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A simple density functional theory for inhomogeneous liquids Wetting by gas at a solid-liquid interface

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A simple free energy functional, which incorporates both 'local' thermodynamics and short ranged correlations, is formulated and applied to the calculation of the density profile of fluids near hard walls. For hard sphere fluids the calculated profiles are in reasonable agreement with Monte Carlo results. For a Lennard-Jones liquid the profiles exhibit the phenomenon of wetting by gas ; the oscillations in the density profiles become much less pronounced and a layer of gas develops near the wall as the bulk density approaches its value at coexistence. Such behaviour was found earlier in Monte Carlo simulations but is not accounted for by existing integral equation theories based on closures of the wall-particle Ornstein-Zernike equation.

1. INTRODUCTION

The density functional approach to the statistical mechanics of inhomogeneous fluids has become increasingly popular during the last few years ; for reviews see [1, 2]. In this approach one constructs a functional, $\Omega_V[\rho]$, of the average particle density $\rho(\mathbf{r})$ and minimizes this with respect to $\rho(\mathbf{r})$ to obtain the equilibrium density of the fluid. The minimum value of $\Omega_V[\rho]$ is the grand potential of the fluid from which relevant thermodynamic properties and correlation functions can be calculated. For real, three-dimensional fluids, $\Omega_V[\rho]$ is not known exactly, and physical intuition must be employed in constructing realistic, yet tractable, approximations for this functional. Several types of functional are currently being used and whilst each of them has met with some success when applied to a specific physical problem they all exhibit failings or difficulties when applied to other problems. A particularly stringent test of such theories is that they should describe correctly the process of wetting at a solid-fluid interface. Recently it has been shown [3] that many widely used integral equation theories 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 Percus-Yevick (PY), hypernetted chain (HNC) and closely related closures of the wall-particle Ornstein-Zernike equation cannot accommodate two coexisting (liquid and gas) phases near the substrate and therefore cannot be used in a self-consistent theory of contact angle and wetting phenomena. These integral equation theories do have the merit, however, of

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providing a rather good description of the density profile of hard sphere fluids near walls, e.g. [4]. By contrast the well-known square-gradient approximation [1, 2] to the density functional does accommodate coexisting phases and does describe wetting [5]. Similar remarks apply to the approach of Sullivan [6], which can also be classed as a density functional theory [7]. These approximate theories incorporate proper 'local' thermodynamics [3] whereas the PY, HNC and related approximations do not. On the other hand the square-gradient approximation and the functional of Sullivan make a purely 'local' approximation to the repulsive force part of the density functional with the result that they cannot describe the oscillatory behaviour of the density profile that is known to occur in the neighbourhood of a wall. Such oscillations, which signify 'layering' or local ordering near the substrate, are especially important in adsorption from dense liquids [8]. The density functional introduced by Ebner *et al.* [9] incorporates 'local' thermodynamics and allows for oscillations in the profile. It has been shown to describe wetting by liquid at a solid-gas interface [10]. Difficulties arise with Ebner *et al.*'s approach because of (a) the necessity of specifying the free energy density and the direct correlation function of a uniform fluid at a density corresponding to a two phase region of the phase diagram and (b) the need to parametrize the density profile of the fluid. A most promising approach is that implemented recently by Nieminen and Ashcroft [11] and by Foiles and Ashcroft [12] for fluids near walls. Unfortunately this appears to have the disadvantage of requiring considerable computational effort which might preclude its application to more complex problems.

In this paper we introduce a *simple* density functional which takes proper account of 'local' thermodynamics and thus accounts for wetting, but which also incorporates the short-ranged correlations that give rise to oscillatory behaviour of the profile. Our density functional is closely related to that studied by Nordholm and coworkers [13, 14] in what these authors termed 'generalized van der Waals theory'. Nordholm *et al.* used coarse-graining arguments to construct a non-local entropy functional, in the same spirit as earlier work by van Kampen [15]. Here we provide a rather different justification for the functional based on its definition as a generating functional for the hierarchy of direct correlation functions [1, 2]. In order to demonstrate the versatility of our density functional approach we apply it to two separate problems. The first is the 'canonical' problem of hard sphere fluids near a purely repulsive (hard) wall. By comparing our results with those of computer simulation we can ascertain the usefulness of the theory for describing local-ordering near walls. The second application concerns a Lennard-Jones 12-6 fluid near a hard wall. This system can exhibit the interesting phenomenon of wetting by gas. When the density of the bulk liquid (far away from the wall) is close to that of the coexisting liquid at the same temperature, the density profile loses its oscillatory character and a layer of gas develops near the wall. Such behaviour is characteristic of wetting by gas [6] and has been found in computer simulations [16, 17]. Integral equation theories cannot describe this behaviour and produce density profiles that are completely different from those obtained by simulation [17, 3]. We show that our theory can describe the erosion of oscillations in the profile and the growth of the wetting layer; this is, to the best of our knowledge, the first successful theoretical treatment of this phenomenon.

