

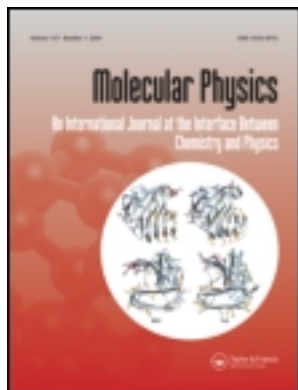
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Choosing the reference system for liquid state perturbation theory

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Choosing the reference system for liquid state perturbation theory

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Minimization of an approximate free energy functional yields the Andersen-Weeks-Chandler approximation $y(r) \equiv g(r) \exp [\beta\phi(r)] \approx y_d(r)$ along with a new criterion for choosing the reference hard sphere diameter d . The new prescription yields thermodynamic consistency and improved numerical results.

1. INTRODUCTION

The perturbation approximation for the pair distribution function $g(r)$ of classical liquids proposed some time ago by Andersen, Weeks and Chandler (AWC) [1],

$$y(r) \equiv g(r) \exp [\beta\phi(r)] \quad (1)$$

$$\approx y_d(r), \quad (2)$$

is especially notable for its simplicity and ease of use. The function $y(r)$ defined in (1) describes correlations between molecular pairs when the direct interaction $\phi(r)$ between them is turned off. The approximation (2) equates this correlation function to that of hard spheres of diameter d at the same density ρ , $y_d(r)$, which is assumed known. A prescription is then needed to specify the diameter d : proceeding from a perturbation expansion of the free energy, AWC proposed the condition

$$\int \{\exp [-\beta\phi(r)] - \exp [-\beta\phi_d(r)]\} y_d(r) \, dr = 0, \quad (3)$$

where $\phi_d(r)$ is the hard sphere potential. The combination of (2) and (3) produced remarkably good results when applied to the repulsive part of the Lennard-Jones potential [1], but was less successful with the softer inverse-12 potential [1, 2].

A fundamental shortcoming inherent in this combination is the lack of thermodynamic consistency; thus, the pressure p obtained from the free energy A ,

$$\frac{\beta p}{\rho} = \rho \frac{\partial(\beta A/N)}{\partial \rho}, \quad (4)$$

is not the same as that found through the usual quadrature,

$$\beta p/\rho = 1 - \frac{1}{6}\rho \int g(r)r\beta\phi'(r) \, dr, \quad (5)$$

the former being more accurate [1], if more troublesome to compute. An alternative criterion for d —directly enforcing consistency of these computed results—was employed by Verlet and Weis [3].

In this note, we show that the basic approximation, (2), can be obtained by minimizing an approximate expression for the free energy. A byproduct of this approach is a new criterion for choosing the hard sphere diameter, namely

$$\int \{ \exp [-\beta\phi(r)] - \exp [-\beta\phi_d(r)] \} \frac{\partial y_d(r)}{\partial d} dr = 0, \quad (6)$$

which eliminates the disagreement between (4) and (5) and leads to improvements in the computed results. Because it implies thermodynamic consistency, (6) is the formal implementation of the Verlet-Weis [3] criterion.

Generalized conditions for the choice of reference system, including energy as well as distance scales but still within the AWC approximation, are obtained in § 2. The improvement in computed results is illustrated with the inverse-12 potential.

2. THEORY AND RESULTS

We begin as in the derivation of the reference-hypernetted chain (RHNC) equation [4], introducing a reference potential $\phi_0(r)$ and defining

$$\phi(r; \lambda) = \phi_0(r) + \lambda\Delta\phi(r), \quad (7)$$

with

$$\Delta\phi(r) = \phi(r) - \phi_0(r). \quad (8)$$

The Helmholtz free energy for the system with potential $\phi(r)$ ($\lambda=1$) can then be written as

$$\beta A/N = \beta A_0/N + \frac{1}{2}\rho \int dr \int_0^1 d\lambda g(r; \lambda) \beta \Delta\phi(r), \quad (9)$$

where A_0 is the free energy of the reference system ($\lambda=0$) and

$$g(r; \lambda) = \exp [-\beta\phi(r; \lambda) + S(r; \lambda) + B(r; \lambda)] \quad (10)$$

