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Improved integral equation for highly supercooled liquids: Numerical tests for soft-sphere fluids

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A new modified hypernetted-chain integral equation for highly supercooled soft-sphere fluids (MHNCS) is introduced. In the MHNCS approximation, the bridge function is approximated by an appropriate interpolation of the bridge function of the Percus-Yevick hard-sphere model and the leading term of the elementary diagrams, which was first successfully applied to classical one-component plasmas. We have obtained solutions of the MHNCS equation for highly supercooled fluids with sixth- and twelfth-inverse-power potentials. These results are compared with those of molecular-dynamics or Monte Carlo simulations and the solutions of two well-known thermodynamically consistent integral equations, i.e., the Rogers-Young (RY) equation and the reference hypernetted-chain (RHNC) equation. Below the freezing temperature, the solution of the MHNCS equation is found to show a splitting of the second peak of the pair distribution function (PDF) compatible with the computer simulations, while the RY or RHNC equation shows no such a splitting. Using the PDF thus obtained, thermodynamic and structural properties of the highly supercooled soft-sphere fluids are investigated.

I. INTRODUCTION

The pair distribution function (PDF) of a liquid in which particles interact through a spherically symmetric pair potential $u(r)$ is uniquely determined from the solution of the integral equation, i.e., the simultaneous solution of the Ornstein-Zernike relation[1]

$$h(r)=c(r)+\rho\int d\mathbf{r}'h(r')c(|\mathbf{r}-\mathbf{r}'|) \tag{1.1}$$

and the closure relation

$$g(r)=e^{-\beta u(r)+\gamma(r)+B(r)}\ , \tag{1.2}$$

where $g(r)$ is the PDF, $h(r)=g(r)-1$ the pair correlation function, $\gamma(r)-h(r)-c(r)$ the so-called sum of the nodal diagrams, ρ the number density, and β the inverse temperature $1/k_BT$. The resultant PDF allows the calculation of the internal energy U, equation of state $P\beta/\rho$, and the compressibility χ_T as follows:[1]

$$\frac{\beta U}{N}=\tfrac{3}{2}+2\pi\beta\rho\int g(r)u(r)r^2dr\ , \tag{1.3}$$

$$\frac{P\beta}{\rho}=1-\tfrac{2}{3}\pi\beta\rho\int g(r)r^3\frac{du(r)}{dr}dr\ , \tag{1.4}$$

$$\rho k_BT\chi_T=1+4\pi\rho\int[g(r)-1]r^2dr\ , \tag{1.5}$$

where N is the total number of particles. In calculations of the PDF using the integral equation, one needs the bridge function $B(r)$ in Eq. (1.2). It is well known that $B(r)$ can be expanded in terms of highly connected h-bond elementary diagrams as[1]

$$B(r)=\sum_{n=4}^{\infty}\{\varepsilon_n(r)\}\ , \tag{1.6}$$

where $\{\varepsilon_n(r)\}$ represents a set of n-point elementary diagrams. However, the convergence of Eq. (1.6) is generally too slow to be applicable to practical calculations for a highly dense liquid state. For such a difficulty in the calculation of $B(r)$, various approximations for the integral equation have been proposed. For example, well-known classical hypernetted-chain (HNC) and Percus-Yevick (PY) approximations are equivalent to substituting in Eq. (1.6) $B(r)=0$ and $-\gamma(r)+\ln[1+\gamma(r)]$, respectively.[1]

The reliability of such approximate integral equations can be tested by comparing their solutions with the "exact" results obtained by computer simulations for a wide range of density. It has been shown that both the HNC and PY approximations break down when the density or temperature approach the freezing point.[1] Since the properties of approximations involved in the integral equation are directly related to the approximation for $B(r)$, a more reliable approximation could be obtained by modifying $B(r)$ in some manner.

Recently proposed thermodynamically consistent approximations with some parametrized bridge function have been found to yield a better approximation up to the freezing point over the HNC or PY approximation.[2] Among these approximations, the Rogers-Young[3] (RY) and reference HNC (RHNC) (Ref. 4) equations have most extensively been studied for various potentials, including one-component plasmas (OCP), hard-sphere, soft-sphere, and 12-6 Lennard-Jones fluids. In our previous paper, it has been shown that even in an equilibrium supercooled liquid regime, the thermodynamic properties predicted by the RY integral equation agree well with the computer simulation data for soft-sphere fluids.[5] However, the PDF's obtained by these integral equations do not reproduce a correct behavior at both intermediate- and long-range distances. It has been shown that the PDF's calculated by computer simulations yield a clear splitting of the second peak near and below the glass transition temperature and a broader second peak in an equilibrium supercooled regime.[6] The PDF's calculated from the RY and RHNC equations for soft-sphere fluids, however, yield no broadening of the second peak in an equilibrium supercooled state, nor splitting below the glass transition temperature, in disagreement with the computer simulations.