Our paper is arranged as follows: in § 2 we describe the non-local density functional, in § 3 we present the results of calculations of the density profile for model fluids near a hard wall and we conclude, in § 4, with some final remarks.

2. DESCRIPTION OF THE DENSITY FUNCTIONAL

For a one-component fluid in an external potential $V(\mathbf{r})$ the equilibrium density $\rho(\mathbf{r})$ is given by minimizing the functional

$$\Omega_V[\rho] = \mathcal{F}[\rho] + \int d\mathbf{r} (V(\mathbf{r}) - \mu)\rho(\mathbf{r}), \quad (1)$$

where μ is the chemical potential and $\mathcal{F}[\rho]$ is the intrinsic Helmholtz free energy functional [1]. $\mathcal{F}[\rho]$ includes ideal gas contributions as well as contributions from interactions between the atoms in the fluid. Many treatments of inhomogeneous fluids begin by writing

$$\mathcal{F}[\rho] = \int d\mathbf{r} f(\bar{\rho}(\mathbf{r})) + \{\text{explicitly non-uniform terms}\} \quad (2)$$

where $f(\rho)$ is the Helmholtz free energy density of a uniform fluid of density ρ and the remaining bracketed terms vanish for a uniform fluid. Such a separation appears natural for weakly non-uniform fluids where the density varies slowly in space. Even in this case, however, difficulties arise in specifying $f(\rho)$ when ρ corresponds to a two-phase region. These can be surmounted by dividing, somewhat arbitrarily, $\mathcal{F}[\rho]$ into parts representing the free energy due to repulsive forces, $\mathcal{F}_R[\rho]$, and attractive forces, $\mathcal{F}_A[\rho]$, between the atoms. If we model the former by hard spheres with suitably chosen diameters and treat the latter in a mean field or random phase approximation we can write, as an approximation,

$$\mathcal{F}[\rho] = \mathcal{F}_{\text{hs}}[\rho] + \frac{1}{2} \int \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r})\rho(\mathbf{r}')\phi_A(|\mathbf{r} - \mathbf{r}'|), \quad (3)$$

where $\mathcal{F}_{\text{hs}}[\rho]$ is the intrinsic free energy functional for an inhomogeneous hard sphere fluid and $\phi_A(r)$ is the attractive part of the pairwise potential between two atoms in the fluid. As emphasized by Sullivan [6] this type of division is very much in the spirit of a van der Waals approach to the theory of fluids and avoids the difficulties associated with the free energy density in a two-phase region. If $\mathcal{F}_{\text{hs}}[\rho]$ is approximated by $\int d\mathbf{r} f_{\text{hs}}(\rho(\mathbf{r}))$ (3) reduces to the functional [7] employed by Sullivan [6] in his theory of wetting; $\rho(\mathbf{r})$ then refers to his long ranged density profile. Several subsequent authors have used this approach in calculations of wetting transitions at various interfaces [7, 18]. By making a local density approximation to $\mathcal{F}_{\text{hs}}[\rho]$ one throws away any possibility of layering in the density profile near a repulsive wall. Clearly one requires a more satisfactory prescription for $\mathcal{F}_{\text{hs}}[\rho]$. This functional is known exactly for hard rods in one dimension [19] but not for the three dimensional fluid.

