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Density Functional Theory of Homogeneous States

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We consider the weighted density approximation of the density functional description of systems in thermal equilibrium. We show that knowledge of the intermolecular potential puts constraints on the theory which take the form of a small number of nonlinear integral equations of unusual type. We show that for homogeneous states of systems with purely repulsive potentials these equations are sufficient to determine the free energy functional completely, at least at densities where the virial expansion of the theory converges. We have not been able to find either analytic or numerical solutions of these equations at arbitrary densities. We have solved the equations in the density expansion to the lowest order in which it disagrees with the exact virial expansion of the system. This extended weighted density approximation (EWDA) gives the exact virial expansion of the pressure to third order and the pair distribution function to first order in the density, as do the other standard integral equation theories. In the next order the EWDA is not exact, but it gives very good numerical results for the pressure and pair distribution and for both hard and soft repulsive potentials. In addition, the difference between the pressure and the compressibility equations of state is numerically very small, indicating a high degree of thermodynamic consistency. Were these properties to persist at higher densities, the EWDA would be clearly preferred to the usual integral approach, at least for repulsive potentials. For potentials with an attractive part the EWDA becomes singular at low temperatures in a way that suggests there is a structural flaw in the assumed form of the free energy functional.

KEY WORDS: Density functional; weighted density approximations; fluids.

1. INTRODUCTION

There has been a rather large number of articles (e.g., refs. 1–3) in which the density functional$^{(4)}$ formalism of the statistical mechanics of thermal equilibrium has been applied to the problems of inhomogeneous dense fluids of various sorts. These applications have been both qualitatively and,

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to varying degrees, quantitatively successful. It is characteristic of these methods that they predict the properties of an inhomogeneous state (i.e., a solid, an interfacial region, a boundary region) given enough properties of a "reference" homogeneous state. Typically one requires at least an equation of state and the direct correlation function of the reference homogeneous state as input, and these come from "other" theories of the dense liquid, but not from the density functional theory itself. Thus, the intermolecular potential does not directly appear in these calculations and one avoids a fundamental question of how the free energy functional is related to the intermolecular potential. It is that question we address here.

In this paper we consider one of the most quantitatively successful of these theories, the weighted density approximation (WDA), proposed by Tarazona,(2) and also extensively investigated by Curtin and Ashcroft.(3) We give in Section 2 an extension of this theory where the density functional is related to the intermolecular potential, in a natural way, by a small set of nonlinear equations. In Section 3 we argue that, to all orders in a density expansion, these equations determine the free energy functional and thus completely specify the theory, at least where the density expansion converges. This result holds for all purely repulsive potentials, but fails at low temperatures for potentials with an attractive part. With this result the WDA theory provides a method for computing the equilibrium properties of most states, both homogeneous and inhomogeneous, for systems with arbitrary intermolecular and external potentials without any reference to other theories of dense fluids. We show that this theory gives the first two terms of the density expansion of the pair distribution function correctly for all repulsive intermolecular potentials. The third term in the expansion is not exact and can only be computed numerically once the intermolecular potential is chosen. In Section 4 we give our results for this term for two cases, the strongly repulsive hard-sphere system and the weakly repulsive Gaussian model, and show that it reproduces the exact virial expansion result with remarkable accuracy. A comparison of these results to both the exact results and the results of other standard integral equation theories of fluids is given. The thermodynamic consistency of the theory is examined. We conclude with a brief discussion of the strengths and weaknesses of this theory.

2. EXTENSION OF THE WDA THEORY

The basic assumption of the WDA theory is that the free energy, as a functional of the local density $\rho(r)$, can be written as

$$\beta F[\rho] = \int \rho(\mathbf{r})[\ln \rho(\mathbf{r}) - 1]\, d\mathbf{r} + \int \rho(\mathbf{r})\, \Psi(\tilde{\rho}(\mathbf{r}))\, d\mathbf{r} \tag{2.1}$$

where $\tilde{\rho}$ is a local functional of the local density implicitly defined by the form

$$\tilde{\rho}(\mathbf{s}) = \int w(\mathbf{s}-\mathbf{u}, \tilde{\rho}(\mathbf{s}))\, \rho(\mathbf{u})\, d\mathbf{u} \tag{2.2}$$

It is assumed that for constant ρ, w satisfies the normalization condition

$$\int w(\mathbf{r}, \rho)\, d\mathbf{r} = 1 \tag{2.3}$$

so that for homogeneous states, $\rho(\mathbf{r})$, ρ, and $\tilde{\rho}(\mathbf{r})$ are identical and Ψ/β has the interpretation of the equilibrium value of the excess free energy per particle. Reasons for choosing these particular forms are given in refs. 2 and 3 (our Ψ/β is their Ψ).

