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Theory of supercooled liquids and glasses for binary soft-sphere mixtures via a modified hypernetted-chain integral equation

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We discuss the equilibrium properties of highly supercooled binary soft-sphere fluids by a modified hypernetted-chain (MHNCS) equation proposed recently by us. The MHNCS approximation is made by a proper interpolation of the bridge functions of the Percus-Yevick hard-sphere model and the leading term of the elementary diagrams that were first successfully applied to classical one-component plasmas. The MHNCS approximation has been found to work well for one-component soft-sphere fluids above and below the freezing point. For a more crucial test, the MHNCS equation is extensively studied for the binary soft-sphere fluids. We have obtained numerical solutions of the MHNCS equation for a binary mixture of the 12th-inverse power potential with different core diameters. These results are compared with those of computer simulations and the Rogers-Young approximation. Below the freezing temperature, the solution of the MHNCS equation reproduces a splitting of the second peak of the pair distribution function (PDF) for various core size ratios, compatible with the computer simulations. Using the PDF thus obtained, thermodynamic and structural properties of the highly supercooled binary soft-sphere fluids are investigated.

I. INTRODUCTION

Integral equations of fluid theory have played an important role in the investigation of structural and thermodynamic properties of liquids.[1] For a multicomponent fluid in which particles interact through spherically symmetric pair potentials $u_{ij}(r)$, where the subscripts denote the species indices, the integral equation results from the combination of two relations. The first one is the Ornstein-Zernike relation

$$h_{ij}(r)=c_{ij}(r)+\rho\sum_{k=1}^{M}x_k\int d\mathbf{r}'h_{ik}(r')c_{kj}(|\mathbf{r}-\mathbf{r}'|)\ , \tag{1.1}$$

where $h(r)$ is the pair correlation function, $c(r)$ the direct correlation function, ρ the number density, M the number of components, and x_i the number concentration of the ith species. The second one is the closure relation

$$g_{ij}(r)=e^{-\beta u_{ij}(r)+\gamma_{ij}(r)+B_{ij}(r)}\ , \tag{1.2}$$

where $g(r)=h(r)+1$ is the pair distribution function (PDF), $\gamma(r)=h(r)-c(r)$ the so-called sum of the nodal diagrams, $B(r)$ the bridge function, and β the inverse temperature $1/k_BT$. The PDF allows one to calculate the internal energy U, equation of state $P\beta/\rho$, and the compressibility χ_T as follows:[1]

$$\beta U/N=\tfrac{3}{2}+2\pi\beta\rho\sum_{i}^{M}\sum_{j}^{M}x_ix_j\int g_{ij}(r)u_{ij}(r)r^2dr\ , \tag{1.3}$$

$$P\beta/\rho=1-\tfrac{2}{3}\pi\beta\rho\sum_{i}^{M}\sum_{j}^{M}x_ix_j\int g_{ij}(r)r^3\frac{du_{ij}(r)}{dr}dr\ , \tag{1.4}$$

$$\rho k_BT\chi_T=1+4\pi\rho\sum_{i}^{M}\sum_{j}^{M}x_ix_j\int[g_{ij}(r)-1]r^2dr\ , \tag{1.5}$$

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

$$B_{ij}(r)=\sum_{n=4}^{\infty}[\epsilon_{n,ij}(r)]\ , \tag{1.6}$$

where $[\epsilon_{n;ij}(r)]$ 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. (1.2) $B(r)=0$ 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 concluded that neither the

HNC nor PY approximation works quantitatively far before the freezing point.[1,2] Since the properties of approximations involved in the integral equation are directly related to the approximation for $B(r)$, better approximations could be obtained by modifying $B(r)$ in some way.

