

A comparison of perturbative schemes and integral equation theories with computer simulations for fluids at high pressures

J. Talbot and J. L. Lebowitz

Department of Mathematics, Rutgers University, New Brunswick, New Jersey 08903

E. M. Waisman

S-Cubed, P.O. Box 1620, La Jolla, California 92038

D. Levesque and J.-J. Weis

Laboratoire de Physique Théorique et Hautes Energies,^{a)} Université Paris-Sud, F-91405 Orsay, France

(Received 27 February 1986; accepted 7 May 1986)

We test some refined perturbation and integral equations theories for predicting the equilibrium properties of spherical fluids, with nonstandard interactions at high densities and temperatures. The perturbation theories are fast and convenient to use and give good results for the thermodynamic properties, but not for the structure. The integral equations require more computer time, but yield thermodynamics and structure that are in very good agreement with simulations. In fact there appears to be no need for computer simulations of classical systems of particles interacting with spherical potentials in the fluid regime—at least away from transitions.

I. INTRODUCTION

The properties of equilibrium classical fluids, interacting via spherical potentials close to the triple point can be predicted to a high degree of accuracy with perturbation theories developed in the 1960's and early 1970's.¹⁻⁴ The standard integral equation theories while useful, tend to be less accurate.⁵ In this paper we investigate the extension of these techniques to the high density part of the fluid phase diagram.

A central idea in all perturbation theories¹⁻⁴ is to divide the intermolecular potential $\phi(r)$ into a stiff reference potential $\phi_0(r)$ and a soft perturbation $\phi_1(r)$:

$$\phi(r) = \phi_0(r) + \phi_1(r).$$

The difference between the various theories lies essentially in their choice of the reference potential $\phi_0(r)$. However most of them approximate the reference system with a hard sphere (HS) fluid, whose diameter D is chosen "appropriately." At higher pressures these standard perturbation theories have some serious shortcomings. The HS diameter becomes so large that the HS fluid is far into the metastable region and it is impossible to obtain a physically reasonable form for its radial distribution function which is needed in the perturbation scheme.

Recent refinements have extended the useful range of fluid perturbation theories, at least for the "standard spherical potentials." In this paper we test two such refined schemes: Ross' semiempirical variational theory⁶ and an extension of the WCA theory by Kang, Lee, Ree, and Ree (KLRR)⁷ for some nonstandard spherical potentials. We also test two refined integral equation theories: the reference hypernetted chain (RHNC) theory⁸⁻¹⁰ and the recently proposed hybrid integral equation of Zerah and Hansen.¹¹ Our aim is to obtain information about the accuracy and efficiency of the theories, as compared to computer simulation results, for potentials not considered in developing the approximations. These are the Aziz potential frequently

used for helium¹² and various sphericalized (median) potentials for molecular fluids.¹³⁻¹⁵

We find the perturbation schemes to be highly convenient and as accurate as simulations for calculating the thermodynamic properties. However the structural predictions of simple extensions of both Ross and KLRR are poor. The integral equations on the other hand, while rather more demanding than the perturbation schemes in terms of the computer time they require, give excellent results for structural as well as thermodynamic properties. We therefore conclude that, aside from transitions and critical point behavior there is no longer any need for simulations of one component spherical fluids. This holds *ipso facto*, for nonspherical fluids which can be represented well by effective spherical potentials and for mixtures which can be described by one-fluid approximations.

In Sec. II we give a brief outline of the Ross and KLRR theories and point out a convenient simplification in the application of the former.

