A note about the comparison of the WCA and self-consistent WCA perturbation methods

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Among the methods of determination of equations of state of fluids from statistical physics, the perturbation methods are of great interest because they lend themselves to fast computations. In this paper, we deal with the case of pairwise additive spherical interactions between molecules with $u(r)$ denoting the intermolecular potential. In this framework, a perturbation method is theoretically characterized by two elements: the definition of a reference intermolecular potential $u_0(r)$ about which the thermodynamical properties are calculated by a functional Taylor expansion using the quantity $[u(r)-u_0(r)]$, and the method of determination of the reference thermodynamical properties corresponding to the mainly repulsive potential $u_0(r)$.

The WCA perturbation method[1] and the self-consistent WCA perturbation method[2] differ from each other by the latter element. Both approaches express the excess free energy A_0 of the reference system in terms of that of hard-spheres by a first order functional Taylor expansion in the blip-function defined in Ref. 1. The difference lies in the criterion for the choice of d, the diameter of the reference hard-sphere potential about which the expansion is carried out. Andersen *et al.*[1] show that, in the WCA method, A_0 contains errors of order ξ^4 only, where ξ is a softness parameter characterizing the range of intermolecular distances in which the blip-function is nonzero. For other choices of d, as in the self-consistent WCA method, the error on A_0 is of order ξ^2. Therefore, although the value of ξ is not strictly the same in each method for a given potential, it may seem surprising that the self-consistent method is generally regarded as superior to the WCA method[2,3] for the determination of the properties of the reference system at high densities. We investigate this point in this paper.

We first note that the results obtained in Refs. 1 and 2 with the WCA method in the case of an inverse-12 potential are different regardless of the difference in the definitions chosen for the pressure computed. We then remark that the difference in the numerical implementations of Refs. 1 and 2 lies only in the representation of the hard-sphere indirect correlation function $y_d(r)$ for $r<d$.

We further investigate the influence of the representation of $y_d(r)$ on the results yielded by the WCA and self-consistent WCA methods by considering the following plausible options for $y_d(r)$.

(V1): Henderson–Grundke representation[4] used by Lado.

(V2): Verlet–Weis representation[5] of $y_d(r)$ for $r \geqslant d$ and quadratic extrapolation of $y_d(r)$ in the parameter $(r-d)$ about $r=d$ for $r<d$.

Expression (V2), contrary to (V1), is compatible with the continuity of the second derivative of y_d at $r=d$;[6] it is also compatible with the order of the errors in A_0 expected with either the WCA method or the self-consistent WCA method [a higher order expansion, involving third and higher order derivatives of $y_d(r)$, is not necessary in view of the error expected]. We also consider the Verlet–Weis approaches of both methods[5,7] whose results we designate by VW for the WCA method and by VWSC for the self-consistent WCA method. The results we find for the inverse-12 potential [defined by $u(r)=4\epsilon(\sigma/r)^{12}$] with these various implementations of the WCA and self-consistent WCA methods are indicated in Tables I and II. Only the compressibility factors, which show the greatest differences, are displayed as functions of the single parameter ρa^3 with $a=\sigma(\beta\epsilon)^{1/12}$ where ρ is the density, σ and ϵ characterize the inverse-12 potential, and $\beta=1/kT$ with k being the Boltzmann constant and T the temperature. The exact results are found in the articles by Hansen[8] and by Hoover *et al.*[9] In order to take full advantage of the accuracy of the WCA method, the pressure is calculated by differentiating the excess free energy,[1] that is with equation (3.6) of Ref. 1. In this expression, the value of $(\partial d/\partial\rho)_T$ is calculated directly by differentiation of the WCA criterion[1] with respect to density in order to minimize the numerical error. For values of ρa^3 greater than 0.6, the hard-sphere diameter becomes so large in the WCA method that the parametrization of Verlet and Weis[5] (*a priori* valid up to a packing fraction of 0.49) for $y_d(r)$ is not applicable. We have therefore not considered higher densities.

