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LETTER TO THE EDITOR

For fluids adsorbed at walls the MWDA density functional theory is equivalent to an HNC approach

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Abstract. The modified weighted density approximation (MWDA) introduced by Denton and Ashcroft in 1989 in a density functional theory of inhomogeneous fluids is applied to the case of fluid adsorption at planar walls. It is shown that the MWDA is completely equivalent to the hypernetted-chain closure of the wall–particle Ornstein–Zernike equation (HNCWP) for such problems. Because of the nature of the uniform fluid higher-order direct correlation functions within the MWDA, this theory of adsorption consititutes a truncation of the functional expansion of the free energy. The MWDA can also be used as the basis of a theory for the radial distribution function of a homogeneous fluid, where it is equivalent to the bulk HNC. For fluids confined in pores, however, the MWDA is not identical to the HNCWP.

Density functional methods for determining the equilibrium structure and thermo-dynamic properties of highly inhomogeneous fluids have become increasingly popular during the last decade (see, e.g., Evans 1979, 1989). The key idea behind such methods is the Hohenberg–Kohn–Mermin result that the intrinsic Helmholtz free energy $\mathcal{F}$ of a fluid is a unique functional of the average one-particle density $\rho(r)$. $\mathcal{F}[\rho]$ then acts as a generating functional for the hierarchy of direct correlation functions. Practical appli-cations to fluid interfaces (Evans 1989) or to the theory of freezing (Baus 1987 and references therein) require some explicit approximation for $\mathcal{F}[\rho]$ and the implicit assumption that the variational principle applies to approximate, as well as exact, functionals. A plethora of approximations exist. Some, such as the SDA (smoothed density approximation) of Tarazona (1984, 1985), have been implemented successfully for a wide variety of problems, while others have been applied to a specific type of inhomogeneity. Relationships between different approximations are, if they exist, often obscure. One of the more soundly based approaches is the WDA (weighted density approximation) of Curtin and Ashcroft (1985). As with Tarazona's SDA, the WDA introduces a coarse-grained or weighted average, $\bar{\rho}(r)$, of the local density $\rho(r)$ that is sufficiently smooth to be used in the local density approximation for the local excess (over ideal) free energy per particle. The determination of the weight function is computationally laborious in the WDA, however, and this feature has restricted its use. Very recently Denton and Ashcroft (1989) have introduced a modification (the MWDA)

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which retains many of the good features of the original WDA but which requires considerably less computational effort. Denton and Ashcroft showed that, when applied to the freezing of the hard-sphere liquid, the MWDA was about as accurate as the WDA, which is known to yield results in good agreement with simulation. Since the MWDA involves only a position independent average density $\hat{\rho}$, rather than $\bar{\rho}(r)$, it is not obvious how such an approach can be applied to interfacial problems, where the inhomogeneity is generally of finite range (Denton and Ashcroft 1989). The present letter addresses this issue. More specifically we investigate the predictions of the MWDA for the density profile and free energy of an inhomogeneous fluid at a planar wall exerting an external potential $V(r) \equiv V(z)$ on particles in the fluid. We find, rather surprisingly, that for this type of interfacial problem the MWDA is completely equivalent to the well-known (HNCWP) hypernetted-chain closure of the wall–particle Ornstein–Zernike (OZ) equation. It follows that the MWDA shares the strengths of the HNCWP, that is it will provide a reasonably accurate description of an oscillatory profile near the wall, as well as the weakness, which is that it fails to account for the exact contact condition, and this has repercussions for the description of phase transitions at interfaces. For some other types of adsorption problem, such as occur for fluids in pores, the MWDA will not be equivalent to the HNCWP.

We recall that the basic assumption of the MWDA is that the excess free energy per particle $F_{\text{ex}}[\rho]/N$, which is independent of position, can be expressed directly in terms of $\hat{\rho}$:

$$(\mathscr{F}[\rho] - \mathscr{F}_{\text{id}}[\rho])/N \equiv F_{\text{ex}}^{\text{MWDA}}[\rho]/N \equiv f_0(\hat{\rho}) \tag{1}$$

where N is the total number of particles and f_0 is the excess free energy per particle of a uniform fluid.