II. ROSS AND KLRR PROCEDURES

As mentioned in the Introduction, standard perturbation theories suffer from the fact that at high densities the HS reference fluid tends to be unrealistically dense. It is therefore replaced in the Ross theory by the softer inverse-12th power fluid. The convenient scaling properties of the HS fluid are retained by employing it as the reference fluid for the inverse-12 fluid. In order to obtain free energies that agree with simulations it is necessary to add an empirical function of the HS packing fraction to the variational equation. This accurate free energy then serves as input to a variational theory for the general potential $\phi(r)$. Specifically the Ross theory sets

$$A = \min \left[A_0 + 2\pi \rho N \int_D^\infty g_{PY}(r/D, \eta) \times \phi(r) r^2 dr + F(\eta) NkT \right], \quad (1)$$

^{a)} Laboratoire associé au Centre National de la Recherche Scientifique.

where $F(\eta) = -(\eta^4/2 + \eta^2 + \eta/2)$, $\eta = (\pi/6)\rho D^3$ is the HS packing fraction expressed in terms of the HS diameter D , and A_0 is the Carnahan–Starling free energy of the HS reference system. $g_{PY}(r/D, \eta)$ is the HS Percus–Yevick (PY) radial distribution function. When the minimization is carried out with respect to the parameter D we obtain a hard sphere reference fluid with diameter D^* . Thus

$$A_{\text{Ross}} = A_0(\eta^*) + 2\pi\rho N \int_1^\infty g_{PY}(x, \eta^*) \times \phi(xD^*) D^{*3} x^2 dx + F(\eta^*) N k T, \quad (2)$$

where $\eta^* = \pi\rho D^{*3}/6$. The use of the Percus–Yevick (PY) radial distribution function is particularly convenient as there is a simple, easily programmable, algorithm available¹⁶ (slight improvements can be obtained by using tables of the inverse-12 radial distribution function, but it is doubtful that the small improvement is worth the sacrifice of the simplicity). We note that for state independent potentials the excess internal energy per particle, U_{ex} , and the compressibility factor $\beta P/\rho$ ($\beta = 1/kT$ and P is the pressure) are given by the usual quadrature expressions without the need to numerically differentiate the free energy, i.e.,

$$\beta U_{\text{ex}} = 12\beta\eta^* \int_1^\infty g_{PY}(x, \eta^*) x^2 \phi(xD^*) dx, \quad (3)$$

$$\beta P/\rho = 1 - 4\beta\eta^* \int_1^\infty g_{PY}(x, \eta^*) x^3 D^* \phi'(xD^*) dx. \quad (4)$$

This route is convenient computationally since if one wants U and P at just one ρ, T point it is necessary to perform only one minimization rather than the three to five required for an accurate numerical derivative. Equations (3) and (4) are the usual energy and virial expressions. They would be exact if the true $g(r)$ for the fluid rather than $g_{PY}(x, \eta^*)$ were used. It is a remarkable fact that a value of D^* can be found, so that Eqs. (1) and (2) are excellent approximations for dense and very dense simple classical fluids.

The KLRR perturbation theory divides the pair potential $\phi(r)$ into a reference potential $\phi_0(r)$ and a perturbation potential $\phi_1(r)$ specified in a particular form:

$$\phi_0(r) = \begin{cases} \phi(r) - F(r), & r < \lambda \\ 0, & r > \lambda, \end{cases} \quad (5)$$

$$\phi_1(r) = \begin{cases} F(r), & r < \lambda \\ \phi(r), & r > \lambda. \end{cases} \quad (6)$$

Both λ and $F(r)$ are arbitrary. For the choice $\lambda = r^*$ and $F(r) = \phi(r^*)$, where r^* is the intermolecular separation at the minimum of $\phi(r)$, the scheme reduces to the WCA theory.⁴ KLRR define

$$\lambda = \min(a_{\text{fcc}}, r^*), \quad (7)$$

where a_{fcc} is the fcc lattice distance, $2^{1/6}\rho^{-1/3}$ and introduce various schemes for specifying $F(r)$. In what follows we use the $F(r)$ corresponding to scheme 1 of Ref. 7, i.e.,

$$F(r) = \phi(\lambda) - \phi'(\lambda)(\lambda - r). \quad (8)$$

For the calculation of thermodynamic quantities both the Ross and KLRR schemes are easy to program and are fast in execution time. More recently KLRR¹⁷ introduced a still different method of decomposing the potential.