Now, to complete the theory one must specify the two functions Ψ and w and our purpose is to show how to do this in terms of the intermolecular potential $\phi(\mathbf{r})$. In the presence of a *external* single-particle potential $u(\mathbf{r})$ the equilibrium state of the system is given by the extremal condition

$$\begin{aligned}\beta\mu - \beta u(\mathbf{r}) - 3\beta \ln \lambda = \beta \frac{\delta F[\rho]}{\delta\rho(\mathbf{r})} &= \ln \rho(\mathbf{r}) \\ &\quad + \int \rho(\mathbf{s})\, \Psi'(\tilde{\rho}(\mathbf{s}))\, \frac{\delta\tilde{\rho}(\mathbf{s})}{\delta\rho(\mathbf{r})}\, d\mathbf{s} + \Psi(\tilde{\rho}(\mathbf{r}))\end{aligned} \tag{2.4}$$

where β is the inverse temperature, μ is the chemical potential, $\lambda = (2\pi m/\beta h^2)^{1/2}$, and the form (2.1) has been used for F. From (2.2) we have

$$\frac{\delta\tilde{\rho}(\mathbf{s})}{\delta\rho(\mathbf{r})} = \frac{w(\mathbf{s}-\mathbf{r}, \tilde{\rho}(\mathbf{s}))}{1 - \int w'(\mathbf{s}-\mathbf{u}, \tilde{\rho}(\mathbf{s}))\, \rho(\mathbf{u})\, d\mathbf{u}} \tag{2.5}$$

where w' is the derivative of w with respect to the second (ρ) argument. If (2.5) is evaluated for a uniform state $\rho(\mathbf{r}) = \rho = \tilde{\rho}(\mathbf{r})$, then the normalization condition (2.3) requires the integral in the denominator of (2.5) to vanish and we have

$$\frac{\delta\tilde{\rho}(\mathbf{s})}{\delta\rho(\mathbf{r})} = w(\mathbf{s}-\mathbf{r}, \rho) \tag{2.5h}$$

where the h after the equation number indicates a functional which has been evaluated in a homogeneous state. If $u(\mathbf{r}) = 0$ and the equilibrium state is homogeneous, then (2.4) becomes

$$\beta\mu - 3\beta \ln \lambda = \ln \rho + \rho\Psi'(\rho) + \Psi(\rho) \tag{2.4h}$$

The direct correlation functional is the second functional derivative of F and, for homogeneous states, takes the form$^{(3)}$

$$C(\mathbf{r}-\mathbf{s},\rho)=-2\Psi'(\rho)\,w(\mathbf{r}-\mathbf{s},\rho)-\rho\Psi''(\rho)\int w(\mathbf{t}-\mathbf{r},\rho)\,w(\mathbf{t}-\mathbf{s},\rho)\,d\mathbf{t}$$
$$-\rho\Psi'(\rho)\int[w(\mathbf{s}-\mathbf{t},\rho)\,w'(\mathbf{r}-\mathbf{t},\rho)+w(\mathbf{r}-\mathbf{t},\rho)\,w'(\mathbf{s}-\mathbf{t},\rho)]\,d\mathbf{t} \tag{2.6h}$$

If we integrate (2.6h) over $\mathbf{r}$ and use the normalization condition (2.2), we obtain the usual compressibility sum rule

$$\int C(\mathbf{r},\rho)\,d\mathbf{r}=-2\Psi'(\rho)-\rho\Psi''(\rho) \tag{2.7h}$$