Let us consider a dense hard sphere liquid near a hard wall. Simulations indicate that the maxima of the density $\rho(z)$ can take values which are much larger than the bulk liquid density. Thus an approximation to $\mathcal{F}_{\text{hs}}[\rho]$ which involves the *local* free energy density $f_{\text{hs}}(\rho(z))$ acquires contributions from the maxima that are pathologically large; $f_{\text{hs}}(\rho)$ is a rapidly increasing function of ρ for large ρ which diverges at the limit of close packing. However the maxima in $\rho(z)$, which occur near the wall, are separated by rather deep minima so that

the density averaged over a local volume of molecular dimensions is never very large. This suggests that it should be useful to introduce a 'smoothed' density $\bar{\rho}(\mathbf{r})$ which *could* be treated sensibly in a local density approximation. We define a suitable density by

$$\bar{\rho}(\mathbf{r}) = \int d\mathbf{r}' \rho(\mathbf{r} + \mathbf{r}') w(\mathbf{r}'), \quad (4)$$

where the weight function $w(\mathbf{r}')$ must approach zero rapidly as $r' = |\mathbf{r}'| \rightarrow \infty$ and is normalized as follows :

$$\int d\mathbf{r}' w(\mathbf{r}') = 1. \quad (5)$$

For a uniform fluid $\bar{\rho}(\mathbf{r}) = \rho(\mathbf{r}) = \rho$, a constant. Physical intuition must be employed to specify $w(\mathbf{r}')$ further. Foiles [20] has suggested that $w(\mathbf{r}')$ might be chosen by requiring that the free energy density local in $\bar{\rho}(\mathbf{r})$ be equivalent to the square-gradient approximation in $\rho(\mathbf{r})$, that is

$$\int d\mathbf{r} f(\bar{\rho}(\mathbf{r})) = \int d\mathbf{r} [f(\rho(\mathbf{r})) + f_2(\rho(\mathbf{r}))(\nabla\rho(\mathbf{r}))^2]. \quad (6)$$

The right-hand side of this equation would form an accurate approximation for the free energy of an inhomogeneous fluid in which the density varied slowly and exhibited only small deviations from some mean value. In this case $f_2(\rho)$ is proportional to the second moment of the direct correlation function of a uniform fluid with density ρ [1]. Whilst such a procedure would guarantee that *long* wavelength density fluctuations are treated in self-consistent fashion it is not clear that short-ranged correlations of the type that occur in hard sphere fluids near walls would be treated adequately.

Here we adopt a different and simpler prescription for $w(\mathbf{r}')$ that focuses attention on short ranged correlations. First we separate $\mathcal{F}_{\text{hs}}[\rho]$ into the ideal gas contribution, which is given exactly by local density form ;

$$\mathcal{F}_{\text{id}}[\rho] = k_{\text{B}} T \int d\mathbf{r} \rho(\mathbf{r}) (\ln(\Lambda^3 \rho(\mathbf{r})) - 1), \quad (7)$$

where T is the temperature and Λ is the thermal de Broglie wavelength, and a contribution from interactions which we treat in terms of the smoothed density :

$$\mathcal{F}_{\text{hs}}[\rho] = \mathcal{F}_{\text{id}}[\rho] + \int d\mathbf{r} \rho(\mathbf{r}) \Delta\psi(\bar{\rho}(\mathbf{r})). \quad (8)$$

$\Delta\psi(\rho)$ is the configurational part of the free energy per atom, i.e.

$$\Delta\psi(\rho) = \frac{f_{\text{hs}}(\rho) - f_{\text{id}}(\rho)}{\rho} = \frac{f_{\text{hs}}(\rho)}{\rho} - k_{\text{B}} T (\ln(\Lambda^3 \rho) - 1). \quad (9)$$

We now use the fact that $\mathcal{F}[\rho]$ is a generating functional for the direct correlation functions [1]. In particular, the two-body direct correlation function is given by

$$c(\mathbf{r}, \mathbf{r}') = \frac{-\delta^2}{k_{\text{B}} T \delta\rho(\mathbf{r}) \delta\rho(\mathbf{r}')} (\mathcal{F}[\rho] - \mathcal{F}_{\text{id}}[\rho]), \quad (10)$$