On the other hand, for the OCP fluids, Iyetomi and Ichimaru[7] have shown that an approximated $B(r)$ based on the leading term of Eq. (1.6), i.e.,

$$\varepsilon_4(r)=\tfrac{1}{2}\rho^2\int d\mathbf{r}'d\mathbf{r}''h(r')h(r'')h(|\mathbf{r}'-\mathbf{r}''|)\times h(|\mathbf{r}-\mathbf{r}'|)h(|\mathbf{r}-\mathbf{r}''|)\ , \tag{1.7}$$

together with a rescaling assumption,[8] could be in a good agreement with computer simulations, leading to a splitting of the second peak of the PDF in a highly supercooled state. Similar results have successfully been obtained for two-component plasmas by Ballone, Pastore, and Tosi.[9]

Noting the difference of the potentials between OCP and soft-sphere fluids, it is our intention to study a better approximation for the integral equation in highly supercooled soft-sphere fluids. We first present the results of the RY and RHNC approximations for one-component soft-sphere supercooled liquids, interacting through sixth- or twelfth-inverse-power potentials. With these results we proceed to propose a better approximation for the integral equation whose solution will be found to agree well with that of computer simulations in both stable and supercooled fluids.

II. THE MODEL

We consider the soft-sphere model in which constituent particles interact through a purely repulsive inverse power potential,

$$u(r)=\varepsilon\left[\frac{\sigma}{r}\right]^n\ , \tag{2.1}$$

where n (≥ 3) is the softness parameter of the potential. The limit of $n=\infty$ corresponds to a hard-sphere potential with core diameter σ. The advantage of inverse power potentials is due to their scaling property. According to this property, all reduced equilibrium properties in excess of their ideal-gas counterparts depend only on one coupling parameter, not on the temperature and the number density of the system separately. We take the following Γ as this coupling parameter:

$$\Gamma=\rho\sigma^3(\varepsilon\beta)^{3/n}\ . \tag{2.2}$$

The freezing points of the inverse power potentials for $n=4$, 6, 9, and 12 were calculated by Hoover *et al.* with Monte Carlo (MC) simulations, and found to be $\Gamma=5.54$, 2.18, 1.33, and 1.15 for $n=4$, 6, 9, and 12, respectively.[10] This model has been found to work well for various real liquids, in which short-range repulsive forces are dominant, by choosing a suitable softness parameter n; for example, $n=15$ reproduces the properties of liquidified inert gases and $n=5$ those of liquid alkali metals.[11] In the present work, the softness parameter n is taken to be $n=6$ and 12.

The pure repulsive nature of the soft-sphere potential leads to an unphysically high pressure of the system. However, thermodynamic properties in more realistic conditions can be obtained by adding the Kac potential, i.e., by the generalized van der Waals model.[5,11] The Kac potential, however, exerts no influence on the properties of the structures. Therefore we take only pure soft-sphere potentials in the present work, where we focus our attention to the structural properties of liquids.

III. THERMODYNAMICALLY CONSISTENT APPROXIMATIONS

Adjustable parameters contained in thermodynamically consistent approximations are usually determined from a consistency between the virial and compressibility equations of state or a criterion with which the free energy of the system is minimized.[2] For example, the RY and RHNC approximations use, respectively, the following bridge functions:[3,4]

$$B(r)=-\gamma(r)+\ln\left[1+\frac{\exp[f(r)\gamma(r)]-1}{f(r)}\right]\leq 0\ ,$$

$$B(r)=B_0(r,d)\ ,$$

where $f(r)=1-\exp(-\alpha r)$ is a mixing function with a mixing parameter α, and $B_0(r,d)$ the bridge function of a reference hard-sphere fluid with an adjustable core diameter d. The parameter α in the RY approximation is adjusted by requiring a self consistency between the equaitons of state obtained separately from Eqs. (1.4) and (1.5), while the parameter d in the RHNC is determined so that the free energy of the reference hard-sphere fluid becomes self consistent:[4]

$$0=\rho\int d\mathbf{r}[g(r)-g_0(r)]\delta B_0(r,d)\ ,$$

where $g_0(r)$ is the PDF of the reference system. Usually, for $g_0(r)$ and $B_0(r)$ the Verlet and Weis (VW) parametrized functions[12] are used, which yield the equation of state for the hard-sphere model consistent to the Carnahan-Starlig formula.[13]

