \mu} \right)_T = \frac{1}{\beta} \left(\frac{\partial N^{\mathrm{ex}}}{\partial \mu} \right)_T \tag{35}$$

where $\langle N \rangle \equiv \int d\mathbf{r} \, \rho(\mathbf{r})$ is the mean number of molecules in the fluid, $N^{\mathrm{ex}} \equiv \int d\mathbf{r} \, (\rho(\mathbf{r}) - \rho_0)$ and V is the volume of the fluid. This equation is identical to (3.110 *b*) of [3], where it was derived using fluctuation theory arguments. Its physical significance was not discussed in [3].

The sum rule (34) should provide a useful, and possibly stringent, test for theories of inhomogeneous fluids. A properly self consistent theory will satisfy this sum rule. Density functional theories do this automatically since they construct the pairwise distribution function from the free energy functional by the procedure outlined above. Theories which attempt to approximate $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$ *directly* will almost certainly fail to satisfy (34).

For our present purposes we are concerned primarily with (34) in the limit of complete wetting. If $T_w < T < T_c$ the bulk quantity κ_T remains finite in this limit and (34) implies that $(\partial\Gamma/\partial\mu)_T$ must diverge in the same fashion as $H(z, 0)$. The nature of this divergence reflects the form of the attractive part of the solid–fluid potential $V(z)$. When the latter decays exponentially with distance z the coverage Γ diverges as $-\ln|\mu-\mu_{\text{sat}}|$, where μ_{sat} is the chemical potential of the coexisting fluid at the given temperature [13, 26]. It follows from (34) that $H(z, 0)$ must diverge as $|\mu-\mu_{\text{sat}}|^{-1}$. Explicit calculations and analysis [26] for Sullivan's [14] model confirm this last result. When $V(z)$ exhibits inverse power law decay for large z, i.e. $V(z) \sim -z^{-m}$, where m is an integer >1, Γ diverges as $|\mu-\mu_{\text{sat}}|^{-1/m}$ [13], and (34) predicts that $H(z, 0)$ should diverge as $|\mu-\mu_{\text{sat}}|^{-(1+1/m)}$. For simple fluids at simple substrates the dominant forces for large distances are attractive van der Waals forces so we expect $m=3$ to be the relevant exponent. Thus we predict that $H(z, 0)$ should diverge as $|\mu-\mu_{\text{sat}}|^{-4/3}$ for real solid–fluid interfaces in the approach to complete wetting, i.e. much faster than the coverage itself.

The last result would appear to have important repercussions for computer simulations of the thick liquid films which occur in near complete wetting situations. We digress a little to explain this. The left hand side of (34) or (35) can be re-expressed in terms of the mean square fluctuation of the coverage using standard manipulations. The equations can then be rewritten as

$$\langle\hat{\Gamma}^2\rangle - \langle\hat{\Gamma}\rangle^2 = \frac{1}{A\beta}\left(\frac{\partial\langle\hat{\Gamma}\rangle}{\partial\mu}\right)_T \tag{36}$$

where $\hat{\Gamma} = \int d\mathbf{r}\,(\hat{\rho}(\mathbf{r}) - \rho_0)$ and equilibrium quantities are given by grand canonical configuration averages, i.e. $\Gamma = \langle\hat{\Gamma}\rangle$, $\rho(\mathbf{r}) = \langle\hat{\rho}(\mathbf{r})\rangle$ etc. A is the surface area. Note the analogy between (36) and the well known result for the mean square fluctuation in the number of particles, or particle density, in a bulk fluid. If Γ varies as $|\mu-\mu_{\text{sat}}|^{-1/m}$ then (36) implies that the root mean square fluctuation $\Delta\Gamma \equiv (\langle\hat{\Gamma}^2\rangle - \langle\hat{\Gamma}\rangle^2)^{1/2}$ should vary as $A^{-1/2}|\mu-\mu_{\text{sat}}|^{-(1+1/m)/2}$. The growth of $\Delta\Gamma$ as $\mu \to \mu_{sat}$ is, of course, limited by the factor $A^{-1/2}$. In a computer simulation, where A is finite, it would be necessary to increase the area as μ increases in order that $\Delta\Gamma$ remain less than Γ, which is itself diverging. This requires $A \sim |\mu-\mu_{\text{sat}}|^{1/m-1}$. In order to make some estimate of the magnitude of the fluctuations we have analysed the results of Ebner and Saam's [10, 8] density functional calculations. Their density profiles (plotted in figure 2 of [10]) for a reduced temperature $T^* \equiv k_B T/\epsilon = 1{\cdot}1$ lying above the surface critical temperature, show the growth of thick liquid films. By estimating the area under these profiles we find that for the highest coverages (largest bulk densities) $\Gamma\sigma^2 \sim 1{\cdot}1\delta_g^{-1/3}$ where $\delta_g \equiv (\rho_g - \rho_0)/\rho_g$ is the relative undersaturation of the bulk gas and σ is the molecular diameter characterizing the Lennard-Jones fluid. (We obtain a similar approximation from the results of our calculations [12].) If we assume that the bulk gas is sufficiently dilute that it obeys the ideal gas law then $\delta_g = \beta(\mu_{\text{sat}} - \mu)$. Combining these relations we have, from (36),