These equations are the usual$^{(2,3)}$ results of density functional theory with the WDA assumption. The theory is completed by specifying the two functions w and Ψ. To do this, we follow an idea used by Percus$^{(4)}$ in deriving the Percus–Yevick and the hypernetted chain equations. The idea is that the pair distribution function $g(\mathbf{r},\mathbf{t},\mu)$ of a system at chemical potential μ and zero external potential is simply related to the local density $\rho(\mathbf{r},\mu)$ of the same system with an external potential $u(\mathbf{r})$ provided by a fixed particle at $\mathbf{t}$ interacting with the system particles by the intermolecular potential $\phi(\mathbf{r},\mathbf{t})$. Specifically,

$$\rho(\mathbf{r},\mu)_0\,g(\mathbf{r},\mathbf{t},\mu)_0=\rho(\mathbf{r},\mu)_{\phi(\mathbf{r},\mathbf{t})} \tag{2.8}$$

where the subscripts are meant to indicate that quantities on the left are evaluated in zero external field while the local density on the right is evaluated in the external field $u(\mathbf{r})=\phi(\mathbf{r},\mathbf{t})$. It would seem, in general terms, that (2.8) puts some condition on the choice of w and Ψ, since given them, both sides of (2.8) can, in principle, be computed. It is perhaps surprising that (2.8) appears to completely determine w and Ψ, at least for a fairly large class of intermolecular potentials and states.

To see this, we assume that the state $(\mu,0)$ is homogeneous, so that $\rho(\mathbf{r},\mu)_0=\rho$, and that (2.4$h$) applies and determines μ. We then use (2.8) in (2.4) for the state (μ,ϕ) and eliminate μ between this equation and the previous one to obtain

$$\ln g(\mathbf{r},\mathbf{t})=\Psi(\rho)-\Psi(\tilde\rho(\mathbf{r},\mathbf{t}))+\rho\Psi'(\rho)$$
$$-\rho\int g(\mathbf{s},\mathbf{t})\,\Psi'(\tilde\rho(\mathbf{s},\mathbf{t}))\frac{\delta\tilde\rho(\mathbf{s},\mathbf{t})}{\delta\rho(\mathbf{r})}\,d\mathbf{s}-\beta\phi(\mathbf{r},\mathbf{t}) \tag{2.9}$$

where from (2.2) and (2.5) we have

$$\tilde{\rho}(\mathbf{r}, \mathbf{t}) = \rho \int w(\mathbf{r}-\mathbf{s}, \tilde{\rho}(\mathbf{r}, \mathbf{t}))\, g(\mathbf{s}, \mathbf{t})\, d\mathbf{s} \tag{2.10}$$

and

$$\frac{\delta\tilde{\rho}(\mathbf{s}, \mathbf{t})}{\delta\rho(\mathbf{r})} = \frac{w(\mathbf{s}-\mathbf{r}, \tilde{\rho}(\mathbf{s}, \mathbf{t}))}{1 - \rho \int w'(\mathbf{s}-\mathbf{u}, \tilde{\rho}(\mathbf{s}, \mathbf{t}))\, g(\mathbf{u}, \mathbf{t})\, d\mathbf{u}} \tag{2.11}$$

In addition we have the usual Ornstein–Zernike relation between the direct correlation and the pair distribution functions,

$$C(\mathbf{r}, \mathbf{s}) - [g(\mathbf{r}, \mathbf{s}) - 1] + \rho \int C(\mathbf{r}, \mathbf{t})[g(\mathbf{t}, \mathbf{s}) - 1]\, d\mathbf{t} = 0 \tag{2.12}$$

Now one can see that the six equations (2.6*h*), (2.7*h*), and (2.9)–(2.12) produce some kind of consistency constraints on the functions w and Ψ. For, suppose we knew w and Ψ; then (2.9)–(2.11) would result in an equation involving only the unknown g and the intermolecular potential ϕ. If it could be solved for g, then C would follow from (2.12). But then C would have to satisfy (2.6*h*) and (2.7*h*) with the given w and Ψ and that seems unlikely for arbitrary w and Ψ. It is nevertheless surprising that the consistency of these six equations is apparently a strong enough requirement to completely determine w and Ψ for a large class of intermolecular potentials, at least at those densities for which the virial expansion converges. We show in Section 3 that these six equations determine the formal density expansion of w, Ψ, C, and g to all orders and we explicitly give the equations determining the first three terms in the expansion of g.