We have solved both the RY and RHNC integral equations for stable and supercooled soft-sphere liquids. These results are found to be in excellent agreement with those of computer simulations in a stable liquid, as shown in Tables I and II. It is found that the adjusted parameter d in the RHNC equation fits a simple relation to the soft-sphere coupling constant Γ, as plotted in Fig. 1, that is,

$$\eta=\eta_f+A(\Gamma-\Gamma_f)\ , \tag{3.1}$$

TABLE I. Thermodynamic properties calculated from various integral equations and the MC simulation for the sixth-inverse-power potential. The first line of each Γ shows the equation of state $P\beta/\rho$ and the second line the reduced inverse compressibility χ_T^{*-1}. The values in parentheses are the hard-sphere parameter d/l for the MHNCS integral equation. The MC data were taken from a numerical interpolation of the simulation data in Ref. 10.

Γ	MC	MHNCS	(d/l)	RY	RHNC
1.4	18.368	18.772	(0.904 02)	18.639	18.600
		42.698		49.523	48.520
1.8	24.144	28.680	(0.937 25)	28.577	28.422
		66.265		78.152	76.812
2.6		55.198	(0.978 10)	55.147	54.559
		128.56		155.91	154.58
3.0		71.778	(0.993 61)	71.789	70.684
		167.80		204.86	210.10
3.4		90.574	(1.0068)	90.668	
		212.37		260.51	
3.6		101.01	(1.0068)	100.95	
		233.03		290.86	

where $\eta=(\pi/6)\rho d^3$ is the packing fraction of the reference system, A is a constant depending on softness parameter n, η_f indicates the freezing point of the hard-sphere system, and Γ_f that of the soft-sphere system. We obtained $A=0.148$ and 0.291 for $n=6$ and 12, respectively. Equation (3.1) means that the freezing point of the soft-sphere system coincides with that of the reference hard-sphere system, and thus the VW hard-sphere reference system fulfills its mission as a "reference" system.

In a highly supercooled regime, however, the RHNC approximation with the VW bridge function has been found to yield an unphysical solution leading to a too small first peak of the PDF and too large inverse compressibility. This shortcoming is partly caused by the Carnahan-Starling formula, which has no theoretical evidence in highly supercooled hard-sphere fluids. Both the RHNC and RY approximations are found to be insufficient to predict a correct $g(r)$ in the range of supercooled soft-sphere fluids, as shown in Fig.2 and Tables I and II. The PDF's obtained yield no broadening of the second peak in the range of moderately supercooled fluids, nor splitting of the second peak below the glass transition temperature, in disagreement with the computer simulations.

IV. THE MHNCS APPROXIMATION

As we have seen above, neither the RY nor RHNC approximations works well in the range of supercooled liquids. There are considerable discrepancies of the PDF between, in both intermediate and long distances, these approximations and the computer simulations. For this reason, below, we will attempt to propose a better bridge function.

The property of the short-range-distance part of $B(r)$ was extensively studied by Rosenfeld and Ashcroft for various pair potentials.[2] According to their work, it has been shown that the form of $B(r)$ at short interparticle distances has a universality whose form can be expressed in terms of the PY bridge function of the hard-sphere sys-

TABLE II. Thermodynamic properties calculated from various integral equaitons and the MD simulation (Ref. 25) for the twelfth-inverse-power potential. The values in parentheses are the hard-sphere parameter d/l for the MHNCS integral equation. The first line of each Γ shows the equation of state $P\beta/\rho$ and the second line the reduced inverse compressibility χ_T^{*-1}.