$$\Delta\Gamma = \left(\frac{1}{A\beta}\left(\frac{\partial\Gamma}{\partial\mu}\right)_T\right)^{1/2} = \left(\frac{1{\cdot}1}{3A\sigma^2}\right)^{1/2}\delta_g^{-2/3}. \tag{37}$$

In the Monte Carlo simulations of Lane *et al.* [5] the dimensions of their box in the x and y directions were both 40 Å. Taking $\sigma = 3{\cdot}405$ Å the area of their surface is $A = 138{\cdot}0\sigma^2$. Inserting this value into (37) we find $\Delta\Gamma/\Gamma \sim 0{\cdot}047\delta_g^{-1/3}$. Thus, for a relative undersaturation $\delta_g = 0{\cdot}02$ we expect that $\Delta\Gamma/\Gamma \sim 0{\cdot}17$, while for $\delta_g = 0{\cdot}01$ this ratio is $\sim 0{\cdot}22$. Fluctuations clearly become very important at these small undersaturations but they are also significant for slightly higher values of δ_g. It is clear that any attempt at simulation of thick wetting films must employ large surface areas. (Note that the film thickness for $\delta_g \sim 0{\cdot}02$ is about 6 or 7 molecular diameters [10].)

The problem is essentially the same as that encountered in computations of bulk properties near the critical point. Indeed, as remarked earlier, the bulk coexistence curve, for $T_w < T < T_c$, can be regarded as a line of critical points for interfacial quantities.

We return now to our discussion of the integral equation theories. It is evident that since these cannot account for the growth of thick wetting films they cannot predict divergent coverages and, therefore, cannot describe the divergence of the transverse structure factor. The reason for this failing becomes clear when we examine (31). The square bracket contains information about a single (bulk) phase only ; c_0 refers explicitly to a single phase and we have already demonstrated that the profile $\rho(z)$ cannot describe a coexisting fluid interface in these theories. Consequently the transverse structure factor $H(z, Q)$ calculated from (31) contains no information about a second phase. This equation should be contrasted with the corresponding equation obtained from Sullivan's model—see (34) or (36) of [26]. The direct correlation function $c(\mathbf{r}, \mathbf{r}')$ depends explicitly on the local density in Sullivan's model—see § 5.

The integral equation (13) based on a closure approximation to the YBG equation also fails to describe the divergence of the transverse structure factor. The approximation

$$\rho^{(2)}(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r})\rho(\mathbf{r}')g_0(|\mathbf{r}-\mathbf{r}'|) \tag{38}$$

obviously implies that the total pairwise correlation function of the inhomogeneous fluid, $h(\mathbf{r}, \mathbf{r}')$, is $h_0(|\mathbf{r}-\mathbf{r}'|)$, the corresponding function for the bulk fluid. Whilst this approximation is similar in spirit to that used in derivations of the HNC and PY theories, (13) differs from these theories in several important respects. First, as mentioned earlier, we cannot expect the approximation (38), to satisfy the surface compressibility sum rule (34) when the density profile is calculated from (13). Secondly, unlike the HNC or PY theories, (13) is not consistent with linear response theory. For an infinitesimal potential, $\delta V(\mathbf{r})$, (13) does not reduce to (25). This is equivalent to the statement that $-\beta S(r) \neq c_0(r)$. Although the equality holds asymptotically (see § 2) it is not valid for small r. There are other significant consequences of the differences between (13) and the other theories. We can illustrate these by reference to (6) or (7) for the ' tail ' of the density profile. Neglecting the external potential $V(z)$ these predict (see also [9] and references therein) that the density profile of the fluid should decay exponentially to its bulk value with a decay length

$$\xi = \left(\frac{\rho_0 b(\rho_0)}{1-\rho_0 a(\rho_0)}\right)^{1/2}. \tag{39}$$