III. THERMODYNAMIC PROPERTIES

A. Aziz potential

A comparison of these theories with simulation has been carried out for the Aziz potential¹²:

$$\begin{aligned} \phi(r) &= \epsilon\phi^*(R), \\ \phi^*(R) &= B \exp(-aR) \\ &\quad - \{C_6/R^6 + C_8/R^8 + C_{10}/R^{10}\} f(R), \\ f(R) &= \begin{cases} \exp[-(D/R - 1)^2], & R < D \\ 1, & R > D. \end{cases} \end{aligned} \quad (9)$$

$R = r/r_m$, $r_m = 2.9673 \text{ \AA}$, $B = 0.5448504 \times 10^6$, $\alpha = 13.353384$, $C_6 = 1.3732412$, $C_8 = 0.4253785$, $C_{10} = 0.178100$, $D = 1.241314$, $\epsilon/k = 10.8 \text{ K}$. All thermodynamic quantities are expressed in terms of the ⁴He Lennard-Jones parameters, $\epsilon_0/k = 10.22 \text{ K}$ and $\sigma_0 = 2.556 \text{ \AA}$.¹²

The molecular dynamics (MD) simulations are performed in the isobaric–isoenthalpic ensemble according to the method proposed by Andersen.¹⁸ In this scheme the system volume is allowed to fluctuate in response to the imbalance between the system pressure and the (constant) external pressure. The conserved quantity is no longer the total internal energy but rather the enthalpy (to order $1/N$). Our simulations are performed for systems of 250 and 432 particles interacting via the Aziz potential. Starting from the last configuration of a previous fluid run, the system is allowed to equilibrate for 2000 time steps of 1.2 fs. This is followed by a production period of 4000 time steps during which the thermodynamic and structural properties are calculated. Long range corrections to the energy, which for a cutoff of $2.5\sigma_0$ are less than 1% of the total energy, are included in our results. A complete description of the simulations is given in Ref. 19.

Table I is a list of the state points for which simulation data is available together with the hard sphere diameters used in the integral and perturbation theories. Table II compares the thermodynamic predictions of these theories with MD and Monte Carlo (MC) simulations. We make two observations about this data. It appears that state 4 is metastable and consequently the agreement between simulation and theory is not as good as the other state points. Also there is a

TABLE I. Simulations performed with the Aziz potential and the values of the HS diameter obtained with the Ross, KLRR, and RHNC theories at these state points. $P^* = P\sigma_0^3/\epsilon_0$, $\rho^* = \rho\sigma_0^3$, $T^* = kT/\epsilon_0$.

State	Simulation	P^*	ρ^*	T^*	d_{HS}/σ		
					Ross	KLRR	RHNC
1	MD 432	1800	2.327	39.13	0.7192	0.7449	
2	MD 432	1800	2.337	37.09	0.7213	0.7461	
3	MD 432	1800	2.343	36.00	0.7224	0.7469	0.7384
4	MD 432	1800	2.370	38.24	0.7173	0.7422	
5	MD 250	1540	2.248	34.17	0.7300	0.7555	
6	MD 250	1300	2.169	28.39	0.7430	0.7680	
7	MC 108	1200	2.098	32.0	0.7410	0.7684	0.7575
8	MC 108	1300	2.149	32.0	0.7383	0.7649	
9	MC 108	1400	2.198	32.0	0.7356	0.7613	
10	MC 108	1500	2.243	32.0	0.7332	0.7582	0.7495

TABLE II. A comparison of the thermodynamic properties of the Ross, KLRR, RHNC, and HMSA theories with simulation for the Aziz potential. The figures in parentheses are the HMSA values.

State	$\beta P / \rho$				$\beta H / N$				$\beta A / N$		
	Ross	KLRR	RHNC	Sim.	Ross	KLRR	RHNC	Sim.	Ross	KLRR	RHNC
1	19.9	20.0		19.8	26.6	26.7		26.6	8.77	8.64	
2	20.9	21.0		20.8	27.9	27.9		27.8	9.14	9.01	
3	21.5	21.6	21.3	21.3	28.6	28.7	28.3	28.3	9.36	9.23	9.17
4	21.1	21.1		19.9	28.2	26.7		26.4	9.25	9.12	
5	20.3	20.3		20.1	26.9	26.9		26.6	8.81	8.69	
6	21.4	21.3		21.1	28.1	28.1		27.8	9.07	8.95	
7	18.0	17.9	17.8 (17.7)	17.9	24.0	23.8	23.7 (23.6)	23.8	7.87	7.75	7.71
8	19.1	18.9		18.9	25.3	25.1		25.0	8.30	8.18	
9	20.1	20.0		20.0	26.7	26.5		26.6	8.72	8.59	
10	21.2	21.2	20.9	20.9	28.0	28.1	27.7	27.8	9.11	8.99	8.93