3. THE DENSITY EXPANSION

We assume⁽²⁾ the function $w(\mathbf{r}, \rho)$ is analytic in the second variable and has the expansion

$$w(\mathbf{r}, \rho) = w_0(\mathbf{r}) + \rho w_1(\mathbf{r}) + \rho^2 w_2(\mathbf{r}) + \cdots \tag{3.1}$$

The normalization condition (2.3) requires that $\int w_i(\mathbf{r})\, d\mathbf{r} = \delta_{i,0}$. If this expansion is substituted into (2.2) and solved iteratively for $\rho(\mathbf{r})$, we find the density expansion

$$\tilde{\rho}(\mathbf{s}) = \int w_0(\mathbf{s}-\mathbf{u})\, \rho(\mathbf{u})\, d\mathbf{u}$$

$$+ \int w_0(\mathbf{s}-\mathbf{u})\, \rho(\mathbf{u})\, d\mathbf{u} \int w_1(\mathbf{s}-\mathbf{v})\, \rho(\mathbf{v})\, d\mathbf{v} + \cdots \tag{3.2}$$

An examination of the form of the general term in this expansion shows that w_p occurs first in the $p+1$ term and always linearly in the form

$$\left[\int w_0(\mathbf{s}-\mathbf{u})\,\rho(\mathbf{u})\,d\mathbf{u}\right]^p \int w_p(\mathbf{s}-\mathbf{v})\,\rho(\mathbf{v})\,d\mathbf{v}$$

From (3.2) it follows that

$$\frac{\delta\tilde{\rho}(\mathbf{s})}{\delta\rho(\mathbf{r})}=w_0(\mathbf{s}-\mathbf{r})+\left[w_0(\mathbf{s}-\mathbf{r})\int w_1(\mathbf{s}-\mathbf{v})\,\rho(\mathbf{v})\,d\mathbf{v}\right.$$
$$\left.+\,w_1(\mathbf{s}-\mathbf{r})\int w_0(\mathbf{s}-\mathbf{u})\,\rho(\mathbf{u})\,d\mathbf{u}\right]+\cdots \tag{3.3}$$

and in this expansion w_p will occur first in the pth order term. When (3.2) and (3.3) are evaluated using the density function of (2.8), we obtain the density expansions of (2.10) and (2.11),

$$\tilde{\rho}(\mathbf{s},\mathbf{t})=\rho\int w_0(\mathbf{s}-\mathbf{u})\,g(\mathbf{u}-\mathbf{t})\,d\mathbf{u}$$
$$+\,\rho^2\int w_0(\mathbf{s}-\mathbf{u})\,g(\mathbf{u}-\mathbf{t})\,d\mathbf{u}\int w_1(\mathbf{s}-\mathbf{v})\,g(\mathbf{v}-\mathbf{t})\,d\mathbf{v}+\cdots \tag{3.4}$$

$$\frac{\delta\tilde{\rho}(\mathbf{s},\mathbf{t})}{\delta\rho(\mathbf{r})}=w_0(\mathbf{s}-\mathbf{r})+\rho\left[w_0(\mathbf{s}-\mathbf{r})\int w_1(\mathbf{s}-\mathbf{v})\,g(\mathbf{v}-\mathbf{t})\,d\mathbf{v}\right.$$
$$\left.+\,w_1(\mathbf{s}-\mathbf{r})\int w_0(\mathbf{s}-\mathbf{u})\,g(\mathbf{u}-\mathbf{t})\,d\mathbf{u}\right]+\cdots \tag{3.5}$$

In these equations we have assumed that the intermolecular potential is translationally invariant, so that $g(\mathbf{s},\mathbf{r})=g(\mathbf{s}-\mathbf{r})$.

Now we assume that g, C, and Ψ have density expansions like (3.1) and we require (2.9) to be satisfied at each order in the density. Using (3.4) and (3.5) in (2.9), we obtain

$$\ln g_0(\mathbf{r}-\mathbf{t})=-\beta\phi(\mathbf{r}-\mathbf{t}) \tag{3.6a}$$

$$\frac{g_1(\mathbf{r}-\mathbf{t})}{g_0(\mathbf{r}-\mathbf{t})}=2\Psi_1\left[1-\int w_0(\mathbf{r}-\mathbf{u})\,g_0(\mathbf{u}-\mathbf{t})\,d\mathbf{u}\right] \tag{3.6b}$$