Γ	MD	MHNCS	(d/l)	RY	RHNC
0.8	8.414	8.343	(0.907 36)	8.315	8.410
	22.5±0.5	22.034		24.940	24.897
1.0	13.770	13.791	(0.948 76)	13.604	13.768
		38.441		45.936	45.670
1.2	21.940	22.179	(0.981 63)	21.687	21.863
		64.014		80.257	79.305
1.4	34.105	34.561	(1.0087)	33.674	33.146
		102.16		133.70	139.18
1.5	42.499	42.598	(1.0207)	41.538	
		127.05		169.57	
1.6	52.753	52.099	(1.0314)	50.887	
		156.01		212.67	

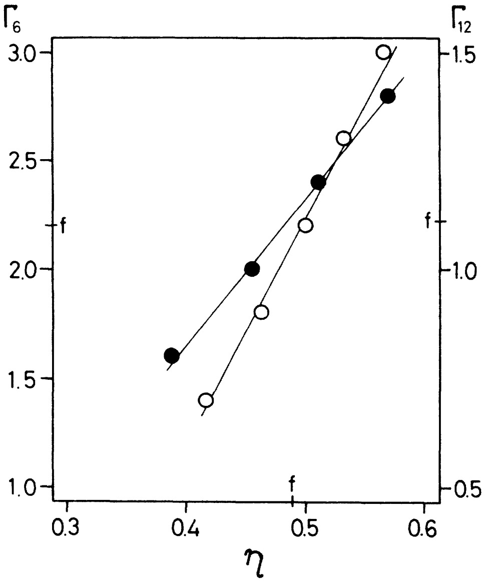

FIG. 1. Hard-sphere packing fraction η calculated with the RHNC approximation for the soft-sphere system ($n=6$ and 12). Points marked by ○ and ● are those of the sixth- and twelfth-inverse-power potentials, respectively. Γ_n indicates the coupling constant of the softness parameter n. f indicates the freezing point for the respective system.

tem $B_H^{\mathrm{PY}}(r,d)$, irrespective of the choice of potentials for repulsive cores. On the other hand, there have been two different approaches proposed to approximate the form of the bridge function at intermediate and long distances, namely, the mean spherical approximation[1] (MSA) and improved HNC (IHNC) approximations for OCP fluids.[7] The MSA assumes $c(r)=-\beta u(r)$ for $r>\sigma$, where σ is the size of the potential core, and the bridge function of the form

$$B^{\mathrm{MSA}}(r)=1-g(r)+\ln[g(r)]\le 0 \quad (r>\sigma) .$$

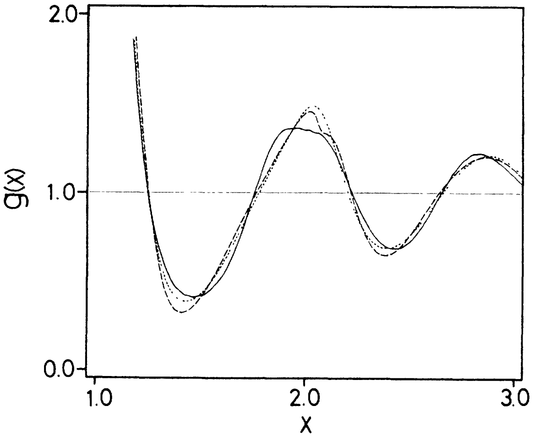

FIG. 2. Pair distribution functions of computer simulation (solid curve), the RY equation (dotted curve), and the RHNC equation (dashed curve) for the twelfth-inverse-power potential at $\Gamma=1.4$.

The form of $B^{\mathrm{MSA}}(r)$ is similar to that of the PY or RY approximation, and consequently the MSA will not be useful for a highly supercooled liquid regime, as we have seen in Sec. III. On the other hand, the IHNC approximation uses $B(r)$ based on the leading term of Eq. (1.6), $\varepsilon_4(r)$, together with a rescaling assumption, and could be in a good agreement with computer simulations, leading to a splitting of the second peak of the PDF in a highly supercooled OCP fluid state.[7] The form of $\varepsilon_4(r)$ is significantly different from that of the PY or RY approximation; the former can have both positive and negative values (oscillation around zero value), which will turn out to be responsible to the splitting of the second peak of PDF's.

From the above considerations, a better empirical bridge function may be assumed as the linear combination of the universal short-range-distance part $B_H^{\mathrm{PY}}(r)$ and the long-range-distance part $\varepsilon_4(r)$.[9] Therefore we assume that

$$B(r,d)=[1-f(r,d)]B_H^{\mathrm{PY}}(r,d)+f(r,d)\varepsilon_4(r) , \tag{4.1}$$

where d is an adjustable hard-sphere diameter and $0\le f(r,d)\le 1$ a continuous mixing function. The mixing function is conveniently taken to be of the form[14–16]

$$f(r,d)=\frac{1}{2}\left[1+\tanh\left[\frac{r-d}{W}\right]\right] , \tag{4.2}$$

where W is a dumping parameter which may be determined from the magnitude of the thermal vibration of particles (root-mean-square amplitude) or the width of the first peak of the PDF. We call our approximation MHNCS.