$$\mathscr{F}_{\text{id}}[\rho] = \beta^{-1} \int \mathrm{d}r\, \rho(r)(\ln \Lambda^3 \rho(r) - 1)$$

is the free energy of the ideal gas; $\beta^{-1} = k_{\text{B}}T$ and Λ is the thermal de Broglie wavelength. The weighted density is defined by

$$\hat{\rho} \equiv \frac{1}{N} \int \int \mathrm{d}r\, \mathrm{d}r'\, \rho(r)\rho(r')w(r - r'; \hat{\rho}) \tag{2}$$

where $w(r; \rho)$ is the weight function. In the limit of a uniform fluid, $\rho(r) \rightarrow \rho_0$, (1) implies that $\hat{\rho}$ must reduce to ρ_0 and it follows that w must be normalised:

$$\int \mathrm{d}r'\, w(r - r'; \hat{\rho}) = 1. \tag{3}$$

w is specified uniquely by requiring that the defining relation (Evans 1979) for the two-particle direct correlation function be satisfied exactly in the uniform limit, i.e.

$$-\beta \lim_{\rho \rightarrow \rho_0} \left(\frac{\delta^2 F_{\text{ex}}^{\text{MWDA}}[\rho]}{\delta\rho(r)\, \delta\rho(r')} \right) = c_0^{(2)}(r - r'; \rho_0) \tag{4}$$

where $c_0^{(2)}$ is the two-particle direct correlation function of the uniform fluid. Denton and Ashcroft (1989) show that

$$w(r - r'; \rho_0) = -(1/2f_0'(\rho_0))[\beta^{-1}c_0^{(2)}(r - r'; \rho_0) + (1/V_0)\rho_0 f_0''(\rho_0)] \tag{5}$$

where the prime denotes differentiation with respect to the density. V_0 is the total

volume. Unlike the original WDA, where the weight function can only be obtained numerically by solving a differential equation, w is now given directly in terms of $c_0^{(2)}$, which is assumed to be known for a given fluid. Note that the compressibility sum rule is satisfied automatically (Denton and Ashcroft 1989). This result follows by integrating both sides of (5) and using (3). With this prescription for w, $F_{ex}^{MWDA}[\rho]$ is determined completely. In any application ρ must be calculated self-consistently by minimisation of the (approximate) grand potential functional

$$\Omega_V[\rho] = \mathscr{F}_{id}[\rho] + F_{ex}^{MWDA}[\rho] + \int d\mathbf{r}\, \rho(\mathbf{r})(V(\mathbf{r}) - \mu) \tag{6}$$

where μ is the chemical potential. The equilibrium density $\rho(\mathbf{r})$ satisfies

$$\delta\Omega_V[\rho]/\delta\rho(\mathbf{r}) = 0 \tag{7}$$

and the minimum value of Ω_V is Ω, the grand potential of the inhomogeneous fluid.

For adsorption at a wall it is convenient to re-express (7) as

$$\rho(\mathbf{r}) = \rho_b \exp(-\beta V(\mathbf{r}) + c^{(1)}(\mathbf{r}) - c_0^{(1)}(\rho_b)) \tag{8}$$

where ρ_b is the density of the bulk fluid far from the wall,

$$c^{(1)}(\mathbf{r}) = -\beta\delta F_{ex}^{MWDA}[\rho]/\delta\rho(\mathbf{r}) = -\beta(f_0(\hat{\rho}) + f_0'(\hat{\rho})N\delta\hat{\rho}/\delta\rho(\mathbf{r})) \tag{9}$$

is the one-particle direct correlation function and $c_0^{(1)}$ is the corresponding quantity for the bulk fluid:

$$c_0^{(1)}(\rho_b) = \ln \Lambda^3\rho_b - \beta\mu = -\beta(f_0(\rho_b) + f_0'(\rho_b)\rho_b). \tag{10}$$

The functional derivative in (9) is easily evaluated:

$$N\delta\hat{\rho}/\delta\rho(\mathbf{r}) = \left(2 \int d\mathbf{r}'\, \rho(\mathbf{r}')w(\mathbf{r} - \mathbf{r}'; \hat{\rho}) - \hat{\rho}\right)$$

$$\times \left(1 - \frac{1}{N} \int\int d\mathbf{r}\,d\mathbf{r}'\, \rho(\mathbf{r})\rho(\mathbf{r}')w'(\mathbf{r} - \mathbf{r}'; \hat{\rho})\right)^{-1} \tag{11}$$

where we have used the fact that

$$N = \int d\mathbf{r}\, \rho(\mathbf{r}).$$

Note that in the limit of a uniform bulk fluid, with $V(\mathbf{r}) \equiv 0$, $N\delta\hat{\rho}/\delta\rho(\mathbf{r}) = \rho_b$. This result follows from (11), recognising that, by virtue of (3),

$$\int d\mathbf{r}'\, w'(\mathbf{r} - \mathbf{r}'; \rho_b) = 0.$$

$c^{(1)}(\mathbf{r})$ in (9) then reduces to the standard bulk result (10) in this limit.