discrepancy of about 1.5% between the Ross and KLRR excess free energies. However because the difference is roughly constant this is consistent with the smaller differences between the other thermodynamic properties (which are derivatives of the free energy). Otherwise the agreement is equally good for both approximations. The present results and those of KLRR⁷ show that their technique, as well as Ross', works very well for dense fluids of LJ and other potentials. We conclude that both schemes are excellent tools in calculating thermodynamic quantities to within an accuracy of a few percent for dense classical fluids with smooth potentials.

B. Median potentials

We have also investigated how well these approximations work for potentials resulting from the sphericalization of the angular dependent intermolecular interactions in simple molecular fluids, such as those of homonuclear diatomic molecules. Ross' procedure has been applied to the median and split median sphericalized potential for such fluids with satisfactory results,¹⁵ although not as good as those for fluids of molecules interacting via central forces.

Here we compare the two procedures for the N₂ median potential which is well approximated by the exponential-6 form

$$\phi(r) = \epsilon \{ 6 \exp[\alpha(1 - r/r_m)] - \alpha(r_m/r)^6 \} / (\alpha - 6) \quad (10)$$

with $\epsilon/k = 75\text{K}$, $r_m = 4.251 \text{ \AA}$, and $\alpha = 13.474$.¹⁴ Table III compares the Ross and KLRR theories with Monte Carlo simulations.¹⁴ In this case the Ross procedure is superior. It

appears that the KLRR method is sensitive to the value of the derivative of the potential at the breakpoint and for stiff potentials with any numerical uncertainty the Ross procedure may be the best choice. Recall that Eq. (10) is only an approximation to the actual median potential. Attempts to apply the KLRR procedure to the numerical CO₂ median potential employed in Ref. 13 [this potential is even steeper than Eq. (9)] lead to the same problem.

IV. STRUCTURE

In the WCA theory a reasonably accurate description of the fluid structure may be obtained from the high temperature approximation for $g(r)$, i.e.,

$$g_0(r) = \exp[-\beta\phi_0(r)] y_{\text{HS}}(r/D, \eta), \quad (11)$$

where $\phi_0(r)$ is the reference fluid potential. We have tested this approximation for the KLRR theory with $\phi_0(r)$ given by Eq. (5). The value of D used in Eq. (11) is calculated for each (ρ, T) point from

$$\int dr [g_{\text{HS}}(r/D) - g_0(r/D)] = 0. \quad (12)$$

Figure 1 shows that the agreement with simulation is reasonably good, though far from quantitative. There is no simple application of Eq. (11) within the framework of the Ross theory that gives a physically acceptable form of $g_0(r)$.

Another approach to the structure is as follows. For a given value of the packing fraction, we can determine the inverse 12 reference potential $\phi_{12}(r) = \epsilon(\sigma/r)^{12}$. The free energy of this fluid is

TABLE III. A comparison of the Ross and KLRR procedures applied to an analytic representation of the median potential for N₂ with Monte Carlo simulations.

$\rho (g \text{ cm}^{-3})$	$T(\text{K})$	d_{HS}/r_m		U_{ex}/ϵ			$\beta P / \rho$		
		Ross	KLRR	Ross	KLRR	MC	Ross	KLRR	MC
1.9	977	0.6735	0.6914	80.5	81.1	79.9	27.9	27.7	28.2
2.1	2972	0.6161	0.6413	158.0	160.7	160.7	15.6	15.4	15.8