the pair distribution function for the intermediate system with potential (7). In (10), S and B are the corresponding series (or nodal) and bridge (or elementary) functions for the same generalized potential. From (10) we have immediately

$$\frac{\partial g(r; \lambda)}{\partial \lambda} = -g(r; \lambda) \Delta\phi(r) + g(r; \lambda) \frac{\partial}{\partial \lambda} [S(r; \lambda) + B(r; \lambda)], \quad (11)$$

or

$$g(r; \lambda) \Delta\phi(r) = -\frac{\partial}{\partial \lambda} \{ g(r; \lambda) - g(r; \lambda) \ln g(r; \lambda) \exp [\beta\phi(r; \lambda)] \} \\ - [S(r; \lambda) + B(r; \lambda)] \frac{\partial g(r; \lambda)}{\partial \lambda}, \quad (12)$$

and (9) becomes

$$\beta A/N = \beta A_0/N - \frac{1}{2}\rho \int dr \{ g(r) - g(r) \ln g(r) \exp [\beta\phi(r)] \\ - g_0(r) + g_0(r) \ln g_0(r) \exp [\beta\phi_0(r)] \} \\ - \frac{1}{2}\rho \int dr \int_0^1 d\lambda [S(r; \lambda) + B(r; \lambda)] \frac{\partial g(r; \lambda)}{\partial \lambda}. \quad (13)$$

The integral over λ of the term involving $S(r; \lambda)$ in (13) can be evaluated exactly [4]. We shall not do so here, however, but instead follow a simpler, though approximate, procedure. The plausibility argument for this is that, as with the bridge function $B(r; \lambda)$ [5], the series function $S(\lambda; r)$ should not be greatly sensitive to the change in potential from $\phi_0(r)$ to the final $\phi(r)$. If we then ignore such changes in both S and B , the last term in (13) becomes

$$\begin{aligned} & -\frac{1}{2}\rho \int dr [S_0(r) + B_0(r)][g(r) - g_0(r)] \\ & = -\frac{1}{2}\rho \int dr \{\ln g_0(r) \exp [\beta\phi_0(r)]\} [g(r) - g_0(r)] \end{aligned} \quad (14)$$

and (13) now reads

$$\begin{aligned} \beta A/N = \beta A_0/N - \frac{1}{2}\rho \int dr \{ & g(r) - g_0(r) \ln g(r) \exp [\beta\phi(r)] \\ & - g_0(r) + g_0(r) \ln g_0(r) \exp [\beta\phi_0(r)] \}, \end{aligned} \quad (15)$$

which expresses the free energy as a functional of $y(r)$ and $y_0(r)$. Requiring (15) to be extremal with respect to variations in these functions then gives

$$\begin{aligned} \frac{\beta\delta A}{N} = \frac{1}{2}\rho \int dr \left\{ \left[\exp [-\beta\phi(r)] \ln \frac{y(r)}{y_0(r)} \right] \delta y(r) - [g(r) - g_0(r)] \delta \ln y_0(r) \right\} \\ = 0, \end{aligned} \quad (16)$$

if

$$y(r) = y_0(r) \quad (17)$$

and

$$\int dr [g(r) - g_0(r)] \delta \ln y_0(r) = 0. \quad (18)$$

Equation (17) is the AWC approximation for the arbitrary reference potential $\phi_0(r)$, while (18) imposes a constraint on this potential. For a specific potential $\phi_0(r; \sigma_0, \epsilon_0)$ with distance and energy scales set by σ_0 and ϵ_0 , we may vary these parameters to satisfy (18). With

$$\delta y_0(r; \sigma_0, \epsilon_0) = \frac{\partial y_0}{\partial \sigma_0} \delta \sigma_0 + \frac{\partial y_0}{\partial \epsilon_0} \delta \epsilon_0 \quad (19)$$

and (17), we have then the conditions

$$\int dr \{ \exp [-\beta\phi(r)] - \exp [-\beta\phi_0(r)] \} \frac{\partial y_0(r)}{\partial \sigma_0} = 0, \quad (20 a)$$

$$\int dr \{ \exp [-\beta\phi(r)] - \exp [-\beta\phi_0(r)] \} \frac{\partial y_0(r)}{\partial \epsilon_0} = 0 \quad (20 b)$$

for determining the optimum values of σ_0 and ϵ_0 . Similar constraints have been obtained for the RHNC equation [6].