Substituting (8) into (10) we obtain as our approximation for the direct correlation function of a non-uniform hard sphere fluid

$$c_{\text{hs}}(\mathbf{r}, \mathbf{r}') = \frac{-1}{k_{\text{B}} T} [\Delta\psi'(\bar{\rho}(\mathbf{r})) + \Delta\psi'(\rho(\mathbf{r}'))] w(|\mathbf{r} - \mathbf{r}'|) - \frac{1}{k_{\text{B}} T} \int d\mathbf{r}'' \rho(\mathbf{r}'') \Delta\psi''(\bar{\rho}(\mathbf{r}'')) w(|\mathbf{r} - \mathbf{r}''|) w(|\mathbf{r}'' - \mathbf{r}'|), \quad (11)$$

where $\Delta\psi'$ and $\Delta\psi''$ denote first and second derivatives of $\Delta\psi$ with respect to density. For a uniform fluid of density ρ (11) reduces to

$$k_B T c_{hs}(|\mathbf{r} - \mathbf{r}'|) = -2\Delta\psi'(\rho)w(|\mathbf{r} - \mathbf{r}'|) - \rho\Delta\psi''(\rho) \int d\mathbf{r}'' w(|\mathbf{r} - \mathbf{r}''|)w(|\mathbf{r}'' - \mathbf{r}'|) \quad (12)$$

which suggests that the shape of $c_{hs}(r)$ is determined primarily by the form of $w(r)$. The integrated strength of $c_{hs}(r)$ is, however, independent of the particular form chosen for $w(r)$ since it follows from (12), (5) and (9) that

$$-k_B T \int d\mathbf{r} c_{hs}(r) = 2\Delta\psi'(\rho) + \rho\Delta\psi''(\rho) = f_{hs}''(\rho) - k_B T/\rho,$$

which is merely a statement of the compressibility sum rule. The latter is satisfied automatically in this approach†. The simplest and most natural choice for the weight function is

$$w(r) = \begin{cases} \left(\frac{4\pi}{3} d^3\right)^{-1}, & r \leq d, \\ 0, & r > d, \end{cases} \quad (13)$$

where d is the hard sphere diameter. This corresponds to averaging $\rho(\mathbf{r})$ over a sphere of radius d since, from (4),

$$\bar{\rho}(\mathbf{r}) = \frac{3}{4\pi d^3} \int_{|\mathbf{r}' - \mathbf{r}| < d} d\mathbf{r}' \rho(\mathbf{r}'). \quad (14)$$

Given some prescription for $f_{hs}(\rho)$ we now have an explicit expression for $c_{hs}(r)$. It is instructive to compare the results obtained using (13) in (12) with those obtained from the Percus–Yevick approximation for hard spheres. In figure 1 we present such a comparison for two different densities. $f_{hs}(\rho)$ was obtained from the Carnahan and Starling equation of state [21]. Our present approximation grossly underestimates the magnitude of $c_{hs}(r)$ for $r \leq d$ and yields a finite ‘tail’ for $d < r < 2d$. This ‘tail’ comes from the second, convolution, term in (12); it does not exist in the Percus–Yevick approximation where $c_{hs}(r) = 0$ for $r > d$. Whilst we cannot expect our approximation to provide an accurate theory for the correlation functions of uniform hard sphere fluids it is evident that it does provide a realistic description of the variation of $c_{hs}(r)$ with density and it is this feature which is important in determining the density profile of non-uniform fluids.

By choosing more complicated forms for $w(r)$ it should be possible to construct better approximations for $c_{hs}(r)$.

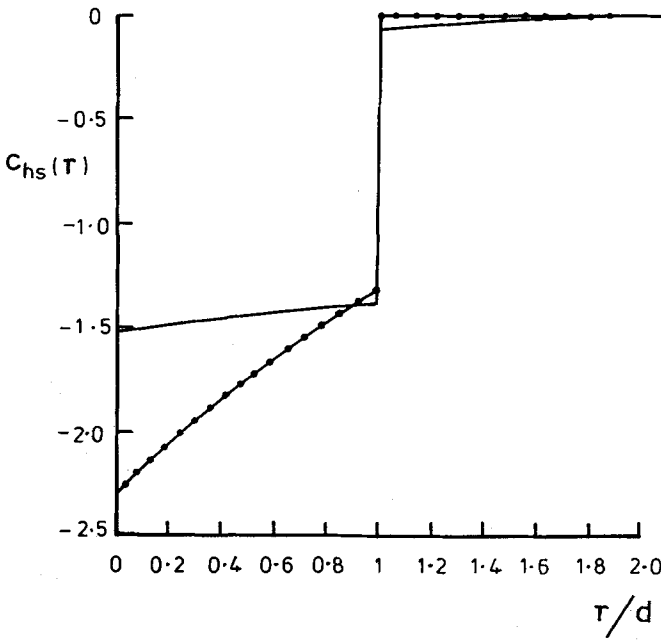
The functional we have used in our calculations can then be written as