The adjustable parameter d in Eq. (4.1) is determined by using the property of the screening potential $H(r)=-\gamma(r)-B(r)$ at $r=0$: $H(0)$ is related to a thermodynamic function of the excess free energy of the system,[2]

$$H(0)=\beta[F^{\mathrm{ex}}(0,N)-F^{\mathrm{ex}}(1,N-2)] , \tag{4.3}$$

where $F^{\mathrm{ex}}(n,m)$ is the excess free energy of the system with n coupled particles and m single particles. Assuming that the entropy difference between two terms in Eq. (4.3) is negligible, $H(0)$ can be evaluated by the respective internal energy $U(0,N)$ and $U(1,N-2)$. In soft-sphere supercooled fluid states the excess internal energy per particle u^{ex} can be written simply as

$$\beta u^{\mathrm{ex}}=\tfrac{3}{2}+b\Gamma^{n/3} , \tag{4.4}$$

where b is a "Madelung" constant[17] which has been found to be $b=3.689$ and 1.655 for $n=6$ and 12, respectively, by using the RY approximation.[5] For the present purpose of calculations of Eq. (4.3), we assume $g(r)\simeq\xi\delta(r-\alpha)$ for the thermodynamic states to which Eq. (4.4) is applicable. We obtain

$$\begin{aligned}\beta u^{\mathrm{ex}}&=\tfrac{3}{2}+2\pi\beta\rho\int u(r)\xi\delta(r-\alpha)r^2dr\\&=\tfrac{3}{2}+2\pi\xi\alpha^{-(n-2)}\Gamma^{n/3} ,\end{aligned} \tag{4.4$'$}$$

and $b=2\pi\xi\alpha^{-(n-2)}$, where ξ is a scaling constant and α

is the distance between a specific particle and nearest-neighbor particles surrounding it (first shell). On the other hand, $u^{\text{ex,coupled}}$ containing two particles (a coupled particle) within the shell can easily be estimated from Eq. (4.4′) by replacing α with $2^{1/3}\alpha$ for the requirement of constant density inside the shell, then we obtain

$$\beta u^{\text{ex,coupled}}=3+(2)2^{-(n-2)/3}b\Gamma^{n/3} . \tag{4.5}$$

Using Eqs. (4.4) and (4.5), Eq. (4.3) is written as

$$H(0)=2b\Gamma^{n/3}(1-2^{-(n-2)/3}) . \tag{4.3′}$$

A set of Eqs. (1.1), (1.2), (4.1), and (4.3′) constructs the MHNCS approximation, which will be solved self consistently. We should note that the MHNCS approximation differs from the usual thermodynamically consistent methods, for we do not use the thermodynamic self-consistency condition.

V. RESULTS

A. Numerical procedures

The method used here to solve the MHNCS integral equation is essentially the same as an iterative procedure proposed by Ng[18] but with some modifications. A number of iterations were made so that the following self-consistent measure Δ is minimized:

$$\Delta=\left(\int |c^{\text{in}}(r)-c^{\text{out}}(r)|^2r^2dr\right)^{1/2} . \tag{5.1}$$

The superscripts in and out denote the input and output functions, respectively. We used $e^{-\beta u(r)}-1$ as an initial input function of $c^{\text{in}}(r)$. It took about 50 iterations for Δ to be less than 5×10^{-10}, which is considered to be small enough, for the present purpose, to ensure the validity of the solutions. $B_H^{\text{PY}}(r)$ in Eq. (4.1) has been calculated with the analytical solution of the PY approximation for the hard-sphere model given by Wertheim and Thiele[19] and Smith and Henderson.[20]

To solve the integral equation, we used dimensionless length $x=r/l$, where $l=\rho^{-1/3}$. The number of grid points and step size used in numerical integrations were chosen to be 2048 points and $\Delta x=0.01$, respectively, and the fast-Fourier-transform routine was used in each iteration step. Iterations have been carried out on a FACOM M-780 scalar processor.