Recently proposed thermodynamically consistent approximations with a parametrized bridge function have been found to yield a better approximation up to the freezing point over the HNC or PY approximation.[3] Among these approximations, the Rogers-Young[4] (RY) and reference HNC (RHNC) (Ref. 5) equations have been studied most extensively for various potentials, including one-component plasmas (OCP's), hard-sphere, soft-sphere, and 12-6 Lennard-Jones fluids. It has been shown that even in an equilibrium supercooled liquid regime the thermodynamic properties predicted by the RY integral equation agree well with computer-simulation data for soft-sphere fluids.[6-8] This is, however, not the case in pair structures. It is well known that the PDF's calculated by computer simulations yield a clear splitting of the second peak near and below the glass-transition temperature for both one- and two-component fluids.[6,7,9] The PDF's by the RY approximation show a different behavior between one- and two-component fluids. For binary mixtures of soft spheres with a specific core-size ratio $\sigma_2/\sigma_1=1.4$, the RY equation yields a behavior of the PDF accompanied by the second peak splitting similar to that of the computer simulation.[6,7] On the other hand, the PDF's for one-component soft-sphere fluids yield no splitting of the second peak below the glass-transition temperature, nor broadening in an equilibrium supercooled state, in disagreement with the results of the computer simulation.[8] For this reason, it is our intention to study a better approximation for the integral equation in both one- and two-component supercooled fluids.

In our previous papers we proposed a modified HNC equation for highly supercooled soft-sphere fluids (MHNCS) and it has been tested for the one-component fluid.[10,11] Near and below the glass-transition temperature, the solution of the MHNCS equation has been found to show a splitting of the second peak of the PDF compatible with the computer simulations. In the MHNCS approximation, the bridge function is approximated by a proper interpolation of the bridge function of the PY hard-sphere model and the leading term of Eq. (1.6), which was first successfully applied to OCP fluids.[12,13] In this paper, we will proceed to test the MHNCS approximation for binary mixtures of soft spheres. We also present the results of our calculations with the RY approximation for supercooled binary fluids of the twelfth-inverse-power potential with different diameters, to be compared with the MHNCS approximation. Thermodynamic properties depending on the core-size ratio and the number concentration will be discussed: $S_{c\text{-}c}(0)$, the concentration-concentration structure factor at q (wave number) equals 0, is of our particular interest in connection with the problem of phase separation, characterized by $S_{c\text{-}c}(0)\rightarrow\infty$.

II. THE MODEL

We consider binary mixtures composed of two species with diameters σ_1 and σ_2, interacting through the purely repulsive twelfth-inverse-power potentials:

$$u_{ij}(r)=\epsilon\left[\frac{\sigma_{ij}}{r}\right]^{12}, \tag{2.1}$$

where the diameters are assumed to be additive, i.e.,

$$\sigma_{ij}=\tfrac{1}{2}(\sigma_i+\sigma_j) . \tag{2.2}$$

The advantage of the inverse-power potential is due to its scaling property. According to this property, all reduced equilibrium properties of binary mixtures, in excess of their ideal-gas counterparts, depend on two independent variables, i.e., the number concentration of species 1, x_1, and the coupling constant Γ, defined as[1]

$$\Gamma=\rho\sigma_1^3(\epsilon\beta)^{1/4} . \tag{2.3}$$

According to the conformal solution theory,[1] an equivalent one-component soft-sphere fluid is introduced with the effective diameter

$$\sigma_{\text{eff}}^3=\sum_i^2\sum_j^2 x_i x_j\sigma_{ij}^3 . \tag{2.4}$$

The corresponding effective coupling constant becomes

$$\Gamma_{\text{eff}}=\Gamma\left[\frac{\sigma_{\text{eff}}}{\sigma_1}\right]^3 . \tag{2.5}$$

Hereafter, we use $\{\Gamma_{\text{eff}}, x_1, \sigma_2/\sigma_1\}$ to assign each thermodynamic state of binary soft-sphere mixtures. The freezing and glass transitions of this model, in the one-component case ($x_1=1$), are found to be at $\Gamma_{\text{eff}}\simeq 1.15$ (Ref. 14) and 1.56 (Refs. 6, 7, 15, and 16), respectively. In the present work, we study the three cases of $\Gamma_{\text{eff}}=0.8$, 1.2, and 1.5, which are stable, moderately supercooled, and highly supercooled liquids, respectively. After having confirmed the validity of our approximation, we discuss the structural properties and stabilities of the alloys, which significantly depend on x_1 and σ_2/σ_1 as well as Γ_{eff}.