$$\mathcal{F}[\rho] = k_B T \int d\mathbf{r} \rho(\mathbf{r}) (\ln(\Lambda^3 \rho(\mathbf{r})) - 1) + \int d\mathbf{r} \rho(\mathbf{r}) \Delta\psi \left(\frac{3}{4\pi d^3} \int_{|\mathbf{r}' - \mathbf{r}| < d} d\mathbf{r}' \rho(\mathbf{r}') \right) + \frac{1}{2} \iint d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) \rho(\mathbf{r}') \phi_A(|\mathbf{r} - \mathbf{r}'|) \quad (15)$$

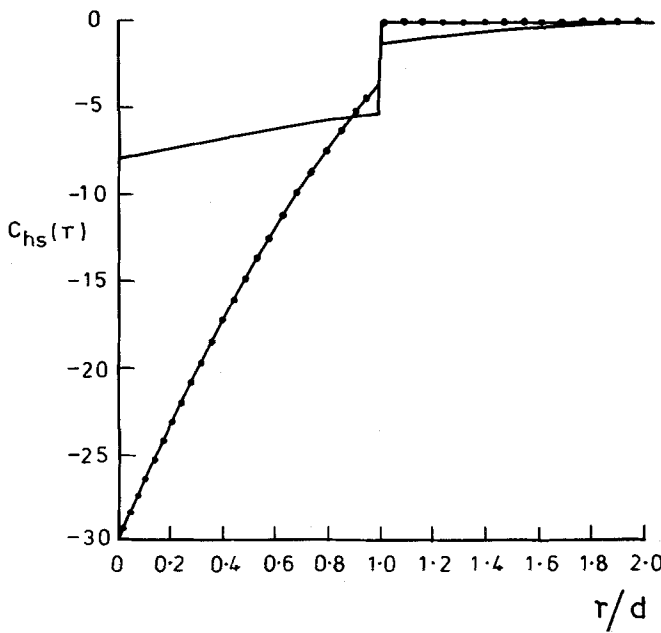
with the Carnahan and Starling result for $\Delta\psi$, i.e.

$$\Delta\psi(\rho) = \frac{k_B T \eta (4 - 3\eta)}{(1 - \eta)^2}, \quad (16)$$

† This sum rule remains valid when attractive forces are incorporated in the manner of (3); then $c(r) = c_{hs}(r) - \phi_A(r)/k_B T$.



(a)



(b)

Figure 1. The direct correlation function for a uniform hard sphere fluid at two different densities: (a) $\rho = 0.2 d^{-3}$ and (b) $\rho = 0.8 d^{-3}$. The full line is the result of the present theory and the dotted line is the result of the Percus-Yevick approximation.

where $\eta = \rho\pi d^3/6$ is the packing fraction. As mentioned in the introduction this is similar to a functional employed by Nordholm *et al.* [13, 14]. These authors arrived at what they term a fine-grained density functional theory from a different line of argument. We recover their theory by setting

$$\Delta\psi(\rho) = -\ln(1 - \rho V_0), \quad (17)$$

where V_0 is the excluded volume in a van der Waals treatment of hard spheres. Since our approach makes use of the accurate Carnahan and Starling equation of state we can expect it to be more realistic than that which utilizes the van der Waals approximation (17). We note, moreover, that the present treatment establishes the connections between Nordholm *et al.*'s theory and the density functional approach used by other authors.

3. RESULTS OF CALCULATIONS

If we model the substrate-fluid interactions by an external potential $V(z)$, where z is measured normal to the surface, the density profile of the fluid, $\rho(z)$, satisfies the Euler-Lagrange equation obtained from minimizing $\Omega_V[\rho]$ in (1). Using (15) for $\mathcal{F}[\rho]$ we obtain an integral equation:

$$\begin{aligned} \mu = V(z) + k_B T \ln(\Lambda^3 \rho(z)) + \Delta\psi(\bar{\rho}(z)) + \frac{3}{4\pi d^3} \int_{|\mathbf{r}' - \mathbf{r}| < d} d\mathbf{r}' \rho(z') \Delta\psi'(\bar{\rho}(z')) \\ + \int d\mathbf{r}' \rho(z') \phi_A(|\mathbf{r} - \mathbf{r}'|) \end{aligned} \quad (18)$$

with $\bar{\rho}(z)$ given by (14). We consider only the case of hard walls so that

$$\left. \begin{aligned} V(z) &= \infty, & z < 0, \\ &= 0, & z > 0. \end{aligned} \right\} \quad (19)$$

It follows that

$$\rho(z) = 0, \quad z < 0. \quad (20)$$

The integral equation can be solved numerically using iterative techniques.