The numerical integration of Eq. (4.10) has been carried out on a FACOM VP-100 vector processor, using the Legendre expansion of $h(r)$ obtained from the HNC equation, which was discussed in detail in Ref. 7 originally used for the calculation of the virial coefficients by Barker and Monaghan.[21] In our calculation we have taken the first 11 terms of this expansion, which confirms an expansion error to be smaller than about 1%. A dumping parameter W in Eq. (3.12) is taken to be $0.2l$ for all present calculations, because the magnitude of the root-mean-square amplitude of particles is not significantly changed over a wide range of Γ's in supercooled liquids.[5,6]

B. Solutions

Calculations of the MHNCS integral equation have been made for six different Γ's for both $n=6$ and 12. For the study of thermodynamical and structural properties of these systems, we examined the equation of state $P\beta/\rho$, the reduced inverse compressibility $\chi_T^{*-1}=\beta(\rho\chi_T)^{-1}$, the so-called Wendt-Abraham ratio R (the ratio of the first minimum to the first maximum of the PDF),[22] and the coordination number N_c as defined by

$$N_c=4\pi\rho\int_0^{r_m}g(r)r^2dr , \tag{5.2}$$

where r_m is the position of the first minimum of the PDF. Our results are summarized in Tables I and II and Figs. 3 and 4, together with comparison with computer simulations,[10,25] the RY approximation,[5,6] and the RHNC approximation. From Tables I and II it is clearly seen that the equation of state obtained from the MNCS equation agrees very well with the computer simulation results up to a highly supercooled regime. χ_T^{*-1} obtained from the MHNCS equation is systematically smaller than that of the RY or RHNC equation for all Γ's in both cases of n,

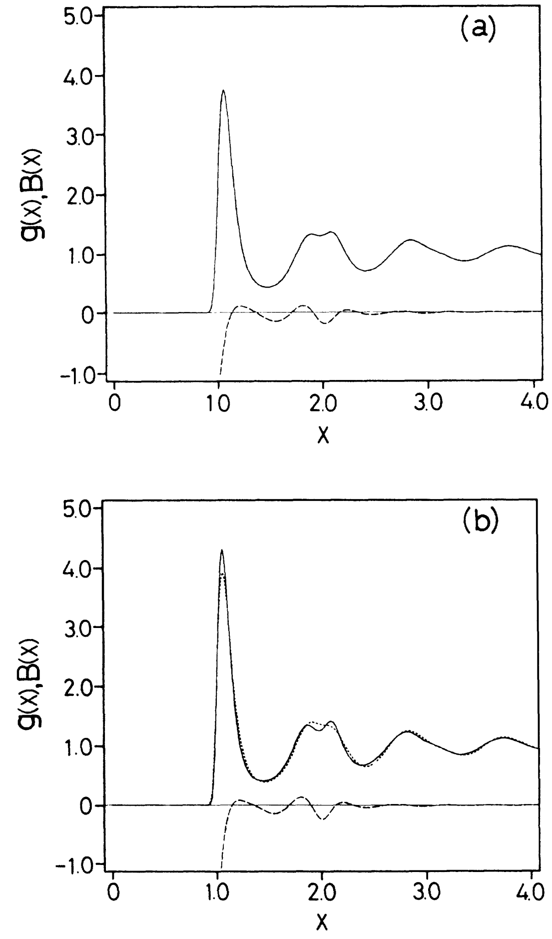

FIG. 3. Pair distribution (solid curve) and bridge (dashed curve) functions of the MHNCS integral equation in highly supercooled regime. (a) $n=6$ and $\Gamma=3.6$; (b) $n=12$ and $\Gamma=1.5$. The MD result of the PDF is shown by the dotted curve (Ref. 25).

