Calculation of a corrected pair distribution function

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In recent publications,^{1,2} we have pointed out that a generalization of the hypernetted-chain formalism of classical fluids provides a simple way of incorporating the effects of an additional term φ_1 in the intermolecular potential when the behavior of a reference system with potential φ_0 is known.³ In this note, we report briefly on a numerical test of this generalization for the corrected pair distribution function (PDF) g obtained from the equations¹

$$\Delta C(r) = g_0(r)[e^{H(r) - \beta\varphi_1(r)} - 1] - H(r), \quad (1a)$$

$$\tilde{H}(k) = \frac{[1 + \rho \tilde{G}_0(k)]^2 \Delta \tilde{C}(k)}{1 - \rho [1 + \rho \tilde{G}_0(k)] \Delta \tilde{C}(k)} - \Delta \tilde{C}(k), \quad (1b)$$

where

$$H(r) \equiv \ln[g(r)e^{\beta\varphi_1(r)}/g_0(r)]. \quad (1c)$$

In these expressions, $g_0 \equiv G_0 + 1$ is the known PDF from φ_0 alone, ρ is the number density, and $\beta \equiv (k_B T)^{-1}$; the tilde denotes a Fourier transform.

The test applied below illustrates one of the uses of Eqs. (1), namely, approximate continuation of Monte Carlo and molecular dynamics (MD) calculations to cases not directly computed. Other uses for a corrected g

occur in some quantum-fluid theories,⁴ where g_0 is the ideal gas PDF and the perturbation φ_1 is associated with pair-correlated wave functions, and in the inversion of scattering data to obtain an experimental potential,⁵ where improved accuracy could be achieved by solving for just φ_1 with φ_0 an assigned potential whose PDF g_0 is known.

We consider here only the first of these applications. Let $g_0(r/\sigma)$ be a PDF for the potential $\varphi_0(r) \equiv \epsilon \Phi(r/\sigma)$ calculated by a numerical experiment at the density ρ and temperature T ; we seek the PDF for the same potential at neighboring values ρ' , T' . This function is obtained as a correction to g_0 by noting that it corresponds to the PDF at ρ , T for a potential $\varphi(r) = \epsilon' \Phi(r/\sigma')$ with $\rho'/\rho = (\sigma'/\sigma)^3$ and $T'/T = \epsilon/\epsilon'$. Thus, with g_0 given and $\varphi_1 = \varphi - \varphi_0$, Eqs. (1) yield a corrected function $g_c(r/\sigma) = g(r/\sigma')$.

We have computed g in this way for the Lennard-Jones potential at $\rho'\sigma^3 = 0.75$, $kT'/\epsilon = 0.827$ using as input Verlet's⁶ MD g for $\rho\sigma^3 = 0.85$, $kT/\epsilon = 2.888$. Since the computed solution has also been obtained by Verlet,⁶ this

FIG. 1. The reference LJ potential φ_0 and perturbing potential φ_1 , defined in text, both in units of $k_B T$. The sum $\varphi_0 + \varphi_1$ is another LJ potential.

FIG. 2. Corrected pair distribution function g obtained from the input g_0 and φ_1 of Fig. 1, compared with the correct MD solution.

affords a direct test of Eqs. (1).

The range of g_{MD} used as input was first suitably extended using the method described in Ref. 6. Equations (1a, b) were then solved iteratively until the largest difference between successive iterates of rH was less than 10^{-4} ; numerical techniques appropriate for this solution are similar to those described elsewhere.⁷

Figure 1 shows the reference and "perturbing" potentials φ_0 and φ_1 , with the abscissa in units of σ as employed in the calculation. The corrected g obtained from Eqs. (1) is shown in Fig. 2, along with the input g_0 and the correct MD solution, all plotted against a rescaled abscissa r/σ' . The agreement between the computed g and g_{MD} is seen to be quite good, particularly in view of the strength of φ_1 .

It may be anticipated that Eqs. (1) will be highly accurate for softer potentials φ_1 .

¹F. Lado, Phys. Rev. A 8, 2548 (1973).

²F. Lado, J. Chem. Phys. 59, 4830 (1973). This paper deals with the generalization to mixtures of the single-component formalism in Ref. 1.

³The analogous Percus-Yevick generalization is obvious [see, e.g., F. Lado, Phys. Rev. 135, A1013 (1964)] though undoubtedly not as useful for weak corrections φ_1 .

⁴T. Dunn and A. A. Broyles, Phys. Rev. 157, 156 (1967); F. A. Stevens, Jr. and M. A. Pokrant, Phys. Rev. A 8, 990 (1973); and other references therein.

⁵M. D. Johnson, P. Hutchinson, and N. H. March, Proc. R. Soc. A 282, 283 (1964).

⁶L. Verlet, Phys. Rev. 165, 201 (1968).

⁷F. Lado, J. Chem. Phys. 47, 4828 (1967); J. Comput. Phys. 8, 417 (1971).