In figure 2 we plot the density profiles for hard spheres ($\phi_A \equiv 0$) at two different bulk densities. We compare our results with those obtained from Monte Carlo simulations [22] and with those from the fine-grained theory of Nordholm *et al.* [13]. At both densities our results represent a distinct improvement on those of [13]. In particular the density at contact $\rho(0^+)$ is almost exactly the same as that obtained in the simulation whereas the contact values obtained in [13] are considerably smaller. The improvement can be traced to our use of an accurate equation of state for hard spheres. For fluids at hard walls there is a well-known exact sum rule relating $\rho(0^+)$ to the bulk pressure p :

$$k_B T \rho(0^+) = p. \quad (21)$$

Our theory, and that of [13], satisfy this sum rule. Given that the Carnahan and Starling equation of state is much more accurate than the van der Waals equation it follows that our values for $\rho(0^+)$ are much better. The amplitudes of the oscillations in the simulated $\rho(z)$ are also better accounted for by our present theory. For the higher density fluid we overestimate these amplitudes

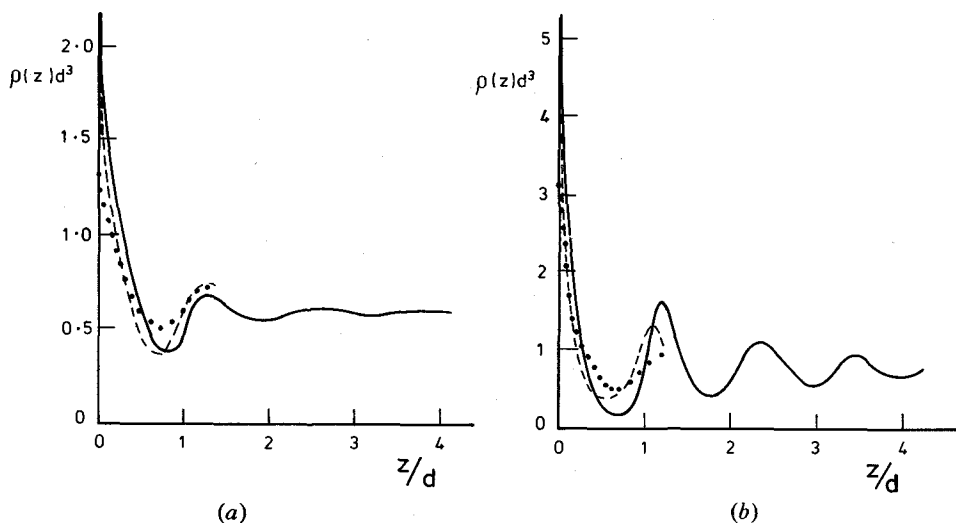


Figure 2. The density profiles $\rho(z)$ for a hard sphere fluid near a hard wall for two different bulk densities: (a) $\rho_B = 0.57 d^{-3}$ and (b) $\rho_B = 0.755 d^{-3}$. The full line is the result of the present theory, the dashed line is the Monte Carlo result [22] and the dotted line is the result of Nordholm *et al.* [13].

and the positions of the maxima, however. This deficiency of the theory, which can be attributed to our overestimation of the range of $c_{hs}(r)$, could be remedied, as discussed in § 2, by making a different choice of $w(r)$. We conclude from these comparisons that our simple density functional theory gives a good qualitative, but not particularly accurate, account of the 'layering' found in dense, hard sphere fluids.