$$\begin{aligned}\frac{g_2(\mathbf{r}-\mathbf{t})}{g_0(\mathbf{r}-\mathbf{t})}=\frac{1}{2}\left[\frac{g_1(\mathbf{r}-\mathbf{t})}{g_0(\mathbf{r}-\mathbf{t})}\right]^2 &+ \Psi_2\left\{3-\left[\int w_0(\mathbf{r}-\mathbf{u})\, g_0(\mathbf{u}-\mathbf{t})\, d\mathbf{u}\right]^2\right.\\ &\left.-2\int g_0(\mathbf{s}-\mathbf{u})\int w_0(\mathbf{s}-\mathbf{u})\, g_0(\mathbf{u}-\mathbf{t})\, d\mathbf{u}\, w_0(\mathbf{s}-\mathbf{r})\, d\mathbf{s}\right\}\\ &-\Psi_1\left[\int w_0(\mathbf{r}-\mathbf{u})\, g_0(\mathbf{u}-\mathbf{t})\, d\mathbf{u}\int w_1(\mathbf{r}-\mathbf{v})\, g_0(\mathbf{v}-\mathbf{t})\, d\mathbf{v}\right.\\ &\left.+\int g_0(\mathbf{s}-\mathbf{t})\, w_0(\mathbf{s}-\mathbf{r})\int w_1(\mathbf{s}-\mathbf{v})\, g_0(\mathbf{v}-\mathbf{t})\, d\mathbf{v}\, d\mathbf{s}\right]\\ &-\Psi_1\left[\int g_0(\mathbf{s}-\mathbf{t})\, w_1(\mathbf{s}-\mathbf{r})\int w_0(\mathbf{s}-\mathbf{u})\, g_0(\mathbf{u}-\mathbf{t})\, d\mathbf{u}\, d\mathbf{s}\right.\\ &\left.+2\int g_1(\mathbf{s}-\mathbf{t})\, w_0(\mathbf{s}-\mathbf{r})\, d\mathbf{s}\right] \qquad (3.6c)\end{aligned}$$

The pth order term in this expansion will have g_p on the left, Ψ_p and lower order terms on the right, and, most importantly, only g_{p-1}, w_{p-1}, and lower orders on the right.

The density expansion of (2.7*h*) yields

$$\int C_0(\mathbf{r})\, d\mathbf{r}=-2\Psi_1, \qquad \int C_1(\mathbf{r})\, d\mathbf{r}=-6\Psi_2, \qquad \int C_2(\mathbf{r})\, d\mathbf{r}=-12\Psi_3 \qquad (3.7)$$

which show that C_{p-1} determines Ψ_p.

We also need the density expansion of (2.6*h*), which is better expressed in terms of the Fourier transforms of C and w, since the equation involves convolution-type integrals. If $C(\mathbf{k}, \rho)$ and $w(\mathbf{k}, \rho)$ are the transforms, the density expansion gives

$$C_0(\mathbf{k})=-2\Psi_1 w_0(\mathbf{k}) \qquad (3.8a)$$

$$C_1(\mathbf{k})=-4\Psi_2 w_0(\mathbf{k})-2\Psi_2 w_0^2(\mathbf{k})-2\Psi_1[1+w_0(\mathbf{k})]\, w_1(\mathbf{k}) \qquad (3.8b)$$

where we do not indicate the explicit form of the higher order terms. The general pth order term will involve C_p, Ψ_{p+1}, and lower orders, and w_p and lower orders. A generic property of these terms is that, as in (3.8b), w_p always occurs only linearly and always multiplied by $1+w_0$. The important point is that these equations can be solved for $w_p(\mathbf{r})$ provided that $1+w_0(\mathbf{k})$ has no zeros for real $\mathbf{k}$.

Finally, we need the density expansion of the Ornstein–Zernike relation (2.12),

$$C_0(\mathbf{r}-\mathbf{s}) = g_0(\mathbf{r}-\mathbf{s}) - 1 \tag{3.9a}$$

$$C_1(\mathbf{r}-\mathbf{s}) = g_1(\mathbf{r}-\mathbf{s}) - \int C_0(\mathbf{r}-\mathbf{t})[g_0(\mathbf{t}-\mathbf{s}) - 1]\, d\mathbf{t} \tag{3.9b}$$

In the general term, C_p and g_p will appear to the same order.