III. ROGERS-YOUNG APPROXIMATION

Rogers and Young have proposed a thermodynamically consistent integral equation based on an idea of mixing of the HNC and PY approximations.[4] The RY approximation uses the following bridge function:

$$B_{ij}(r)=-\gamma_{ij}(r)+\ln\left[1+\frac{\exp[f_{ij}(r)\gamma_{ij}(r)]-1}{f_{ij}(r)}\right], \tag{3.1}$$

where $f(r)$ is a mixing function with adjustable parameters. According to the work by Hansen and Zerah,[2] we take a single mixing function as

$$f(r)=1-e^{-\alpha r} , \tag{3.2}$$

where α (>0) is an adjustable parameter to be determined by the requirement of a self-consistency condition for the equations of state obtained in two ways, i.e., Eqs. (1.4) and (1.5) to be identical. We have solved the RY integral equation for highly supercooled soft-sphere mixtures at $\{1.5,0.5,1.2\}$, $\{1.5,0.5,1.3\}$, and $\{1.5,0.5,1.4\}$. The resultant PDF's are shown in Fig. 1.

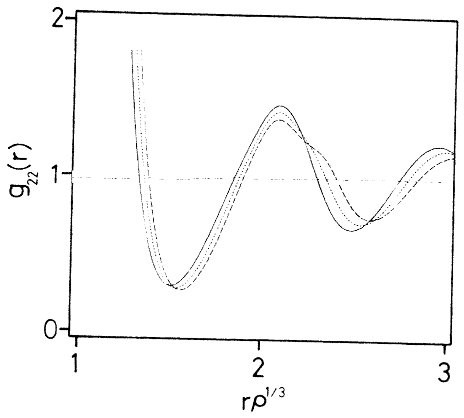

FIG. 1. Partial PDF $g_{22}(r)$ calculated with the RY integral equation in a highly supercooled regime. The thermodynamic states are $\{1.5,0.5,1.2\}$ (solid curve), $\{1.5,0.5,1.3\}$ (dotted curve), and $\{1.5,0.5,1.4\}$ (dashed curve).

In our previous papers,[8,10,11] it has been shown that the PDF's for the RY approximation for one-component soft-sphere fluids do not yield a splitting of their second peak even in the highly supercooled regime, because of the lack of the approximate bridge function which takes a negative value at any distance. Therefore it is anticipated that the PDF's obtained using the RY equation for binary soft-sphere fluids yield no splitting of their second peak either. It is obviously seen from Fig. 1 that such an anticipation is true. However, the PDF's begin to show an asymmetric structure around their second peak as the core size ratio increases. Similar results have been obtained by Bernu *et al.*[6,7] Thus, there are other origins, not directly related to the detailed form of the bridge function, resulting in such asymmetric behavior depending on the core-size ratio: Equation (1.2) is written in the view of the diagramatic expansion as

$$h_{ij}(r)=c_{ij}(r)+x_1\,\underset{i}{\circ}\overset{c}{\text{—}}\underset{1}{\bullet}\overset{c}{\text{—}}\underset{j}{\circ}+x_2\,\underset{i}{\circ}\overset{c}{\text{—}}\underset{2}{\bullet}\overset{c}{\text{—}}\underset{j}{\circ}+\cdots\,, \tag{3.3}$$

where the i, j, and integers attached to circles denote the respective species. For a pure system $(\sigma_1=\sigma_2)$, the second and third terms of Eq. (3.3) are identical. For the binary system $(\sigma_1\neq\sigma_2)$, however, the later term differs from the former term by a factor of about $(\sigma_{i2}+\sigma_{2j})/(\sigma_{i1}+\sigma_{1j})$. For this reason, it may be supposed that an asymmetric structure in the second peak of the PDF appears for a binary mixture for a large core-size ratio.