The second and more important case that we considered was a Lennard-Jones 12-6 fluid near a hard wall. The attractive part of the pairwise potential was extracted via the Weeks-Chandler-Andersen [23] prescription:

$$\left. \begin{aligned} \phi_A(r) &= -\epsilon, & r < 2^{1/6} \sigma, \\ &= 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], & r > 2^{1/6} \sigma. \end{aligned} \right\} \quad (22)$$

The hard sphere diameter d was set equal to σ . As we were concerned primarily with the study of the onset of wetting by gas we investigated the density profiles corresponding to bulk densities that were slightly larger than the density of the coexisting liquid. In figure 3 we present our results for a reduced temperature $k_B T/\epsilon = 0.82$. The density of the coexisting liquid calculated from our theory at this temperature is $\rho_l = 0.760 \sigma^{-3}$. When the bulk density $\rho_B = 0.80 \sigma^{-3}$ (curve (c)) the profile exhibits oscillations for $0 < z \lesssim 5 \sigma$ but acquires a rather small value at contact. The oscillations gradually disappear and $\rho(0^+)$ becomes smaller as $\rho_B \rightarrow \rho_l$. For $\rho_B = 0.77 \sigma^{-3}$ (curve (b)) the density profile is almost smooth and is beginning to mimic the profile of the free liquid-gas interface calculated for the same temperature (curve (a)). At higher densities a 'gas' film of constant density grows near the wall and in the limit $\rho_B = \rho_l$ this film becomes macroscopically thick, corresponding to complete wetting of the wall-liquid interface by gas.

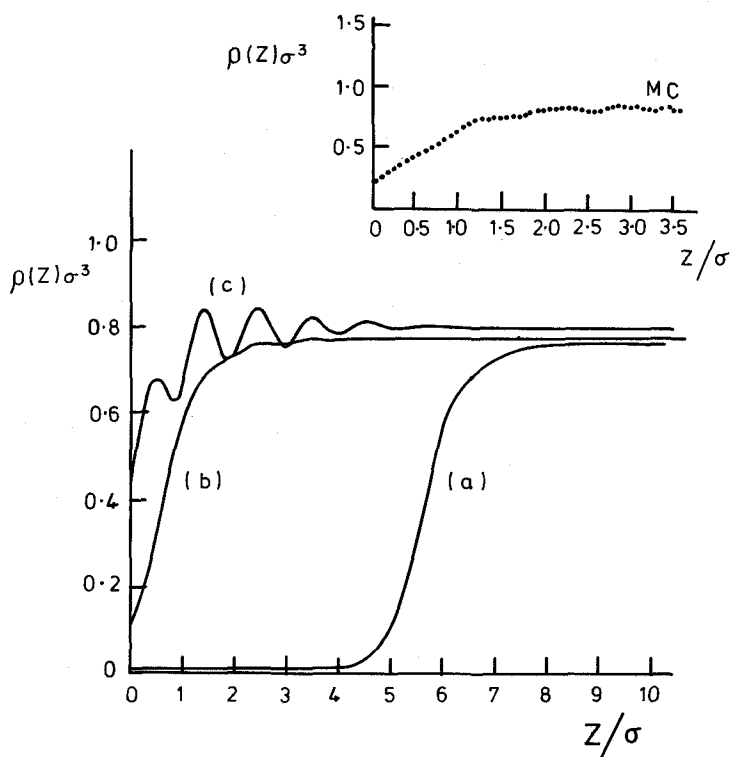


Figure 3. The density profiles for a Lennard-Jones fluid near a hard wall. (a) is the profile of a free liquid-gas interface (located arbitrarily), (b) is the profile for $\rho_B = 0.77 \sigma^{-3}$ and (c) is the profile for $\rho_B = 0.80 \sigma^{-3}$. The inset shows the Monte Carlo result [17] for the same temperature (see text).

Comparing the results of figure 3 with those of figure 2 we see that the inclusion of attractive forces between atoms brings about a dramatic change in the structure of the fluid near the wall. The importance of attractive forces has been emphasized by Sullivan and Stell [24] and is demonstrated clearly in the simulations of Abraham [16] and of Sullivan *et al.* [17] who obtained profiles similar to curve (b) in figure 3 in Monte Carlo studies of a Lennard-Jones fluid near coexistence. Indeed our result has the same *shape* as that found by Sullivan *et al.* [17] for the same temperature—see the inset to figure 3 where we plot their result. Note that the bulk density in the simulation is $\rho_B = 0.83 \sigma^{-3}$ indicating that the coexisting liquid density is about $0.81 \sigma^{-3}$ rather than the value of $0.76 \sigma^{-3}$ obtained from our theory. We remark that whereas our theory gives a rather good description of the onset of wetting by gas, integral equation theories fail completely—see figure 2 of [17].