We can now show that Eqs. (3.6)–(3.9) (and their higher order counterparts) can be solved iteratively for all of the unknowns to every order provided that $1 + w_0(\mathbf{k})$ has no zeros for real $\mathbf{k}$. We exhibit the first few terms and argue that the process continues indefinitely. From (3.6a) we have

$$g_0(\mathbf{r}) = \exp[-\beta\phi(\mathbf{r})] \tag{3.10}$$

which agrees with the lowest order virial result. With (3.10) and (3.9a) we find $C_0 = g_0 - 1$ and then from (3.7) we have for Ψ_1

$$\Psi_1 = -\frac{1}{2}\int [g_0(\mathbf{r}) - 1]\, d\mathbf{r} \tag{3.11}$$

which can be shown to agree with the virial expansion of the pressure. Now, (3.8a) determines w_0 and with these results we can use (3.6b) to find g_1 as

$$\begin{aligned} g_1(\mathbf{r}-\mathbf{t}) &= g_0(\mathbf{r}-\mathbf{t})\left\{-\int [g_0(\mathbf{r}) - 1]\, d\mathbf{r} + \int [g_0(\mathbf{r}-\mathbf{u}) - 1]\, g_0(\mathbf{u}-\mathbf{t})\, d\mathbf{u}\right\} \\ &= g_0(\mathbf{r}-\mathbf{t}) \int [g_0(\mathbf{r}-\mathbf{u}) - 1][g_0(\mathbf{u}-\mathbf{t}) - 1]\, d\mathbf{u} \end{aligned} \tag{3.12}$$

which again agrees with the virial result. Now the same sequence of steps can be repeated. From (3.9b) we determine C_1, and (3.7) gives Ψ_2 (which agrees with the virial result). Then w_1 can be found from (3.8b) and g_2 from (3.6c). We do not give the explicit formula for g_2, as it is messy, but one can show that it is not identical to the virial result. Some thought will show that the structure of the higher order terms in Eqs. (3.6)–(3.9) is such that this solution procedure can be carried out to arbitrary order. Hence, this theory has a unique solution within the region of convergence of the density expansion.

The above solution to the theory is predicated on the assumption that $w_0(\mathbf{k}) \neq 1$ for real $\mathbf{k}$, so that (3.8) and its higher order versions can be solved for a nonsingular $w_p(\mathbf{k})$ to all orders. In terms of the Mayer function

$f(\mathbf{r}) = \exp[-\beta\phi(\mathbf{r})] - 1$, we find $w_0(\mathbf{r}) = f(\mathbf{r})/\int f(\mathbf{r})\,d\mathbf{r}$ and for the transform $w_0(\mathbf{k}) = f(\mathbf{k})/f(\mathbf{k}=0)$. Now it's easy to see that for purely repulsive forces ($\phi > 0$ everywhere) we have $|w_0(\mathbf{k})| < 1$ for all real $\mathbf{k} \neq 0$, so that the above assumption is satisfied. One can also see that the assumption is satisfied for small enough β for any realistic intermolecular potential. On the other hand, it is not hard to show that if ϕ is attractive at intermediate ranges, then the assumption must fail at large β. If $w_0(\mathbf{k}) = 1$ for some real $\mathbf{k}$, then the solutions for $w_p(\mathbf{k})$ are singular for that $\mathbf{k}$ and it is apparently impossible to invert the transform to obtain a physically reasonable short-ranged $w_p(\mathbf{r})$. Thus, this theory seems well defined for purely repulsive potentials, but must be restricted to higher temperatures for more realistic potentials.

4. RESULTS AND CONCLUSIONS

As a first test of the accuracy of the above theory we have computed g_2/g_0 and the fourth pressure virial B_4 for both the hard-sphere fluid and the Gaussian model. These are the lowest order terms for which the theory does not give exact values. The expressions for g_2 have been evaluated numerically to a relative accuracy, we estimate, of 0.5%.