IV. THE MHNCS APPROXIMATION

Recently, we proposed the MHNCS approximation for one-component soft-sphere fluids, which reproduces the correct behavior of the PDF in both stable and supercooled liquids.[10,11] The PDF obtained with the MHNCS approximation yields a clear splitting of the second peak near and below the glass-transition temperature, compatible to that of computer simulations. Our approximation is based on the idea of a universality of the short-range part of $B(r)$, suggested by Rosenfeld and Ashcroft,[3] and the relevant work for the one-component plasmas by Iyetomi and Ichimaru.[12] According to the former, the form of $B(r)$ at short interparticle distances can be expressed in terms of the PY bridge function of the hard-sphere system with an adjustable core diameter d, i.e., $B_H^{\mathrm{PY}}(r,d)$, irrespective of the choice of potentials for repulsive cores. Iyemoti and Ichimaru, on the other hand, have shown that an approximate $B(r)$ based on the leading term of Eq. (1.6), $\epsilon_4(r)$, together with a rescaling assumption[17] could be in good agreement with computer simulations for a highly supercooled OCP fluid state, leading to a splitting of the second peak of the PDF. Similar results have successfully been obtained for two-component plasmas by Ballone, Pastore, and Tosi.[13] Therefore we assume an empirical bridge function of the form of a linear combination of the short-range-distance part $B_H^{\mathrm{PY}}(r,d)$ and the long-range-distance part $\epsilon_4(r)$.[10,11]

The MHNCS approximation is easily extended to binary mixtures[18] assuming three bridge functions as

$$B_{ij}(r,d_1)=[1-f(r,d_{ij})]B_{H;ij}^{\mathrm{PY}}(r,d_1)+f(r,d_{ij})\epsilon_{4;ij}(r)\,, \tag{4.1}$$

where d_1 is an adjustable hard-sphere diameter, $0\leq f(r,d)\leq 1$ a continuous mixing function, and d_{ij} are defined as

$$d_{ij}=\frac{d_1(\sigma_i+\sigma_j)}{2\sigma_1}\,. \tag{4.2}$$

The mixing function is simply taken to be of the form[10,11,18–20]

$$f(r,d)=\frac{1}{2}\left[1+\tanh\left[\frac{r-d}{W}\right]\right]\,, \tag{4.3}$$

where W is a dumping parameter that 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. The leading term of Eq. (1.6), $\epsilon_4(r)$, is explicitly written as

$$\epsilon_{4;ij}(r)=\tfrac{1}{2}\rho^2 x_i x_j \sum_{k}^{2}\sum_{l}^{2}\int\int d\mathbf{r}'d\mathbf{r}''h_{ik}(r')h_{il}(r'')h_{kl}(|\mathbf{r}'-\mathbf{r}''|)h_{kj}(|\mathbf{r}-\mathbf{r}'|)h_{lj}(|\mathbf{r}-\mathbf{r}''|)\,. \tag{4.4}$$

The adjustable parameter d_1 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,[3]

$$H(0)=\beta[F^{\text{ex}}(0,N)-F^{\text{ex}}(1,N-2)]\ , \tag{4.5}$$

where $F^{\text{ex}}(n,m)$ 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. (4.5) 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[6,7,21]

$$\beta u^{\text{ex}}=\tfrac{3}{2}+b\Gamma_{\text{eff}}^4\ , \tag{4.6}$$

where b is a "Madelung" constant. For the present purpose of the calculation of Eq. (4.6), we assume $g(r)\simeq\xi\delta(r-\alpha)$ for the thermodynamic states to which Eq. (4.6) is applicable. Recalling the conformal solution theory, we obtain[10,11]

$$\begin{aligned}\beta u^{\text{ex}}&=\tfrac{3}{2}+2\pi\beta\rho\sum_i^2\sum_j^2 x_ix_j\int g_{ij}(r)u_{ij}(r)r^2dr\\ &\simeq\tfrac{3}{2}+2\pi\beta\rho\sum_i^2\sum_j^2 x_ix_j\left[\frac{\sigma_{ij}}{\sigma_1}\right]^3\int g_0(r/\sigma_1)u_0(r/\sigma_1)(r/\sigma_1)^2d(r/\sigma_1)\\ &=\tfrac{3}{2}+2\pi\xi\alpha^{-10}\Gamma_{\text{eff}}^4\ ,\end{aligned} \tag{4.6$'$}$$