(This result should be valid for a real system provided ξ exceeds the decay length of $V(z)$.) From the definitions (5) of a and b it is easy to show that ξ is the Ornstein–Zernike correlation length of the bulk fluid. This assumes $b > 0$; Evans and Sluckin [28] have argued that b should be positive for all, except the very highest density, states of a Lennard-Jones fluid. Analysis of (13), however, predicts [9] exponential decay with a different length

$$\lambda = \left(\frac{\rho_0 \alpha_2}{1 - \rho_0 K(\rho_0)} \right)^{1/2}, \tag{40}$$

where

$$\alpha_2 = \frac{2\pi}{15} \beta \int_0^\infty dr\, r^5 g_0(r)\, d\phi(r)/dr.$$

This result assumes that $\rho_0 K(\rho_0) < 1$ and that $\alpha_2 > 0$. For many fluid states the pressure is such that $1 < \rho_0 K(\rho_0) < 2$ (see (12)). In these circumstances (13) does not predict exponential decay but would, presumably, predict oscillatory behaviour for the ' tail ' of the density profile—a result completely at odds with the result of the other theories. Note also that λ, as given by (40), does not diverge at the critical point since, in general, $K(\rho_c) \neq 1/\rho_c$. Even if we supposed that $K(\rho_c) = 1/\rho_c$ λ would not diverge in the same way as the Ornstein–Zernike correlation length ξ of (39). This follows since $\alpha_2 \neq b$. α_2 remains finite whilst b diverges in a non-classical theory of the critical point.

The differences between the predictions of (13) and the other theories are not quite so dramatic for hard-sphere fluids, which are the systems which have been studied in most detail. In this case b is negative for all thermodynamic states so that ξ, as defined by (39) is imaginary. The quantity K is negative for hard-sphere fluids but α_2 is also negative so that λ in (40) is imaginary. Nevertheless, we have no reason to suppose that $\lambda = \xi$ in this case either.

We conclude that (13) has some undesirable features in addition to its failure to describe liquid–gas coexistence. In the next section we comment briefly on published attempts at solving (13) and mention closure approximations which improve upon (38).

5. DISCUSSION

The main conclusion which emerges from our study is that the various approximate integral equation theories cannot describe coexisting liquid and gas phases. As mentioned in the introduction this failing had been anticipated, but not explained, previously. Our analysis of the grand potential density makes the failing explicit. It is evident from the discussion in § 3 that the HNC and PY approximations do not incorporate proper ' local ' thermodynamics. Since these theories expand around a single bulk phase they are unable to describe a grand potential density with the two minima necessary to account for coexistence. Density functional theories, on the other hand, incorporate, from the outset, two-phase coexistence by introducing a realistic grand potential density. This is apparent in the theory of Ebner and Saam [7, 8] and in that of Sullivan [14] whose approach can also be regarded as an approximate density functional theory [26, 13]. What is required is that the part of the free energy density arising from repulsive forces in the fluid exhibit the variation with ρ that is characteristic of hard spheres. Sullivan has made this point in several articles, for example, [14, 19]. An equivalent requirement is that, in contrast to what is indicated by (24), the direct correlation of the fluid should depend on the local density. Using Sullivan's model grand potential functional in (23) we find [26] :

$$c(\mathbf{r}, \mathbf{r}') = \left(\frac{1}{\rho(\mathbf{r})} - \beta f''_{\mathrm{h}}(\rho(\mathbf{r}))\right) \delta(\mathbf{r}-\mathbf{r}') - \beta w_2(|\mathbf{r}-\mathbf{r}'|), \qquad (41)$$