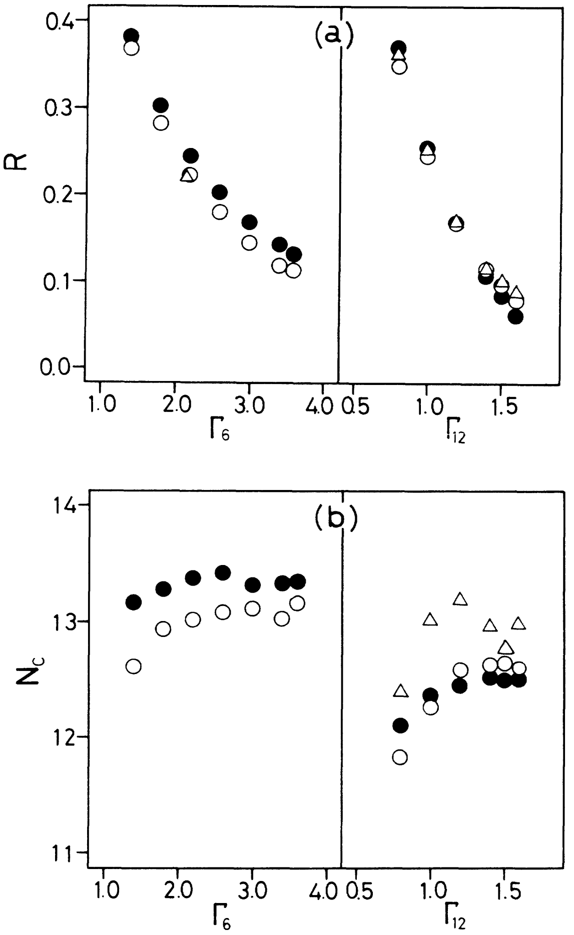

FIG. 4. Γ dependence of (a) the Wendt-Abraham ratio R and (b) coordination number N_c. Points marked by △, ●, and ○ are those obtained from computer simulation (Refs. 25 and 27), the RY equation (Ref. 5), and the MHNCS equation, respectively. Γ_n indicates the coupling constant for the softness parameter n.

which we have studied here. For further tests of the MHNCS approximation, it would be most preferable to compare χ_T^{*-1} with that of computer simulations, but it is difficult to determine χ_T, using Eq. (1.5), directly from the computer simulation data of the PDF because of the truncation of the data at a distance corresponding to the length of the basic cell of the simulation. Because of such a restriction, we calculated a reliable χ_T^{*-1} value with the MD simulation data only for $n=12$ at $\Gamma=0.8$.

The PDF's of the MHNCS equation exhibit a clear splitting of their second peak for a highly supercooled regime, that is, when $\Gamma \gtrsim 1.4$ for $n=12$ and $\Gamma \gtrsim 3.4$ for $n=6$ (Fig. 3). Splitting of the MHNCS PDF's begins to appear at somewhat smaller Γ's compared with the computer simulations, which may be reasonably understood by taking into consideration slow relaxation phenomena near the glass transition.[23] Computer generated samples at the highly supercooled regime are not fully relaxed, due to slow relaxations.[24–26] Therefore, the feature of the PDF may possibly be smeared by biased dynamical fluctuations caused by the nonequilibrium nature of the system. We also note the fact that the PDF calculated from computer simulations with elimination of the thermal vibrations of particles shows a clear splitting of the second peak as well as a sharper first peak even in moderately supercooled liquids. The results of the MHNCS approximation shows a smaller value of R than that of computer simulations for large Γ's, as shown in Fig. 4, and the PDF yields a splitting of the second peak even in an equilibrium supercooled regime. The dependence of PDF's on the softness parameter is significant: Both the first peak and the splitting of the second peak for $n=12$ are found to be sharper than those for $n=6$.

The splitting of the second peak of PDF is essentially dominated by the form of the second term of Eq. (4.1). We note that $\varepsilon_4(r)$ is nearly equal to zero except for the core region in stable liquids, while below the freezing temperature it begins to oscillate around zero value in the intermediate distances, where the second peak of PDF appears (Fig. 3). On the other hand, the bridge function for the RY or PY equation always has a nonpositive value, thus resulting in no splitting of the second peak.

The coordination number calculated from Eq. (5.2), i.e., the population number of the first shell (average number of nearest-neighbor particles surrounding a particle), has a value between 12 and 14 below the freezing temperature, as shown in Fig. 4, which is compatible to that of computer glasses. Therefore, the packing order is quite similar to all thermodynamic states below the freezing temperature.

VI. DISCUSSION

We have proposed a new MHNCS integral equation and obtained its solutions up to the highly supercooled liquid regime of soft spheres. The MHNCS solution results in the same equation of state as that of the computer simulations in both stable and supercooled liquids. The PDF obtained shows a clear splitting of the second peak at a highly supercooled regime, in excellent agreement with the results of the molecular-dynamics simulations. Glasses are nonequilibrium states in nature, in which the structural relaxation time is many orders of magnitude larger than that of an equilibrium liquid. Therefore, structures of computer glasses simulated over too short a time interval compared with the structural relaxation time may depend on the quenching rates and their routes as well as initial configurations. On the other hand, the PDF calculated from the integral equation based on the statistical theory of fluids is that for a fully relaxed "fluid" state, which may be produced by quenching a liquid at an infinitely slow cooling rate. Intermediate- and long-range-distance parts of $B(r)$ can be well approximated by the leading elementary diagram $\varepsilon_4(r)$, which is responsible for the characteristic feature of the PDF at intermediate distances for highly supercooled liquids. Since $\varepsilon_4(r)$ has almost no contribution for stable liquids, the MHNCS integral equation is equivalent to the RHNC and RY approximations above the freezing temperature. On the other hand, for highly supercooled liquids, $\varepsilon_4(r)$, exhibiting a significant oscillatory behavior around zero value, reproduces not only the splitting of the second peak but also a correct gross feature of the PDF which is in excellent agreement with the results of the computer simulations. Thus we conclude that the MHNCS works very well over a wide range of the soft-sphere fluid states, including supercooled liquids and glasses.