We now suppose that the planar wall is infinitely repulsive for $z < 0$ so that $\rho(r) \equiv \rho(z) = 0$, $z < 0$. It is convenient to introduce the quantity $\Delta(z) \equiv \rho(z) - \rho_b$. Then Γ, the surface excess number of particles per unit area, can be written as

$$\Gamma \equiv N^{(s)}/A = \int_0^L dz\, \Delta(z) \tag{12}$$

and the weighted density as

$$\hat{\rho} = \rho_b + \rho_b \frac{N^{(s)}}{N} + \frac{A}{N} \int_0^L \int_0^L dz\, dz'\, \Delta(z)\, \Delta(z')\, W(|z - z'|; \hat{\rho}) \tag{13}$$

with

$$W(|z - z'|; \hat{\rho}) \equiv \int_A d\boldsymbol{R}\, w([R^2 + (z - z')^2]^{1/2}; \hat{\rho})$$

the surface integral over the wall.

In deriving (13) we have assumed

$$\lim_{L \to \infty} \int_0^L dz\, W(|z - z'|; \hat{\rho}) = 1$$

i.e. the weight function is normalised over the semi-infinite half-space $z > 0$. In the thermodynamic limit ($L \to \infty$) the second and third terms in (13) make vanishingly small contributions. The second is $O(L^{-1})$ times ρ_b provided the adsorption Γ is *finite*. It is straightforward to show that the double integral in (13) is finite as $L \to \infty$ so the third term is also $O(L^{-1})$ times ρ_b. (The constant term in w (see (5)) makes a contribution $O(L^{-2})$.)

Thus, for fluids near walls we find $\hat{\rho} = \rho_b$, as we would expect intuitively for finite ranged inhomogeneity. The only contentious point in the argument is whether the assumption that the weight function can be normalised (for $z > 0$) is compatible with the requirement (5). That problems of this type can arise in applications of the MWDA has been pointed out by Lutsko and Baus (1990). Here we can avoid the problem by making the (reasonable) assertion that the MWDA for adsorption corresponds to setting $\hat{\rho} = \rho_b$ in the equation for $c^{(1)}(r)$, i.e.

$$-\beta^{-1} c^{(1)}(z) = f_0(\rho_b) + f_0'(\rho_b) \left(2 \int dr'\, \rho(z') w(r - r'; \rho_b) - \rho_b \right) \tag{14}$$

since the double integral in the denominator of (11) is $O(L^{-1})$. Substituting (14) into (8) and making use of (5), (10) and the compressibility sum rule we obtain

$$\rho(z) = \rho_b \exp\left(-\beta V(z) + \int dr'\, c_0^{(2)}(r - r'; \rho_b)(\rho(z') - \rho_b)\right) \tag{15}$$

which is identical to the integral equation for $\rho(z)$ that is obtained from the HNCWP (Perram and White 1975, Henderson *et al* 1976). We should recall that the formally exact wall–particle OZ equation is derived by treating the fluid as a homogeneous binary mixture of particles (the atoms) and large spheres and taking the limit in which only one sphere, with infinite radius, remains. The HNC is one of a variety of closure approximations that have been applied to this equation. That the MWDA should be equivalent to this procedure is quite remarkable.

In order to understand better the equivalence it is instructive to consider (6), the MWDA for the grand potential functional, which can be re-expressed as

$$\Omega_V[\rho] = \Omega[\rho_b] + \int dr\, \rho(z)V(z) + N^{(s)}(\beta^{-1}\ln\Lambda^3\rho_b - \beta^{-1} - \mu)$$

$$+ \beta^{-1}\int dr\, \rho(z)\ln\left(\frac{\rho(z)}{\rho_b}\right) + F_{ex}^{MWDA}[\rho] - N'f_0(\rho_b) \tag{16}$$

where $N' \equiv \rho_b V_0$, i.e. $N^{(s)} = N - N'$, and $\Omega[\rho_b]$ is the grand potential of the bulk fluid. We now make a functional Taylor expansion, in powers of $\Delta(z)$, about $F_{ex}^{MWDA}[\rho_b] = N'f_0(\rho_b)$, and find

