

## PERTURBATION THEORY FOR THE RADIAL DISTRIBUTION FUNCTION FOR SIMPLE POLAR FLUIDS

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The radial distribution function for a fluid whose molecules interact according to the Stockmayer potential was calculated by means of thermodynamic perturbation theory using two different approximations for the perturbation term and was compared with computer simulation results. The approximation based on the Percus-Yevick equation was found to be in much better agreement with the simulations than was the "simplified superposition approximation" to the perturbation term.

The successful application of thermodynamic perturbation theory to simple fluids has recently led several workers to apply this procedure in the determination of the equilibrium properties of a fluid consisting of molecules interacting with a non-spherical pair potential [1-5]. Recently, we proposed [6] a new perturbation technique, based on the Percus-Yevick equation, for determining the radial distribution function. We report here the application of this new technique to a fluid whose molecules interact according to the Stockmayer potential and show that it is superior to a conventional perturbation calculation based on the superposition approximation.

In perturbation theory it is convenient [1] to write the anisotropic pair potential  $u(r_{12}, \omega_1, \omega_2)$ , which is a function of the interparticle separation  $r_{12}$  and the orientations  $\omega_1, \omega_2$  of each particle relative to the interparticle axis, as the sum of an orientation-independent reference potential  $u_0(r_{12})$  and a perturbing potential  $u_a(r_{12}, \omega_1, \omega_2)$ . For the Stockmayer potential, considered here, the reference potential  $u_0(r_{12})$  for the unperturbed system is the Lennard-Jones 12-6 potential,

$$u_0(r_{12}) = 4\epsilon[(\sigma/r_{12})^{12} - (\sigma/r_{12})^6], \quad (1)$$

where  $\epsilon$  is the well depth and  $u_0(\sigma) = 0$ . The perturbing potential  $u_a$  is a dipole-dipole interaction,

$$u_a = -\mu^2 r_{12}^{-3} [2\cos\theta_1 \cos\theta_2 - \sin\theta_1 \sin\theta_2 \cos(\phi_1 - \phi_2)], \quad (2)$$

where  $\mu$  is the dipole moment,  $\theta_i$  is the angle between the dipole of the  $i$ th particle and the interparticle axis, and  $\phi_i$  is the azimuthal angle between the dipole and any reference plane containing the interparticle axis. All multipole interactions are characterized by

$$\langle u_a(r_{ij}, \omega_i, \omega_j) \rangle_{\omega_i} = 0, \quad (3)$$

which causes many of the terms in the perturbation expansion to vanish.

The perturbation expansion through second order of the orientation-dependent pair correlation function  $g(r_{12}, \omega_1, \omega_2)$  is [1]

$$g(r_{12}, \omega_1, \omega_2) = g_0(r_{12}) + \Delta g(r_{12}, \omega_1, \omega_2) + \Delta^2 g(r_{12}, \omega_1, \omega_2), \quad (4)$$

where  $g_0(r_{12})$  is the pair correlation function for the fluid with pair potential  $u_0(r_{12})$ ;  $\Delta g$  is linear in  $u_a$ , and  $\Delta^2 g$  is quadratic in  $u_a$ . The radial distribution function (RDF)  $\bar{g}(r_{12})$  is the unweighted average of the anisotropic pair correlation function over the orientations of molecules 1 and 2,

$$\begin{aligned}\bar{g}(r_{12}) &= \langle g(r_{12}, \omega_1, \omega_2) \rangle_{\omega_1, \omega_2} \\ &= g_0(r_{12}) + \Delta \bar{g}(r_{12}) + \Delta^2 \bar{g}(r_{12}).\end{aligned}\quad (5)$$

For our choice of  $u_0(r_{12})$ , the orientation average of  $\Delta g$  vanishes.

