A 3, 340 (1971).

[4] G. Ahlers, Phys. Rev. Letters 22, 54 (1969).

[5] K. D. Erben and F. Pobell, Phys. Letters 26A, 368 (1968).

[6] P. Leiderer and F. Pobell, J. Low-Temp. Phys. 3, 577 (1970).

[7] In the range of power densities used here the thermal resistance of the superfluid is attributable to several dissipative processes. In addition to the usual normal fluid viscosity and mutual friction effects, there is a large contribution from another mechanism which has sometimes been described in terms of a superfluid eddy viscosity [see, for example, C. E. Chase, in *Superfluid Helium*, edited by J. F. Allen (Academic, London, 1966), p. 219]. For this reason the temperature dependences in Figs. 1 and 2 should not be interpreted in terms of mutual friction alone.

[8] G. Ahlers, Phys. Rev. Letters 21, 1159 (1968).

PHYSICAL REVIEW A VOLUME 4, NUMBER 2 AUGUST 1971

Perturbation Theory and the Equilibrium Structure of Simple Liquids*

J. A. Barker and D. Henderson
IBM Research Laboratory, Monterey and Cottle Roads, San Jose, California 95114

(Received 4 March 1971)

Monte Carlo studies of the reference fluid used by Chandler, Weeks, and Andersen (CWA) are reported. Although the CWA theory gives good values for the total thermodynamic properties, in its original form it gives less satisfactory values for the individual terms in their perturbation expansion. This results in part from the use of the Percus-Yevick theory in the CWA calculation of the radial distribution function.

Recently, Chandler, Weeks, and Andersen[1] (CWA) have developed an interesting perturbation theory of liquids. In their publications to date, they apply their theory to the 6 : 12 fluid in which the total potential energy results from the additive contributions of pair interactions of the form

$$u(R)=4\epsilon[(\sigma/R)^{12}-(\sigma/R)^{6}]. \tag{1}$$

Their theory can be applied to more general systems. However, for simplicity we also confine our attention to this fluid.

In their theory, $u(R)$ is written as

$$u(R)=u_0(R)+u_1(R), \tag{2}$$

where

$$u_0(R)=\begin{cases} u(R)+\epsilon, & R<R_m \\ 0, & R>R_m \end{cases} \tag{3}$$

and

$$u_1(R)=\begin{cases} -\epsilon, & R<R_m \\ u(R), & R>R_m \end{cases} \tag{4}$$

where R_m is the value of R for which $u(R)$ is a minimum. For the 6 : 12 potential, $R_m = 2^{1/6}\sigma$.

They then consider $u_1(R)$ as a perturbation on the reference fluid defined by $u_0(R)$. Expanding the Helmholtz free energy, they obtain

$$A=A_0+\tfrac{1}{2}N\rho\int u_1(R)g_0(R)\,d\vec{R}, \tag{5}$$

where A_0 and g_0 are, respectively, the free energy and radial distribution function (RDF) of the reference fluid. The right-hand side of (5) is actually an upper bound on the free energy but this fact is not used in their theory

The difficulty with the CWA theory is that the properties of the reference fluid are not well known. To overcome this, they assume that the free energy of the reference fluid is equal to that of a hard-sphere system,

$$A_0=A_{\mathrm{HS}}, \tag{6}$$

and that the RDF of the reference system is given by

$$g_0(R)=e^{-\beta[u_0(R)-u_{\mathrm{HS}}(R)]}g_{\mathrm{HS}}(R), \tag{7}$$

where $u_{\mathrm{HS}}(R)$ and $g_{\mathrm{HS}}(R)$ are the hard-sphere potential and RDF, respectively. They define the hard-sphere diameter d by

$$\int_d^{R_m} R^2 e^{\beta u_{\mathrm{HS}}(R)} g_{\mathrm{HS}}(R)\,dR = \int_0^{R_m} R^2 e^{\beta[u_{\mathrm{HS}}(R)-u_0(R)]} g_{\mathrm{HS}}(R)\,dR. \tag{8}$$

This approach gives results which are in very good agreement with the results of quasiexperimental computer simulations. However, the CWA theory rests on untested approximations for their reference fluid. To test these approximations we have made Monte Carlo (MC) simulation studies of their reference fluid. The results of (7), calculated using the Percus-Yevick (PY) g_{HS},[2] are compared with our MC results in Fig. 1. The agreement is fair.