Another conclusion of the present paper is the softness (n) dependence of the structural properties in the supercooled regime. The splitting of the second peak of the PDF has a tendency to be smeared for a softer potential. This is reasonably understood by considering a weak-distance-dependent character of a softer potential, which should tend to allow an increase of a number of possible configurations of particles.

Finally, we mention that the MHNCS integral equation can be easily extended to binary mixtures. Calculations for the binary soft-sphere mixtures are being undertaken.

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[1] J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids,* 2nd ed. (Academic, London, 1987).

[2] Y. Rosenfeld and N. W. Ashcroft, Phys. Rev. A **20**, 1208 (1979).

[3] F. J. Rogers and D. A. Young, Phys. Rev. A. **30**, 999 (1984).

[4] F. Lado, Phys. Lett. **89**, 196 (1982); F. Lado, S. M. Foiles, and N. W. Ashcroft, Phys. Rev. A **28**, 2374 (1983).

[5] S. Kambayashi and Y. Hiwatari, Phys. Rev. A **37**, 852 (1988).

[6] A. Rahman, M. J. Mandell, and J. P. McTague, J. Chem. Phys. **64**, 1564 (1976).

[7] H. Iyetomi and S. Ichimaru, Phys. Rev. A **27**, 3241 (1983).

[8] Q. N. Usmani, B. Friedman, and V. R. Pandharipande, Phys. Rev. B **25**, 4502 (1982).

[9] P. Ballone, G. Pastore, and M. P. Tosi, J. Chem. Phys. **81**, 3174 (1984).

[10] W. G. Hoover *et al.*, J. Chem. Phys. **52**, 4931 (1970); W. G. Hoover, S. G. Gray, and K. W. Johnson, *ibid.* **55**, 1128 (1971).

[11] H. Matsuda and Y. Hiwatari, Prog. Theor. Phys. **47**, 741 (1972); in *Cooperative Phenomena,* edited by H. Haken and M. Wagner (Springer-Verlag, Berlin, 1973).

[12] L. Verlet and J. J. Weis, Phys. Rev. **45**, 939 (1972).

[13] N. F. Carnahan and K. E. Starling, J. Chem. Phys. **51**, 635 (1969).

[14] S. M. Foiles, N. W. Ashcroft, and L. Reatto, J. Chem. Phys. **80**, 4441 (1984).

[15] P. D. Poll and N. W. Ashcroft, Phys. Rev. A **32**, 1722 (1985).

[16] P. D. Poll and N. W. Ashcroft, Phys. Rev. A **35**, 866 (1987).

[17] J. O. Hirshfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[18] K. C. Ng, J. Chem. Phys. **61**, 2680 (1974).

[19] M. S. Wertheim, Phys. Rev. Lett. **10**, 321 (1963); E. Thiele, J. Chem. Phys. **39**, 474 (1963).

[20] W. R. Smith and D. Henderson, Mol. Phys. **19**, 411 (1970).

[21] J. A. Barker and J. J. Monaghan, J. Chem. Phys. **36**, 2564 (1962); see also A. D. J. Haymet, S. A. Rice, and W. G. Madden, *ibid.* **74**, 3033 (1981).

[22] H. R. Wendt and F. F. Abraham, Phys. Rev. Lett. **41**, 1244 (1978).

[23] M. Kimura and F. Yonezawa, in *Topological Disorder in Condensed Matter,* edited by F. Yonezawa and T. Ninomiya (Springer-Verlag, Berlin, 1983).

[24] J. J. Ullo and S. Yip, Phys. Rev. Lett. **54**, 1509 (1985).

[25] S. Kambayashi and Y. Hiwatari, J. Phys. Soc. Jpn. **56**, 2788 (1987).

[26] H. Miyagawa, Y. Hiwatari, B. Bernu, and J. P. Hansen, J. Chem. Phys. **88**, 3879 (1988).

[27] J. P. Hansen and D. Schiff, Mol. Phys. **25**, 1281 (1973).