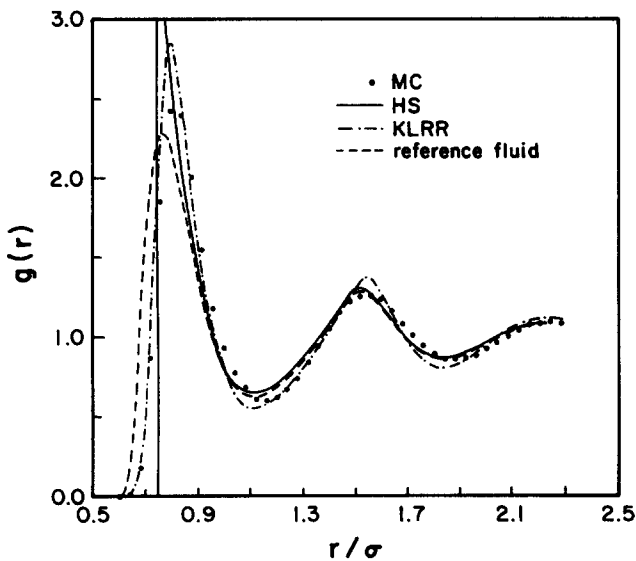


FIG. 1. The high temperature approximation, Eq. (11), compared with Monte Carlo results for the state point $T^* = 32.0, \rho^* = 2.098$. Also shown is the HS radial distribution function with the Ross value of the HS diameter.

$$A(\alpha) = \min \left[A_0(\eta) + F(\eta)NkT + \frac{\alpha^4 2\pi^4}{(6\eta)^3} \int_1^\infty g(x, \eta) x^{-10} dx \right], \quad (13)$$

where $\alpha = \rho\sigma^3(\epsilon/kT)^{1/4}$. By performing the minimization at different values of α one obtains $\eta(\alpha)$. This tabulation gives α for a given value of η . Finally the inverse 12 reference potential parameters are related to α as

$$\epsilon\sigma^{12} = \alpha^4 kT / \rho^4. \quad (14)$$

The structure of the reference fluid is calculated with the high temperature approximation, Eq. (11), with $\phi_0(r)$ re-

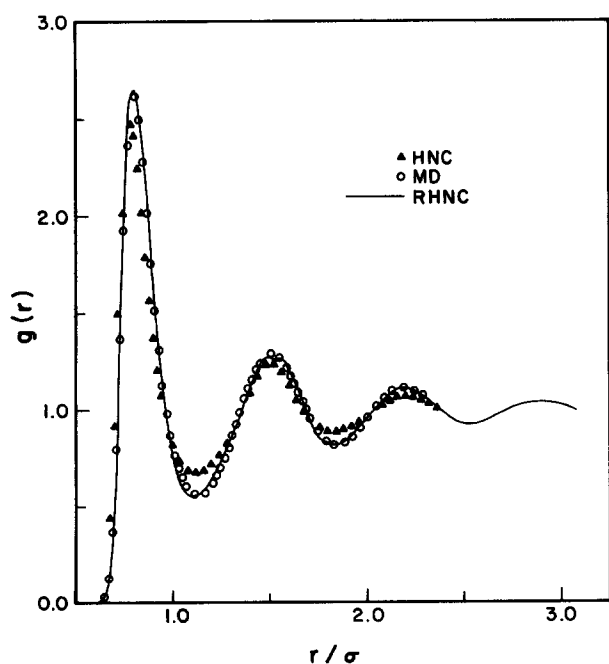


FIG. 2. A comparison of the radial distribution functions for the state point $T^* = 32, \rho^* = 2.243$.

placed with $\phi_{12}(r)$. Figure 1 compares this radial distribution function with the Monte Carlo results for the Aziz potential. Again in this case the agreement is far from quantitative and we conclude that these simple approaches to the fluid structure are of little value.