With (17), the approximate free energy now reads

$$\begin{aligned} \beta A/N = \beta A_0/N - \frac{1}{2}\rho \int dr [g(r) - g_0(r)] \\ = \beta A_0/N - \frac{1}{2}\rho \int dr \{ \exp [-\beta\phi(r)] - \exp [-\beta\phi_0(r)] \} y_0(r), \end{aligned} \quad (21)$$

in agreement with the first-order AWC expansion [1]. By explicit differentiation, we then have

$$\begin{aligned} \frac{\beta p}{\rho} &= \rho \frac{\partial(\beta A/N)}{\partial \rho} \\ &= \frac{\beta p_0}{\rho} - \frac{1}{2} \rho \int dr \Delta e(r) y_0(r) - \frac{1}{2} \rho \int dr \Delta e(r) \rho \frac{\partial y_0(r)}{\partial \rho}, \end{aligned} \quad (22)$$

where

$$\Delta e(r) \equiv \exp[-\beta \phi(r)] - \exp[-\beta \phi_0(r)]. \quad (23)$$

But $y_0(r)$ is a dimensionless function of r/σ_0 , $\rho\sigma_0^3$ and $\beta\epsilon_0$, so that

$$\sigma_0 \frac{\partial y_0(r)}{\partial \sigma_0} = 3\rho \frac{\partial y_0(r)}{\partial \rho} - r \frac{\partial y_0(r)}{\partial r} \quad (24)$$

and (22) becomes

$$\begin{aligned} \frac{\beta p}{\rho} &= \frac{\beta p_0}{\rho} - \frac{1}{2} \rho \int dr \Delta e(r) y_0(r) - \frac{1}{6} \rho \int dr \Delta e(r) \left[\sigma_0 \frac{\partial y_0(r)}{\partial \sigma_0} + r y_0'(r) \right] \\ &= 1 - \frac{1}{6} \rho \int dr y_0(r) \exp[-\beta \phi(r)] r \beta \phi'(r) - \frac{1}{6} \rho \int dr \Delta e(r) \sigma_0 \frac{\partial y_0(r)}{\partial \sigma_0}, \end{aligned} \quad (25)$$

after an integration by parts. It is now evident that consistency in the pressure is achieved within the AWC approximation when σ_0 is chosen to satisfy (20 a).

In the same way, (20 b) ensures a similar consistency for the internal energy E ; explicitly, we have from (21)

$$\begin{aligned} \frac{\beta E}{N} &= \beta \frac{\partial(\beta A/N)}{\partial \beta} \\ &= \frac{3}{2} + \frac{1}{2} \rho \int dr y_0(r) \exp[-\beta \phi(r)] \beta \phi(r) - \frac{1}{2} \rho \int dr \Delta e(r) \epsilon_0 \frac{\partial y_0(r)}{\partial \epsilon_0}. \end{aligned} \quad (26)$$

At present, only the hard sphere model is sufficiently well known to serve as reference system. For this choice, (20 b) is trivially satisfied since there is no energy scale; the hard sphere diameter $d = \sigma_0$ is then determined by (20 a). For the calculations discussed below, $y_d(r)$ and $\partial y_d(r)/\partial d$ were obtained using the parametrizations of Verlet-Weiss [7] and Henderson-Grundke [8].

To test the effect of using condition (6) rather than (3), the original trial cases [1] have been calculated anew. The greatest numerical change occurs for the virial pressure, (5), of the inverse-12 potential

$$\phi(r) = 4\epsilon \left(\frac{\sigma}{r} \right)^{12}. \quad (27)$$

The results are shown in table 1, along with the Monte Carlo (MC) values of Hansen [9] and Hoover *et al.* [10], as functions of the single parameter ρa^3 , where

$$a = \sigma(\beta\epsilon)^{1/12}. \quad (28)$$

Also shown in table 1 are the results obtained by Hutchinson and Conkie (HC) [11] from an integral equation method that imposed consistency between the virial and compressibility equations of state. The improvement on using (6)

Table 1. Virial pressure for the inverse-12 potential.