In Table I we give some comparisons for hard spheres of unit diameter. We list values for the ratio $g_2(r)/g_0(r)$ since this is finite in the hard-sphere limit even for $r < 1$ and this is typically where approximate integral equation theories are least exact, as is also the case with this theory. We give values at $r = 0$, $r = 1$, and $r = 2$ rather than a graph because

Table I. Results for Unit-Diameter Hard Spheres[a]

	B_4/B_2^3	$g_2(0)/g_0(0)$	$g_2(1)/g_0(1)$	$g_2(2)/g_0(2)$
Exact	0.2869	12.885	1.259	−0.407
EWDA	0.2935 (*C*) 0.2887 (*P*)	13.269	1.266	−0.402
PY	0.2969 (*C*) 0.2500 (*P*)	8.225	1.097	−0.407
HNC	0.2092 (*C*) 0.4453 (*P*)	16.998	1.953	−0.407
YBG	0.3424 (*C*) 0.2252 (*P*)	14.256	0.988	−0.407

[a] Integral equation values are taken from refs. 5 and 8. Here $B_2 = 2\pi/3$. Values of B_4 are from either the compressibility (*C*) or the pressure (*P*) equation of state.

the difference between our values and the exact virial values could not be seen on a graph to normal scale. We give the exact virial result, the result of this extended weighted density approximation (EWDA), and the results of three standard integral equation theories, Percus–Yevick (PY), hypernetted chain (HNC), and the Yvon–Born–Green (YBG). One sees that the EWDA results for the distribution function are substantially better than the other integral equation results, particularly at small r. We show also the values for the fourth virial coefficient B_4 in Table I. B_4 can be found from $g_2(r)$ using either the compressibility (C) or the pressure (P) equation of state.[5] The well-known thermodynamic inconsistency of the usual integral equations produces different values for B_4, both of which are listed. We have not been able to show that the EWDA is, or is not, thermodynamically consistent in this sense, but we see no formal reason that it should be. Thus, the 1.6% difference between the EWDA values for $B_4(C)$ and $B_4(P)$ is taken to be a real measure of the thermodynamic consistency of the theory and not due primarily to numerical error. Here again the EWDA does much better than the other integral equation approaches.

At the other extreme of a soft repulsive potential, consider the (physically unrealistic) Gaussian model defined by assuming the Mayer function takes the form $f(r) = \exp(-\alpha r^2)$ and for which analytic expressions for the exact B_4 and $g_2(r)$ can be found.[6] Table II shows the results with α chosen so that the second virial coefficient is the same as for the unit-diameter hard-sphere case, $\alpha = (9\pi/16)^{1/3}$. Again we see very good agreement between the EWDA and the exact values and poor results for the other integral equations. In this case the two EWDA values for B_4 do agree to 0.5% and agree with the exact value to that accuracy also, so these differences could be primarily due to numerical errors.

Table II. Results for the Gaussian Model with $\alpha = (9\pi/16)^{1/3}$ [a]

	B_4/B_2^3	$g_2(0)$	$g_2(1)$	$g_2(2)$
Exact	−0.1255	0.471	−0.526	−0.496
EWDA	−0.1247 (C) −0.1251 (P)	0.506	−0.522	−0.496
PY	−0.0732 (C) −0.1540 (P)	−0.238	−1.064	−0.501
HNC	−0.1540 (C) −0.1098 (P)	0.859	−0.736	−0.492

[a] Values are from ref. 6 and from our own calculations. Values of B_4 are from either the compressibility (C) or pressure (P) equation of state.

The remarkably good agreement of the EWDA with the virial expansion for two very different cases is encouraging; however, the real interest in equations of this type is, of course, at higher densities, where the density expansion is not useful. For this we need either analytic or accurate numerical solutions of the unexpanded equations (2.6*h*)–(2.12). We have not yet been able to accomplish this, but the accuracy of these low-density results, along with the success of the WDA theory in treating the hard-sphere freezing transition, seems to justify more effort in this direction.

The theory can, in principle, be extended to inhomogeneous states and the problems of phase coexistence; however, some of the equations take a substantially more complicated form and there may be conceptual difficulties as well. Whether the theory will be an accurate one for a wide range of interactions and states we cannot yet say. The major formal difficulty we see with this theory is its failure at low temperatures for systems whose intermolecular potentials are not purely repulsive. This suggests that there is some structural flaw, perhaps in the assumed WDA form of the free energy. We have tried a number of variations on the WDA assumption, but have not found a version free of all structural difficulties.

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