V. INTEGRAL EQUATIONS

In the integral equation theory of fluids the direct correlation function $c(r)$ plays a central role. It is defined in terms of the total correlation function $h(r) = g(r) - 1$ by the Ornstein-Zernike equation

$$h(r) = c(r) + \rho h(r) * c(r). \quad (15)$$

Here ρ is the number density and $*$ denotes a convolution. A formally exact closure relation is

$$c(r) = h(r) - \log[g(r)] - \beta\phi(r) + B(r), \quad (16)$$

where $B(r)$ is the sum of elementary or "bridge" graphs. If one knew this function then Eqs. (15) and (16) would provide an exact description of a fluid interacting with pair potential $\phi(r)$. Alas $B(r)$ is not known for any ϕ and to proceed we are forced to make approximations. The HNC prescription is to set $B(r) = 0$. This closure is well suited for long range, and, in particular, Coulomb potentials. However in our application simple HNC is not able to give quantitative predictions for the structure or thermodynamics. See Fig. 2. The HNC compressibility factors for the state points 7 and 10 are 19.4 and 22.7, respectively. The corresponding excess internal energies are 4.97 and 6.01.

In recent years attempts have been made to extend the useful range of the standard integral equation theories like PY and HNC. One particularly successful approach based on the ansatz of the "universality of the bridge functions,"⁹ is the reference hypernetted chain (RHNC) theory developed by Lado and others.⁸⁻¹⁰ They noted that if $g(r)$ is

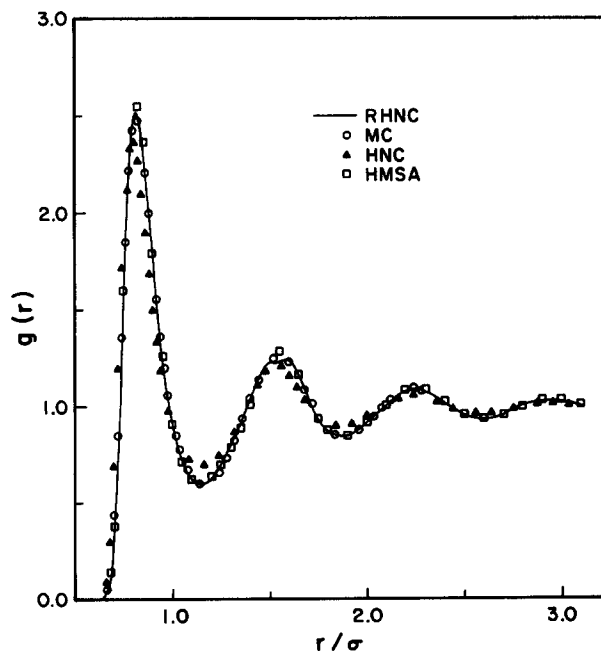


FIG. 3. A comparison of the radial distribution functions for the state point $T^* = 32, \rho^* = 2.098$.

“known” from simulations or some approximate theory for any potential ϕ then from Eqs. (15) and (16) we also know $B(r)$ for that $\phi(r)$. Their technique consists of modeling the bridge function by the (approximate) HS value, and taking a HS diameter that minimizes the free energy. We follow this route, using the Verlet–Weis–Grundke–Henderson parametrization of the HS $g(r)$. All calculations were performed using a fast Fourier transform algorithm with 1024 points and a grid size of $0.01\sigma_0$.

$$g(r) = \exp[-\beta\phi_0(r)] \left[1 + \frac{\exp\{f(r)[h(r) - c(r) - \beta\phi_1(r)]\} - 1}{f(r)} \right], \quad (17)$$

where $\phi_0(r)$ and $\phi_1(r)$ are the repulsive and attractive components of the pair potential and $f(r)$ is the “switching function,” having the properties

$$\lim_{r \rightarrow 0} f(r) = 0 \quad \text{and} \quad \lim_{r \rightarrow \infty} f(r) = 1,$$

but otherwise arbitrary. Following Zerah and Hansen we take $f(r) = 1 - \exp(-\alpha r)$. Consistency between the virial and compressibility routes to the isothermal compressibility is achieved by varying the parameter α . This procedure for solving the HMSA equation is rather time consuming and we have limited our calculations to one point ($T^* = 32.0$, $\rho^* = 2.098$). In this case we find $\alpha\sigma_0 = 0.94$. By using a slightly larger value of α , $\alpha\sigma_0 = 1$, the HMSA can be made to agree with RHNC but with loss of the consistency condition.