and $b=2\pi\xi\alpha^{-10}$, where ξ is a scaling constant, α the distance between a specific particle and nearest-neighbor particles surrounding it (first shell), and the 0 index denotes the equivalent one-component system. Furthermore, $u^{\text{ex,coupled}}$ containing two particles (a coupled particle) within the shell can easily be estimated from Eq. (4.6$'$) by replacing α with $2^{1/3}\alpha$ for the requirement of constant density inside the shell, and then we obtain

$$\beta u^{\text{ex,coupled}}=2(\tfrac{3}{2}+2^{-10/3}b\Gamma_{\text{eff}}^4)\ . \tag{4.7}$$

Using Eqs. (4.6) and (4.7), Eq. (4.5) is written as

$$H(0)=2(u^{\text{ex}}-\tfrac{3}{2})(1-2^{-10/3})\ . \tag{4.8}$$

A set of Eqs. (1.1), (1.2), (4.1), and (4.8) constructs the MHNCS approximation for the binary soft-sphere mixture, which can be solved numerically in a self-consistent way. We should note that the MHNCS approximation differs from the usual thermodynamically consistent methods,[3-5] for we do not use any thermodynamic self-consistency condition.

V. RESULTS

A. Numerical procedures

The method used here to solve the integral equation is essentially the same as an iterative procedure proposed by Ng[22] for the OCP fluids and that used in our previous papers.[10,11,18] A number of iterations were made so that the following self-consistent measure Δ is minimized:

$$\Delta=\left[\sum_i\sum_j\int|c_{ij}^{\text{in}}(r)-c_{ij}^{\text{out}}(r)|^2\,r^2dr\right]^{1/2}\ .$$

The superscripts in and out denote the input and output functions, respectively. We used $e^{-\beta u(r)}-1$ as an initial input function for $c^{\text{in}}(r)$. Successive input functions are replaced by the output functions with

$$c_{ij}^{\text{in}}(r)=[c_{ij}^{\text{out}}(r)]_1-\sum_{k=2}^{6}A_k\{[c_{ij}^{\text{out}}(r)]_k-[c_{ij}^{\text{out}}(r)]_1\}\ ,$$

where $[c^{\text{out}}(r)]_k$ is the output function at kth step before and A_k are calculated by requiring the constraint that $\Delta=0$. It took about 100 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. $B_H^{\text{PY}}(r,d)$ in Eq. (4.1) has been calculated with the analytical solution of the PY approximation for the hard-sphere model given by Lebowitz.[23]

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. (4.4) 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. 12, and originally used for the calculation of the virial coefficients by Barker and Monaghan.[24] 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. (4.3) 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.[8,11,15]

B. Solutions

Calculations of the MHNCS integral equation have been made for three different Γ_{eff}'s, three x_1's and four σ_2/σ_1's. For the study of thermodynamical and structural properties of these systems, we calculated the equation of state $P\beta/\rho$, the reduced inverse compressibility $(\chi_T^*)^{-1}=\beta(\rho\chi_T)^{-1}$, and the concentration-concentration structure factor $S_{c\text{-}c}(q)$ defined as[25]

$$S_{c\text{-}c}(q)=x_1x_2\{1+x_1x_2\rho[\hat{h}_{11}(q)+\hat{h}_{22}(q)-2\hat{h}_{12}(q)]\}\ , \tag{5.1}$$

where $\hat{h}(q)$ is the Fourier transform of $h(r)$. Our results are summarized in Tables I–III and Figs. 2–4.

From Tables I–III, it is clearly seen that the equation of state obtained agrees excellently with the computer-simulation results. The equation of states depends slightly on the number concentration x_1 and the core-size ratio σ_2/σ_1. This means that the equivalent one-fluid approximation works well at least for this quantity.