$$F_{ex}^{MWDA}[\rho] = N'f_0(\rho_b) - \beta^{-1}c_0^{(1)}(\rho_b)\int dr\, \Delta(z)$$

$$- \frac{\beta^{-1}}{2}\int\int dr_1\, dr_2\, c_0^{(2)}(r_1 - r_2; \rho_b)\, \Delta(z_1)\, \Delta(z_2)$$

$$- \frac{\beta^{-1}}{3!}\int\int\int dr_1\, dr_2\, dr_3\, c_0^{(3)}(r_1, r_2, r_3; \rho_b)\, \Delta(z_1)\, \Delta(z_2)\, \Delta(z_3)$$

$$- \ldots - \frac{\beta^{-1}}{n!}\int\ldots\int dr_1\ldots dr_n\, c_0^{(n)}(r_1, r_2\ldots r_n; \rho_b)$$

$$\times \Delta(z_1)\ldots\Delta(z_n) - \ldots. \tag{17}$$

where $c_0^{(n)}$ is the n-particle direct correlation function of the bulk fluid to be evaluated within the MWDA. While the first three terms in the expansion (17) are identical to those that would arise in the corresponding expansion of the exact functional (recall that f_0 and $c_0^{(2)}$ are assumed known), the higher-order terms are, of course, different. The n-particle direct correlation function can be obtained by successive functional differentiation of F_{ex}^{MWDA}. After tedious algebra we find for the three-particle function

$$-\beta^{-1}c_0^{(3)}(r_1, r_2, r_3; \rho_b) = (2/V_0)f_0''(\rho_b)(w(r_1 - r_2; \rho_b)$$

$$+ w(r_1 - r_3; \rho_b) + w(r_2 - r_3; \rho_b)) + (2/V_0)f_0'(\rho_b)$$

$$\times (w'(r_1 - r_2; \rho_b) + w'(r_1 - r_3; \rho_b) + w'(r_2 - r_3; \rho_b))$$

$$+ \rho_b f_0'''(\rho_b)/V_0^2 - 3f_0''(\rho_b)/V_0^2. \tag{18}$$

When this result is inserted into the fourth term in (17) it is easy to show that the largest contribution is $O(L^{-1})$ times the contributions from the second and third terms which are both proportional to the wall area A. Thus, in the thermodynamic limit $L \to \infty$, the term involving $c_0^{(3)}$ makes a vanishing contribution to the interfacial tension. It is straightforward to show that the remaining higher-order terms ($n > 3$) in (17) also make no contribution, and hence that the MWDA grand potential functional (16) reduces to

$$\Omega_V[\rho] = \Omega[\rho_b] + \int dr\, \rho(z)V(z) + \beta^{-1}\int dr\left[\rho(z)\ln\left(\frac{\rho(z)}{\rho_b}\right) - \rho(z) + \rho_b\right]$$

$$- \frac{\beta^{-1}}{2}\int\int dr_1\, dr_2\, c_0^{(2)}(r_1 - r_2; \rho_b)\Delta(z_1)\,\Delta(z_2) \tag{19}$$

where we have used (10). But (19) is precisely the functional that generates the HNCWP (Grimson and Rickayzen 1981), i.e. minimisation of (19) yields the integral equation (15). This exercise demonstrates that the MWDA is completely equivalent to the HNCWP for adsorption at walls.

Note that while the HNCWP simply truncates the expansion of the exact functional $F_{ex}[\rho]$ after the term quadratic in Δ, the MWDA does include (approximations to) all higher-order terms. However, the MWDA for $c_0^{(3)}$, $c_0^{(4)}$ etc is such that for the adsorption problem the higher-order terms make no contribution to the surface tension and have no effect on the density profile. Presumably, for freezing, where the inhomogeneity extends throughout the system, the higher-order terms are non-vanishing and constitute important corrections to the quadratic approximation (Denton and Ashcroft 1989). In this context we should remark that although (18) would appear to be an unrealistic approximation (note the factors of V_0^{-1}) for $c_0^{(3)}(r_1 - r_3, r_2 - r_3; \rho_0)$ it is easy to check that the Fourier transform $c_0^{(3)}(k, k'; \rho_0)$ does have the merit of satisfying the exact sum rule

$$c_0^{(3)}(k, 0; \rho_0) = (\partial/\partial\rho_0)c_0^{(2)}(k; \rho_0). \tag{20}$$

The MWDA should also satisfy the higher-order $(c_0^{(n)})$ generalisations of (20) (Denton and Ashcroft 1989).