Gubbins and Gray [1] have derived an exact expression for  $\Delta^2 g$  in the grand canonical ensemble for "multipole-like" potentials, i.e., for potentials for which eq. (3) applies. When their formula for  $\Delta^2 g$  is averaged over the orientation of molecules 1 and 2 according to eq. (5), the resulting expression for  $\Delta^2 \bar{g}$  becomes identical to the first-order perturbation correction  $\Delta g(r_{12})$  for a system with an *effective* isotropic perturbing potential  $u_1^{\text{eff}}$  given by

$$u_1^{\text{eff}}(r_{12}) = -\frac{1}{2} \beta \langle [u_a(r_{12}, \omega_1, \omega_2)]^2 \rangle_{\omega_1, \omega_2}, \quad (6)$$

where  $\beta = 1/kT$ . The three- and four-particle correlation functions for the reference fluid which appear in this expression for  $\Delta^2 \bar{g}$  are not available, but Smith et al. [7] and Gubbins et al. [8] have evaluated similar integrals using the Kirkwood superposition approximation for these higher-order correlation functions. They also proposed an additional simplification which eliminates the need for the time-consuming calculation of the elementary (fully-connected) cluster integral. When these procedures are applied, the exact  $\Delta^2 \bar{g}$  is approximated in this so-called simplified superposition approximation (SSA) by

$$\begin{aligned}\Delta^2 \bar{g} &= -\beta g_0(r_{12}) \left\{ u_1^{\text{eff}}(r_{12}) + 2\rho \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{---} \end{array} (r_{12}) \right. \\ &\quad \left. + \frac{1}{2} \rho^2 \left[ 2 \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{---} \end{array} (r_{12}) + 3 \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{---} \end{array} (r_{12}) \right] \right\}, \quad (7)\end{aligned}$$

where in cluster notation [8] a straight line represents  $h_0(r_{ij}) = g_0(r_{ij}) - 1$  and a wavy line represents  $u_1^{\text{eff}}(r_{ij})g_0(r_{ij})$ .

Rather than evaluating the exact terms in the perturbation expansion (4) through a series of approximations, we have recently introduced [6] approximate expressions for these terms obtained from the Percus-Yevick (PY) equation for the RDF. Our expressions for  $\Delta^n g^{\text{PY}}$  are readily generalized to a system with an anisotropic pair potential. For "multipole-like" interactions, the first-order term vanishes and the resulting expression for  $\Delta^2 g^{\text{PY}}$  is identical to the first-order term for a system with an *effective* perturbing potential  $u_1^{\text{eff}}$  of eq. (6):

$$\begin{aligned}\Delta^2 \bar{g}^{\text{PY}} &= -\beta u_1^{\text{eff}}(r_{12}) g_0^{\text{PY}}(r_{12}) + \rho \exp[-\beta u_0(r_{12})] \\ &\quad \times \int \left[ -\beta \int u_1^{\text{eff}}(r_{13}) y_0^{\text{PY}}(r_{13}) h_0^{\text{PY}}(r_{23}) d3 \right. \\ &\quad \left. + \int \{1 - \exp[\beta u_0(r_{13})]\} [\Delta^2 \bar{g}^{\text{PY}}(r_{13}) h_0^{\text{PY}}(r_{23}) \right. \\ &\quad \left. + \Delta^2 \bar{g}^{\text{PY}}(r_{23}) g_0^{\text{PY}}(r_{13})] d3 \right], \quad (8)\end{aligned}$$

where the notation is that of ref. [6].

We have calculated the RDF's  $\bar{g}(r)$  for the Stockmayer potential for  $\mu^{*2} = \mu^2/\epsilon\sigma^3$  up to 1.4 at  $T^* = kT/\epsilon = 0.719$ ,  $\rho^* = \rho\sigma^3 = 0.850$  and at  $T^* = 1.036$ ,  $\rho^* = 0.650$  both from the SSA equation (7) and from an iterative solution to eq. (8). The RDF  $g_0(r)$  for the reference system was obtained from the molecular dynamics data of Verlet [9]. The results along with  $g_0(r)$  are shown in figs. 1-3.