where $f''_{\mathrm{h}}(\rho)$ is the second derivative of the Helmholtz free energy density of a uniform hard sphere fluid and $w_2(r)$ is the attractive part of the pairwise potential between fluid molecules. When (41) is employed for a uniform fluid it gives rise to a realistic grand potential density [26]. In Ebner and Saam's approach $c(\mathbf{r}, \mathbf{r}')$ is a rather complicated function of the local density and depends on $c(|\mathbf{r}-\mathbf{r}'|\ ;\ \bar{\rho})$, the direct correlation function of a uniform fluid at some mean density $\bar{\rho}$. Problems arise in practical calculations because of the necessity of specifying this function when $\bar{\rho}$ corresponds to a two phase region of the phase diagram. This difficulty is avoided in Sullivan's approach but the latter is unable to describe any oscillatory behaviour of the density profile in the neighbourhood of the substrate. A purely ' local ' approximation to the repulsive force part of the grand potential functional cannot account for oscillations of this kind which arise from the short range correlations in the fluid. Integral equation theories of the HNC or PY type are quite successful at describing this particular aspect of the interfacial structure. Generalizations of and improvements on the functionals of Sullivan and of Ebner and Saam are required before a reliable and realistic theory, capable of describing complete wetting and short range intermolecular correlations, becomes available. We are currently developing such density functional theories in this laboratory.

Could more sophisticated versions of the HNC or PY closure approximations of the wall-particle Ornstein–Zernike account for complete wetting ? As argued in § 2, we believe that existing closures cannot. The difficulty lies in finding approximations for the wall-particle direct correlation function which retain the necessary information about two phase coexistence. It is not at all obvious how to construct suitable approximations. Experience with closures for bulk fluids is not particularly useful for this purpose.

For completeness we should refer to the papers of Thompson *et al.* [29] and Henderson *et al.* [30]. These authors discuss the results of calculations of the density profiles of a Yukawa fluid, i.e. a fluid in which the particles interact through hard sphere potentials with attractive Yukawa tails, near a hard wall. Their calculations are based on the mean-spherical approximation (MSA) closure of the wall-particle Ornstein–Zernike equation. This closure, with $V(z)=0$, is identical to the PY closure except that $c_0(r)$ is now obtained from the MSA. The grand potential density has the same parabolic form as that given by (22) and cannot, therefore, describe liquid–gas coexistence. As expected, no indication of wetting by gas is found in the calculations corresponding to a bulk liquid near coexistence ; the density profiles exhibit oscillatory behaviour near the wall—see figures 1 and 4 of [29]. They are similar to those obtained from the EXP and MF–EXP approximations applied to a Lennard-Jones fluid near a hard wall for which Monte Carlo calculations

[19] find a wetting film of gas. Henderson *et al.* [30] remark that they find a singularity in the coverage ' which may be interpreted as indicative of wetting ', when the compressibility κ_T is infinite. Their remark is consistent with the argument of § 2. Real wetting, which occurs when κ_T is finite, is not described by the MSA closure.

Finally we return to the defects and deficiencies of the approximate YBG equation (13). There are two distinct problems associated with this. The first concerns the inability of the approximation to describe liquid–gas coexistence—a point noted by Croxton [31], while the second concerns the failure of the approximation to reproduce the results of linear response theory. We first address ourselves to the second problem. A theory which fails in the linear response regime might still be quite accurate for calculations of the density profile arising from the large, ultimately infinite, perturbation introduced by the presence of a wall. Nevertheless we should not be too surprised if, given the arguments of § 4, (13) did not yield realistic density profiles for dense single phase fluids, especially those satisfying the condition $1 < \rho_0 K(\rho_0) < 2$. There is some discussion in the literature which might be relevant. Borštnik and Ažman [32] used (13) for a Lennard-Jones fluid near a hard wall. They found diverging solutions for liquids below the critical temperature. The same group later reported divergent solutions for high density liquids [33]. Navascués [34] was unable to find convergent solutions of (13) below the critical point for a Lennard-Jones liquid near a hard wall with an attractive tail. The question of the existence of stable solutions to (13) and the possible connection with linear response requirements warrant further investigation.