Having shown the equivalence of the MWDA and the HNCWP for adsorption at a planar wall we should enquire how good a theory is the latter. Although there are few numerical results available (Grimson and Rickayzen 1981, Rickayzen and Augousti 1984, Zhou and Stell 1989a, b) it is known that for a hard-sphere fluid near a hard wall the HNCWP yields density profiles fairly close to those from the well-studied Percus–Yevick closure and, hence, to simulation, provided the reduced bulk density $\rho_b d^3 \le 0.4$; d is the hard-sphere diameter. For higher bulk densities the HNCWP over-estimates the amplitude of the first few oscillations in $\rho(z)$. In particular it is known that the HNCWP overestimates $\rho(0^+)$ the density of the fluid at contact with a hard wall. The exact sum rule is $\rho(0^+) = \beta p$ where p is the pressure of the bulk fluid while the HNCWP result is

$$\rho(0^+) = \rho_b\left(1 - \tfrac{1}{2}\rho_b \int dr\, c_0^{(2)}(r; \rho_b)\right).$$

The failure of the HNCWP to account properly for the contact condition can be traced to the truncation of the functional expansion at quadratic order (Evans *et al* 1983). The same truncation is responsible for the failure of the HNCWP (and the Percus–Yevick closure) to describe two-phase (liquid–gas) coexistence and, therefore, macroscopic wetting films, at an interface (Evans *et al* 1983). As presented here, the MWDA will necessarily exhibit the same shortcomings. Notice that in deriving the result $\lim_{L\to\infty} \hat{\rho} = \rho_b$ we restricted the adsorption Γ to being finite. This automatically precludes any complete wetting of the wall–fluid interface. A satisfactory theory of interfacial phase transitions obviously requires a different approach. The more sophisticated density functional approximations, such as the SDA or the WDA, which are based on a spatially varying $\bar{\rho}(r)$, do satisfy the contact condition and do account for complete wetting (Tarazona and Evans 1984, van Swol and Henderson 1989)—see also the approaches of Rickayzen and Augousti (1984) and Zhou and Stell (1989). These approximations give rise to $c_0^{(3)}$ etc which are much more realistic than the MWDA result (18), so the higher-order terms in the expansion of $F_{ex}[\rho]$ are non-vanishing in the appropriate limit.

We conclude by commenting on the nature of the MWDA for other types of inhomogeneity. If the fluid is confined in a pore with finite wall separation (slits) or radius

(cylinders and spheres) $\hat{\rho}$ will differ, in general, from $\rho_b(\mu)$, the density of the bulk fluid with the chemical potential of the adjoining reservoir. This will be the case even for infinitely long pores where the enclosed volume is infinite. Indeed the MWDA may be better suited to the calculation of fluid structure in pores than the HNCWP. The latter requires as input $c_0^{(2)}$ at the pre-assigned (bulk) density whereas the MWDA will determine $\hat{\rho}$ self-consistently, albeit at the expense of more computational effort. Suppose, finally, that the inhomogeneity of the fluid density is caused by fixing one of the particles at the origin. This particle then exerts an external potential $V(r) \equiv \varphi(r)$ on the others; $\varphi(r)$ is the usual pairwise interparticle potential. The average density 'profile' $\rho(r) (= \rho(r))$ can now be identified with $\rho_0 g_0(r)$, where g_0 is the radial distribution function of the (homogeneous) fluid. In this case $\hat{\rho} = \rho_0(1 + O(N^{-1}))$ and we can repeat the steps leading to (15). The resulting integral equation for $g_0(r)$ is

$$\ln g_0(r) = -\beta\varphi(r) + \rho_0 \int d\mathbf{r}' \, c_0^{(2)}(\mathbf{r} - \mathbf{r}'; \rho_0)(g_0(r') - 1) \tag{21}$$

which is just the HNC closure for a homogeneous fluid (see, e.g., Percus 1964). $c_0^{(2)}$ is, as yet, unspecified. If (21) is supplemented by the exact OZ equation we recover the usual HNC integral equation for g_0. Thus, the MWDA applied to the calculation of the radial distribution function is identical to the HNC approximation†. The grand potential functional which, upon minimisation, generates (21) is simply (19) with $\rho(z)$ replaced by $\rho_0 g_0(r)$ and $V(z)$ by $\varphi(r)$. Once again, terms of higher order do not affect the equation for the density profile, or $g_0(r)$ in the present case.

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† After completing this work we received a preprint from Kim and Jones (1990) in which they reach the same conclusion.

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