Wang et al. [10] have recently reported Monte Carlo determinations of the RDF using the Stockmayer potential with values of  $\mu^{*2}$  up to 1.4. Their RDF's differ only slightly from the Lennard-Jones reference  $g_0(r)$  for the same state, showing a slight shift of the first peak toward smaller intermolecular distances with

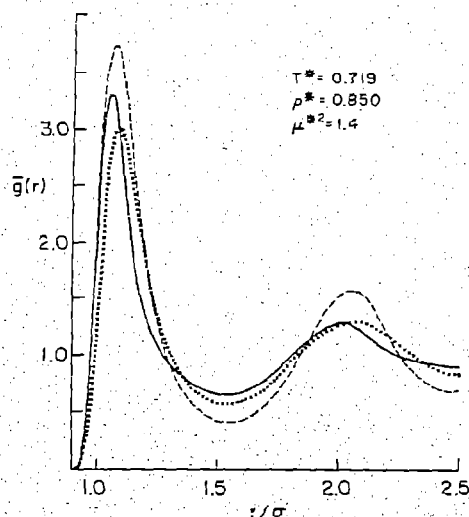


Fig. 1. The radial distribution function for the Stockmayer potential. Solid line is from PY perturbation (7), dashed line from SSA perturbation (8). Dotted line is the Lennard-Jones reference RDF.

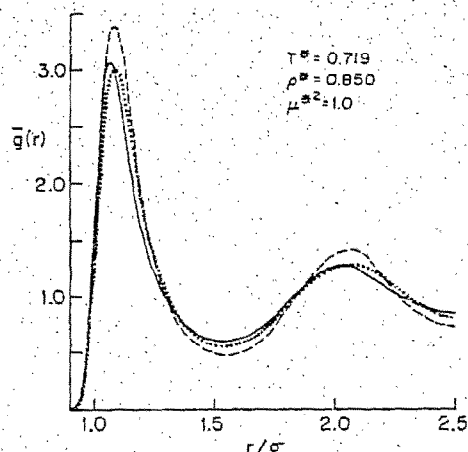


Fig. 2. The radial distribution function for the Stockmayer potential. Key as in fig. 1.

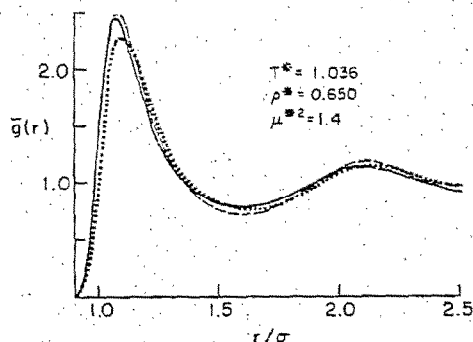


Fig. 3. The radial distribution function for the Stockmayer potential. Key as in fig. 1.

no change in height and a positive deviation in height at the first minimum. Since the Monte Carlo results were obtained at  $T^* = 0.719$  and  $\rho^* = 0.800$ , we are unable to make a direct comparison with our calculations. However, it is expected that a Monte Carlo calculation at  $\rho^* = 0.850$  would show that the Stockmayer RDF is related in a similar manner to the Lennard-Jones RDF at  $\rho^* = 0.850$ .

Fig. 1 shows that for  $\mu^2 = 1.4$  at  $T^* = 0.719$  and  $\rho^* = 0.850$  the PY perturbation (8) predicts the shift of the first peak and the positive correction at the first minimum, although the height of the first peak is larger than the expected Monte Carlo result. The SSA equation (7), on the other hand, gives perturba-

tion corrections which are excessively large and long-ranged and which fail to exhibit the qualitative differences between the Stockmayer and Lennard-Jones RDF's. Fig. 2 shows the calculated and reference RDF's for  $\mu^2 = 1.0$  at the same reduced temperature and density. In this case the PY perturbation (8) gives an RDF that is in excellent qualitative and quantitative agreement with the expected behavior of the Stockmayer RDF. The SSA equation (7) gives results which, though improved, are still poor.

No computer simulations of the Stockmayer RDF are available at any other densities and temperatures. However, at lower densities and elevated temperatures the attractive forces of the Stockmayer potential should play an increasingly important role and produce significant perturbations. An example, for which  $\mu^* = 1.4$ ,  $T^* = 1.036$ , and  $\rho^* = 0.650$ , is presented in fig. 3. We note the close agreement between the two theoretical curves and the large perturbation at the first peak.

We conclude that for "multipole-like" anisotropic potentials the SSA perturbation expansion of the RDF yields perturbations to the reference (isotropic potential) RDF which are both quantitatively and qualitatively incorrect. On the other hand, our new PY perturbation expression (8) gives not only much smaller perturbations, but also the qualitative displacements to the reference RDF in agreement with Monte Carlo results.

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