The inability of the theory to describe coexistence means that (13) cannot form the basis of a self-consistent theory of wetting, contact angles etc. (The work of Berry [23], which is based on (13), makes further approximations in order to obtain a theory of the contact angle θ. We are not convinced that θ calculated from this approach is consistent with its thermodynamic definition in terms of the three interfacial tensions, i.e. Young's equation.) In particular (13) cannot be used for self-consistent calculations of the density profile at a free liquid–gas interface. The only relevant result of which we are aware is that due to Toxvaerd [35] who solved (13) for the planar liquid–gas interface of the square well fluid taking $g_0(r)$ to be the radial distribution function of the bulk liquid calculated in a certain approximation. By construction the profile satisfied the boundary condition $\rho(-\infty) = \rho_l$ but it did not approach the coexisting gas density ρ_g (as calculated from an equation of state) at large z.

It is more usual, in studies of the liquid–gas interface based on the YBG equation, to employ more sophisticated closure approximations for $\rho^{(2)}(\mathbf{r}, \mathbf{r}')$. These are reviewed in [31, 22].

If the distribution function g is defined via the equation

$$\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \equiv \rho^{(2)}(z_1, z_2, z_{12}) \equiv \rho(z_1)\rho(z_2)g(z_1, z_2, r_{12}) \tag{42}$$

then g is often approximated by a linear combination, weighted with the local density, of bulk liquid and bulk gas radial distribution functions. Alternatively g is set equal to $g(r_{12}\,;\ \bar{\rho})$, the radial distribution function of a hypothetical uniform fluid of density $\bar{\rho}$ and some prescription relating $\bar{\rho}$ to $\rho(z_1)$ and $\rho(z_2)$ is assumed. It seems likely that *many* of these more sophisticated approximations are consistent with a grand potential density exhibiting two minima. The work of Toxvaerd [36] is an example which illustrates how an improved closure produces a realistic equation of state. Moreover the ' sum rules ' derived by Lekner and Henderson [37], which relate the coexisting densities to the pressure, appear to be quite realistic. Although these can be regarded as generalizations of (18), they do not exhibit the inconsistencies of the latter. We also note that the density profiles calculated from such closures are monotonic and agree reasonably well with those obtained from other theories or simulations [22] of the liquid–gas interface. The work of Fischer and Methfessel [38] is especially relevant in this context. These authors devised a closure approximation which gave realistic profiles for the liquid–gas interface of a Lennard-Jones fluid at various temperatures and then used the same approximation in calculations of the density profile of the same fluid near a Lennard-Jones 9–3 wall. For a bulk gas at a density very slightly below the coexisting gas density they obtained a thick liquid-like film adsorbed at the interface. This suggests that their theory is capable of describing complete wetting, although the authors do not commit themselves on this issue! What our present work indicates is that it is possible that *some* of the closure approximations which have been employed for the liquid–gas interface might not correspond to a grand potential with two minima. Given the long saga [22, 31] concerning the existence of stable oscillatory profiles at such interfaces it might be worthwhile, in the light of this remark and the discussion in § 4, to re-examine those closures which appear to give rise to oscillations.

Indeed it is instructive at this juncture to enquire how the incorporation of density dependence into g alters the previous results for the ' tail ' of the density profile. Analysis of the YBG equation using a closure which sets $\bar{\rho}=\rho(\frac{1}{2}(z_1+z_2))$ yields a decay length proportional to $[1-\rho_0(K(\rho_0)+\frac{1}{2}\rho_0\, dK(\rho_0)/d\rho_0)]^{-1/2}$ rather than the result given by (40)†. From the virial equation (17) it follows that this decay length is now proportional to $\kappa_T{}^{1/2}$ or $(1-\rho_0 a(\rho_0))^{-1/2}$, which is more consistent with the results of the other theories described in § 4. In particular the decay length diverges at the critical point and there is no longer any special concern for states satisfying $1<\rho_0 K(\rho_0)<2$. The incorporation of density dependence obviously has very significant consequences.

Although more refined closure approximations are able to account for coexistence and, hence, complete wetting, they will not give a realistic description of pairwise correlations in either the liquid–gas interface or in thick adsorbed films at solid substrates. By making any ' local ' approximation to g in (42) we throw away the possibility of the long-ranged transverse correlations discussed in § 4. Since these correlations afford an important signature of the approach to complete wetting, theories which cannot incorporate them are of limited value in large coverage situations. We emphasize once more that closure approximations made for g directly will not, in general, satisfy the surface compressibility sum rule (34).

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