ρa^3	Ref. [9]	$\beta p/\rho$			
		MC Ref. [10]	Eqn. (6)	AWC Eqn. (3)	HC
0.1	1.447	1.448	1.450	1.450	1.450
0.2	2.118	2.121	2.123	2.158	2.123
0.3	3.119	3.101	3.118	3.246	3.113
0.4	4.578	4.557	4.555	4.926	4.540
0.5	6.660	6.641	6.588	7.508	6.560
0.6	9.556	9.460	9.389	11.436	9.366
0.7	13.511	13.469	13.137	17.318	13.20

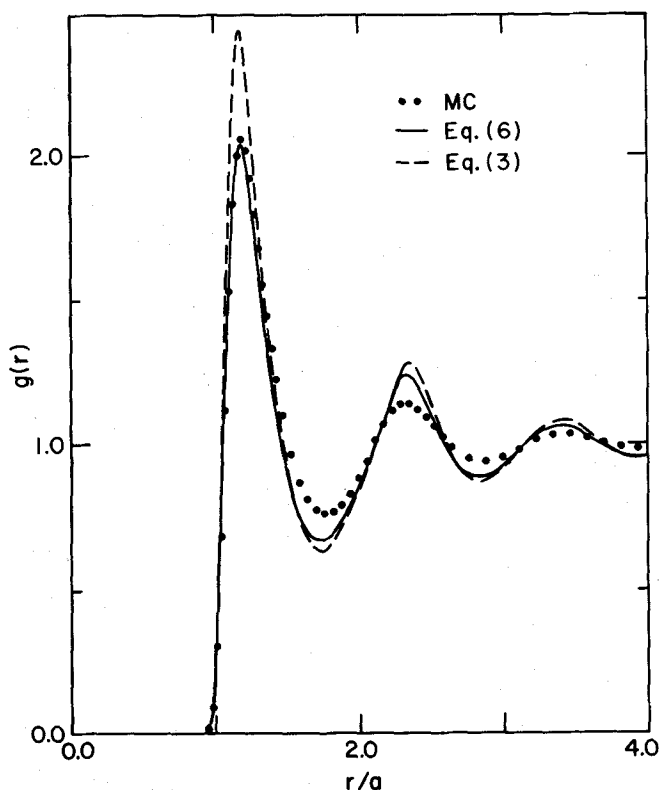
Table 2. Helmholtz free energy and reference hard sphere diameters for the inverse-12 potential.

ρa^3	$\beta A/N$				d/a		
	MC Ref. [9]	MC Ref. [10]	AWC Eqn. (6)	AWC Eqn. (3)	HC	Eqn. (6)	Eqn. (3)
0.1	0.403	0.403	0.404	0.404	0.40	1.1853	1.1969
0.2	0.904	0.906	0.908	0.907	0.91	1.1778	1.1914
0.3	1.533	1.533	1.538	1.536	1.53	1.1689	1.1842
0.4	2.330	2.323	2.332	2.323	2.32	1.1587	1.1750
0.5	3.339	3.328	3.332	3.307	3.32	1.1472	1.1640
0.6	4.613	4.580	4.585	4.528	4.57	1.1346	1.1512
0.7	6.214	6.196	6.146	6.029	6.13	1.1212	1.1368

with the AWC approximation is quite significant; in fact, the new results are comparable with the pressure-consistent HC calculations, though far easier to obtain. The improvement in free energy, shown in table 2, is less dramatic, as this quantity is relatively insensitive to changes in the diameter d . Table 2 also shows the two sets of sphere sizes used in obtaining these results. In all cases studied (6) produces smaller diameters than does (3).

Smaller diameters d in turn lead to reduced structure in the pair distribution function $g(r)$, as illustrated in the figure. The improvement here, compared to MC results [2], is seen to be particularly significant for the main peak of $g(r)$ (which accounts for the good thermodynamic results above) and rather less so for the remaining structure.

A recalculation using the repulsive part of the Lennard-Jones potential yields results following the same pattern as those above but with smaller numerical changes. This was to be hoped for since the original AWC values were already quite good [1].



Pair correlation function for the inverse-12 potential at $\rho a^3 = 0.56921$.

In summary, then, we find that using (6) to fix the hard sphere diameter in the AWC approximation removes a thermodynamic inconsistency and improves the computed results while retaining the simplicity and ease of use of the AWC approximation.

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