We note that, as it is well known, the results significantly depend on the type of WCA method used or on the type of representation chosen for $y_d(r)$ only at high density, say $\rho a^3 > 0.4$. In this domain of density, the Verlet–Weis results,[5,7] which can also be characterized by a certain representation of $y_d(r)$, are poor. As for the other results, we remark that, for a given version of the WCA method, a change in the representation of $y_d(r)$ can bring about a shift of 5% in the compressibility factor. This shift would still be greater with another plausible representation of $y_d(r)$ proposed by Andersen *et al.*[1] Besides, we note that the relative ranking of the WCA method and the self-consistent WCA method depends on the representation of $y_d(r)$ chosen (V1 or V2). The self-consistent WCA method gives better results when (V1) is chosen (though less markedly than shown in Ref. 2) whereas the WCA

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TABLE I. Compressibility factor for the inverse-12 potential calculated with the WCA method for various representations of the indirect correlation function $y_d(r)$; V1: Henderson–Grundke representation of $y_d(r)$[4], V2: $y_d(r)$ is represented by the parametrization of Verlet–Weis (Ref. 5) if $r \geqslant d$ and by quadratic extrapolation about $r=d$ if $r<d$, VW: results obtained using the Verlet–Weis approach (Refs. 5 and 7).

	$\beta P/\rho$				
ρa^3	Monte Carlo (Ref. 8)	Monte Carlo (Ref. 9)	y_d: V1	y_d: V2	VW
0.1	1.447	1.448	1.449	1.450	1.450
0.2	2.118	2.121	2.121	2.124	2.124
0.3	3.119	3.101	3.107	3.119	3.105
0.4	4.578	4.557	4.515	4.562	4.444
0.5	6.660	6.641	6.471	6.627	6.110
0.6	9.556	9.460	9.110	9.557	7.950

TABLE II. Compressibility factor for the inverse-12 potential calculated with the self-consistent WCA method for various representations of the indirect correlation function $y_d(r)$, V1, V2: see Table I, VWSC: results obtained using the Verlet–Weis approach (Ref 7).

	$\beta P/\rho$				
ρa^3	Monte Carlo (Ref. 8)	Monte Carlo (Ref. 9)	y_d: V1	y_d: V2	VWSC
0.1	1.447	1.448	1.450	1.450	1.450
0.2	2.118	2.121	2.124	2.125	2.126
0.3	3.119	3.101	3.117	3.125	3.110
0.4	4.578	4.557	4.554	4.583	4.450
0.5	6.660	6.641	6.583	6.674	6.041
0.6	9.556	9.460	9.378	9.636	7.354

method gives slightly better results when (V2) is chosen.

Our conclusion is that the self-consistent WCA method is not intrinsically better than the WCA method as indicated in Ref. 2. The results obtained by both methods at high density with the classical test potential $u(r) = 4\epsilon(\sigma/r)^{12}$ vary enough with the possible representations of $y_d(r)$ that the relative ranking of the two methods depends on the representation chosen.

This conclusion does not reduce the interest of Lado's method[2] whose results [Table II with the representation (V1) for $y_d(r)$] are very good over a large domain of density and whose domain of validity is a little larger than for the WCA method since it leads to somewhat smaller packing fractions for the reference hard-sphere fluid. Besides, this conclusion enhances the interest of the method proposed by Kang *et al.*[10] whose relative insensitiveness to the representation of $y_d(r)$ we have verified. Then, there is less uncertainty on the numerical results and a simple first order Taylor expansion of $y_d(r)$ about $r=d$ can be used, leading to the computationally inexpensive expressions proposed by Verlet and Weis[5,7] for the diameter of the reference hard-sphere fluid.

[1] H. C. Andersen, J. D. Weeks, and D. Chandler, Phys. Rev. A **4**, 1597 (1971).
[2] F. Lado, Mol. Phys. **52**, 871 (1984).
[3] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 2nd ed. (Academic, London, 1986), p. 160.
[4] D. Henderson and E. W. Grundke, J. Chem. Phys. **63**, 601 (1975).
[5] L. Verlet and J.-J. Weis, Phys. Rev. A **5**, 939 (1972).
[6] D. A. McQuarrie, *Statistical Mechanics* (Harper and Row, New York, 1976), p. 282.
[7] L. Verlet and J.-J. Weis, Mol. Phys. **24**, 1013 (1972).
[8] J. P. Hansen, Phys. Rev. **42**, 221 (1970).
[9] W. G. Hoover, M. Ross, K. W. Johnson, D. Henderson, J. A. Barker, and B. C. Brown, J. Chem. Phys. **52**, 4931 (1970).
[10] H. S. Kang, C. S. Lee, T. Ree, and F. H. Ree, J. Chem. Phys. **82**, 414 (1985).