4. CONCLUDING REMARKS

In this paper we have introduced a free energy functional which incorporates both 'local' thermodynamics and the short ranged correlations that are responsible for 'layering' in the density profile. Besides accounting for the phenomenon of wetting by gas our functional is well-suited to studies of other

wetting phenomena; it should be useful in calculations of the interfacial tensions, contact angles, location of wetting transitions at a variety of solid-fluid and fluid-fluid interfaces [5-7, 10, 18].

The main deficiency of the present theory lies in its failure to yield an accurate bulk direct correlation function $c_{hs}(r)$. As mentioned earlier it is permissible to choose forms for $w(r)$ different from (13) and this should result in an improved theory. The consequences of choosing a linear function (for $r < d$) have been investigated [25]. Note that it is possible to allow $w(r)$ to depend on the local density but the subsequent analysis then becomes more complicated and the essential physics is obscured somewhat. The advantage of the present functional is that it is reasonably easy to implement.

In our earlier paper [3] we listed some of the advantages and disadvantages of various density functional theories and integral equation theories of inhomogeneous fluids. Here we make an additional remark concerning the wall sum rule (21). Integral equation theories of the PY or MSA type do not satisfy this rule, e.g. [24, 26] and references therein, and a GMSA type of closure (Waisman *et al.* [4]) must be imposed in a semiempirical fashion before the sum rule is satisfied. Once again this failing can be attributed to the failure of the integral equation theories to incorporate proper 'local' thermodynamics. We illustrate this by reference to the HNC theory. The well-known HNC integral equation for $\rho(z)$ can be obtained by minimizing a certain grand potential functional [27, 3]. Consequently the HNC theory can be regarded as a density functional theory; the HNC integral equation is just the Euler-Lagrange equation. A self-consistent treatment of the latter is equivalent [1] to satisfying the equation of hydrostatic equilibrium:

$$\frac{dp_N(z)}{dz} = -\rho(z) \frac{dV(z)}{dz},$$

where $p_N(z)$ is the normal component of the pressure tensor. For a hard wall this equation can be integrated (using the property that $\rho(z) \exp(V(z)/k_B T)$ is continuous at $z=0$) to give

$$p_N(\infty) - p_N(-\infty) = k_B T \rho(0^+). \quad (23)$$

Here $p_N(\infty) = p$, is the pressure of the bulk fluid of density ρ_B . In a theory which incorporates proper 'local' thermodynamics $p_N(-\infty)$, the pressure of the fluid inside the wall, must be zero since the density of the fluid is zero and (23) reduces to the usual sum rule (21). Equation (23) remains valid in the HNC approximation but $p_N(-\infty)$ is not zero. From the HNC grand potential functional it follows (see equation (21) of [3]) that the pressure of a uniform fluid with zero density is $p - k_B T \rho_B (1 - \rho_B/2 \int dr c(r))$, where $c(r)$ is the direct correlation function of the bulk fluid. Substituting this result for $p_N(-\infty)$ into (23) we obtain the following result† for the density at contact in the HNC approximation:

$$\rho(0^+) = \rho_B (1 - \frac{1}{2} \rho_B \int dr c(r)). \quad (\text{HNC}). \quad (24)$$

† This result is also implicit in the work of Carnie *et al.* [28]. Equation (A 11) of the Appendix to [28] reduces to the present result (24) in the limit of a hard wall and a single component fluid. We are grateful to U. Marini Bettolo Marconi for bringing [28] to our attention.

Calculations indicate that the contact densities obtained from (24) can differ considerably from those obtained from the exact sum rule (21) or, indeed, from the PY and MSA result [24, 26] :

$$\rho(0^+) = \rho_B(1 - \rho_B \int d\mathbf{r} c(r))^{1/2}. \quad (\text{PY}). \quad (25)$$

Since our present density functional incorporates 'local' thermodynamics it is consistent with $p_N(-\infty) = 0$ and $\rho(0^+)$ satisfies the exact sum rule (21).

Finally we mention that the free energy functional we have described here can be used to develop a theory for crystallization [25].

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