Figures 2 and 3 compare the integral equation theories with the molecular dynamics results. We note that there is a small dip in the RHNC function at about twice the HS diameter. The origin of this artifact, as explained in the paper of Lado *et al.*,¹⁰ is due to analytic deficiencies in the HS $B(r)$.

The HMSA integral equation of Zerah and Hansen¹¹ is an attempt to improve upon the proposal of Rogers and Young (RY).²⁰ Both schemes achieve thermodynamic consistency (i.e., between the virial and compressibility equations of state) by interpolating between two simpler integral equations: HNC and PY in the case of RY and HNC and the mean spherical approximation (MSA) in the case of ZH. The MSA is judged to be the more appropriate choice for systems with attractive interactions. The ZH closure is

However, apart from this the agreement for both the RHNC and HMSA theories is excellent.

With a view to developing a simple melting criterion we have calculated the structure factor $S(k)$ from the RHNC and HMSA $g(r)$'s and directly from the MC $g(r)$. The procedure used to extrapolate the MC $g(r)$ consists of solving

$$\begin{aligned} g(r) &= g_{MC}(r), & r < 2.28\sigma_0, \\ c(r) &= \exp[h(r) - c(r)] - h(r) + c(r) - 1, & r > 2.28\sigma_0, \end{aligned} \quad (18)$$

together with the Ornstein–Zernike relation, Eq. (15). The iteration procedure for solving these equations is quite unstable and we have been able to obtain a solution only for the state $T^* = 32$, $P^* = 1200$. Nevertheless, as Fig. 4 shows, the agreement between $S_{MC}(k)$, $S_{RHNC}(k)$, and $S_{HMSA}(k)$ for this point is very good and we assume that $S_{RHNC}(k)$ is a good representation of the true function for a range of pressures and temperatures. For the state $P^* = 1500$, $T^* = 32.0$, which is close to the freezing line, the maximum in $S_{RHNC}(k)$ is 2.88. This appears to agree well with the Han-

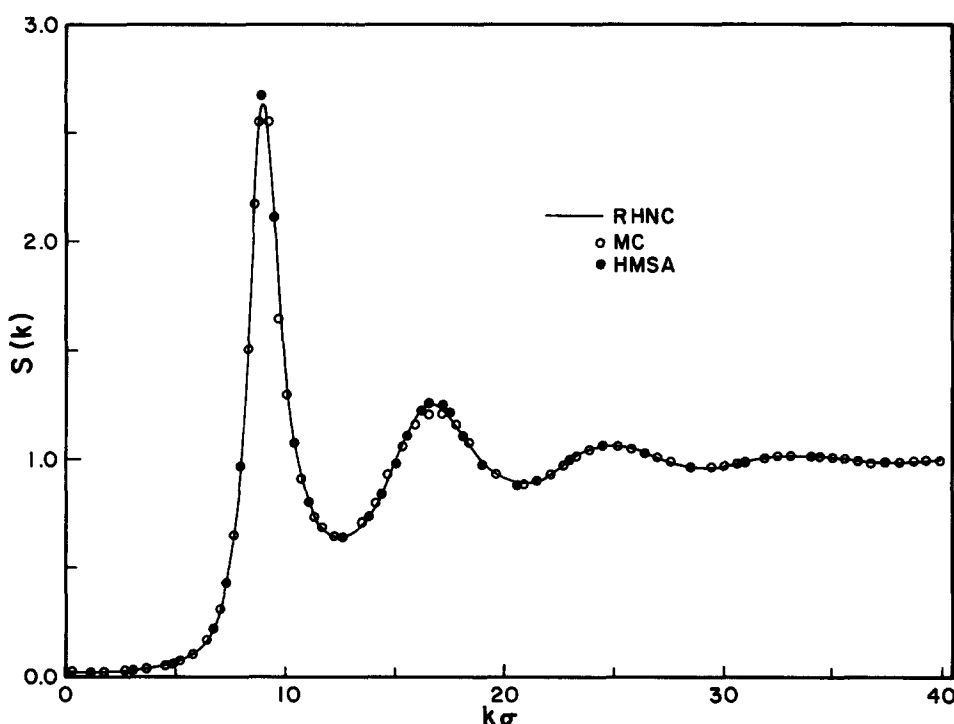


FIG. 4. A comparison of the structure factors for the state point $T^* = 32$, $\rho^* = 2.098$.

sen-Verlet criteria,²¹ i.e., that freezing occurs when the height of the first maximum in the structure factor reaches a value of ~ 2.85 .