The results listed in Table I show that the CWA treatment of the reference fluid overestimates the pressure of the reference fluid p_0. Thus, it is

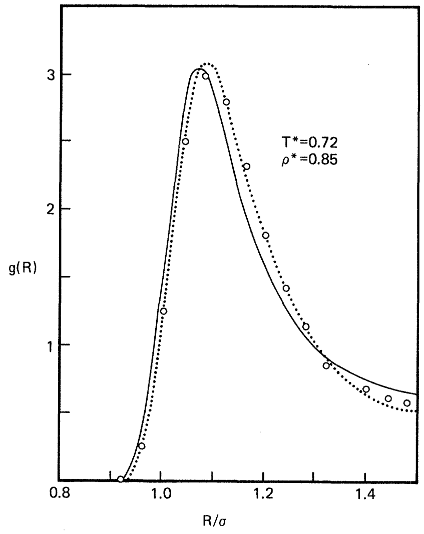

FIG. 1. Radial distribution functions of 6:12 fluid and of reference fluid. The solid and dotted curves give the MC and CWA values for $g_0(R)$ and the points give the simulation results for the 6:12 fluid. The CWA values are calculated from the PY g_{HS}.

TABLE I. Terms in CWA perturbation theory.

	$T^*=1.36$,	$\rho^*=0.5$	$T^*=0.72$,	$\rho^*=0.85$
	MC	CWA[a]	MC	CWA[a]
p_0V/NkT	3.28	3.30	10.87	11.14
A_0/NkT		0.880		4.371
A_1/NkT	−2.624	−2.647	−9.227	−9.395
A_2/NkT	−0.034		−0.043	

[a] Calculated using PY g_{HS}.

reasonable to suppose that CWA also overestimate A_0. However, we cannot verify this, since we have not obtained a complete isotherm. On the other hand, they obtain for the first-order term A_1 a result which is too negative. Thus the good results which they obtain depend in part on a fortuitous cancellation of errors in their treatment of the reference fluid and the first-order term.

If MC values of g_{HS} are used, good results are obtained from (7) and (8).[3] Thus, the errors in the CWA calculation of A_0 and A_1 result, in part, from the use of the PY g_{HS} in (7) and (8).

The CWA perturbation expansion is of considerable interest because, as may be seen from Table I, it is rapidly convergent. Presumably, the reason for this is the slowly varying nature of $u_1(R)$ which reduces the importance of fluctuation terms. On the other hand, as presently formulated the CWA theory has the drawback that the reference fluid is not universal, as is the case with perturbation theories based on hard spheres. Thus, the inclusion of higher-order terms, which are required to give an accurate perturbational treatment of $g(R)$, requires a MC calculation at every temperature and density and for every potential which is considered. It would be no harder to make a MC calculation for the actual fluid under consideration.

One more point deserves mention. As may be seen from Fig. 1, although (7), calculated with the PY g_{HS}, is not a good approximation to $g_0(R)$, it is a good one to the RDF of the 6:12 fluid[4] at high densities (but not at intermediate or low densities). Quite possibly, this is fortuitous. If it is not, then some justification other than that given by CWA is required because they claim this to be a consequence of the approximation $g(R) \simeq g_0(R)$. From Fig. 1 we see that this is only a fair approximation.

---

[*] Work supported in part by a grant from the Department of the Interior, Office of Saline Water.

[1] D. Chandler and J. D. Weeks, Phys. Rev. Letters 25, 149 (1970); J. D. Weeks, D. Chandler, and H. D. Andersen (unpublished report).

[2] M. S. Wertheim, Phys. Rev. Letters 10, 321 (1963); E. J. Thiele, J. Chem. Phys. 38, 1959 (1963).

[3] J. D. Weeks (private communication).

[4] L. Verlet, Phys. Rev. 165, 201 (1968).