VI. CONCLUSIONS

We have applied the Ross and KLRR approximations to the problem of predicting the thermodynamic and structural properties of fluids at high pressures and temperatures. Both schemes give very good results for the thermodynamics but their structural predictions are poor. The more sophisticated RHNC and HMSA theories give excellent results for the structure as well as thermodynamic properties.

Our main conclusion, based on this work and that carried out previously for standard potentials,^{6,7} is that it is no longer necessary to use simulation as a method for calculating the equilibrium properties of classical fluids, away from transitions, interacting via pairwise spherical potentials. If one's interest is restricted to the thermodynamic properties then it is sufficient to use the Ross or KLRR schemes (with a slight preference for the former). The RHNC and HMSA integral equations provide a complete description. Two unresolved problems are to understand why these methods work as well as they do and how to extend them to molecular fluids and mixtures.

ACKNOWLEDGMENTS

Some of the simulations were performed at Los Alamos with a program originally developed by M. Phani and K.

Schmidt. We thank Fred Lado for useful discussions. We are also grateful to Francis Ree for valuable comments. This work was supported by AFOSR 85-0014.

- ¹J. A. Barker and D. Henderson, *J. Chem. Phys.* **47**, 4714 (1967).
- ²D. Henderson and J. A. Barker, *Phys. Rev. A* **1**, 1266 (1970).
- ³J. D. Weeks, D. Chandler, and H. C. Andersen, *J. Chem. Phys.* **54**, 5237 (1971).
- ⁴H. C. Andersen, J. D. Weeks, and D. Chandler, *Phys. Rev. A* **4**, 1597 (1971).
- ⁵J. A. Barker and D. Henderson, *Rev. Mod. Phys.* **48**, 587 (1976).
- ⁶M. Ross, *J. Chem. Phys.* **71**, 1567 (1979).
- ⁷H. S. Kang, C. S. Lee, T. Ree, and F. H. Ree, *J. Chem. Phys.* **82**, 414 (1985).
- ⁸F. Lado, *Phys. Rev. A* **8**, 2548 (1973).
- ⁹Y. Rosenfeld and N. W. Ashcroft, *Phys. Rev. A* **20**, 1208 (1979).
- ¹⁰F. Lado, S. M. Foiles, and N. W. Ashcroft, *Phys. Rev. A* **28**, 2374 (1983).
- ¹¹G. Zerah and J.-P. Hansen, *J. Chem. Phys.* **84**, 2336 (1986).
- ¹²R. Aziz, V. P. S. Nain, J. S. Carley, W. L. Taylor, and G. T. McConville, *J. Chem. Phys.* **70**, 4430 (1979).
- ¹³D. MacGowan, E. M. Waisman, J. L. Lebowitz, and J. K. Percus, *J. Chem. Phys.* **80**, 2719 (1984).
- ¹⁴D. MacGowan, J. D. Johnson, and M. S. Shaw, *J. Chem. Phys.* **82**, 3765 (1985).
- ¹⁵J. D. Johnson and M. S. Shaw, *J. Chem. Phys.* **83**, 1271 (1985).
- ¹⁶J. W. Perram, *Mol. Phys.* **30**, 1505 (1975).
- ¹⁷H. S. Kang, T. Ree, and F. H. Ree, *J. Chem. Phys.* **84**, 4547 (1986).
- ¹⁸H. C. Andersen, *J. Chem. Phys.* **72**, 2384 (1980).
- ¹⁹D. Levesque, J.-J. Weis, and P. Loubeyre (to be published).
- ²⁰F. J. Rogers and D. A. Young, *Phys. Rev. A* **30**, 999 (1984).
- ²¹J. P. Hansen and L. Verlet, *Phys. Rev. Lett.* **184**, 151 (1969).