The PDF's of the MHNC equation exhibit a clear splitting of their second peak at $\Gamma_{\text{eff}}=1.5$ in a highly supercooled regime (Fig. 2), revealing a remarkable contrast to those of the RY approximation (Fig. 1) or a stable liquid state (Fig. 3). The splitting is, however, sharper than that of the computer simulation.[11] This may be reasonably understood by taking into consideration of slow-relaxation phenomena near the glass transition.[26] Computer-generated samples at the highly supercooled regime are not fully relaxed, due to slow relaxation.[27–29] Therefore, the feature of the PDF may be smeared by biased dynamical fluctuations caused by the nonequilibrium nature of the system. The splitting of the second peak of the PDF is essentially dominated by the form of Eq. (4.1).[10,11] We note that $\epsilon_4(r)$ 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 the PDF appears (Figs. 2 and 3). On the other hand, the bridge function for the RY or PY equation always has a nonpositive value everywhere, thus resulting in no splitting of the second peak.

TABLE I. Thermodynamic properties calculated from the MHNCS equation and molecular-dynamics (MD) simulations (Ref. 29) with the twelfth-inverse-power potential at $\Gamma_{\text{eff}}=0.8$. The values in parentheses are the hard-sphere parameters d_1/l for the MHNCS integral equation. The first line of each pair of x_1 and σ_2/σ_1 shows the equation of state $P\beta/\rho$ and the second line the reduced inverse compressibility $(\chi_T^*)^{-1}$.

x_1	σ_2/σ_1	MHNCS		MD
0.1	1.1	8.270	(0.8298)	
		22.458		
0.1	1.2	8.278	(0.7662)	
		22.573		
0.1	1.3	8.298	(0.7109)	
		22.666		
0.1	1.4	8.323	(0.6627)	
		22.746		
0.5	1.1	8.231	(0.8639)	
		22.823		
0.5	1.2	8.246	(0.8238)	8.481
		23.305		
0.5	1.3	8.312	(0.7845)	
		23.759		
0.5	1.4	8.409	(0.7469)	
		24.206		
0.9	1.1	8.267	(0.8958)	
		22.495		
0.9	1.2	8.275	(0.8866)	
		22.709		
0.9	1.3	8.310	(0.8761)	
		22.956		
0.9	1.4	8.365		
0.9	1.4	8.365	(0.8646)	
		23.258		

TABLE II. Thermodynamic properties calculated from the MHNC equation and molecular-dynamics (MD) simulations (Refs. 7 and 29) with the twelfth-inverse-power potential at $\Gamma_{\text{eff}}=1.2$. The values in parentheses are the hard-sphere parameters d_1/l for the MHNCS integral equation. The first line of each pair of x_1 and σ_2/σ_1 shows the equation of state $P\beta/\rho$ and the second line the reduced inverse compressibility $(\chi_T^*)^{-1}$. The MD data for $\sigma_2/\sigma_1=1.4$ were taken from a numerical interpolation of the simulation data in Ref. 7.

x_1	σ_2/σ_1	MHNCS		MD
0.1	1.1	22.232	(0.8935)	
		63.885		
0.1	1.2	22.288	(0.8245)	
		64.115		
0.1	1.3	22.377	(0.7647)	
		64.371		
0.1	1.4	22.482	(0.7127)	
		64.666		
0.5	1.1	22.175	(0.9291)	
		64.811		
0.5	1.2	22.352	(0.8839)	22.243
		65.739		
0.5	1.3	22.684	(0.8402)	
		66.794		
0.5	1.4	23.109	(0.7991)	23.11
		68.204		
0.9	1.1	22.227	(0.9644)	
		63.968		
0.9	1.2	22.302	(0.9536)	
		64.472		
0.9	1.3	22.474	(0.9415)	
		65.225		
0.9	1.4	22.732	(0.9286)	
		66.272		

It is made clear that the detailed structures of the PDF's at same Γ_{eff} depend significantly on the core-size ratio σ_2/σ_1 and the number concentration x_1. For a small number concentration ($x_1=0.1$), the first peak of three partial PDF's yields almost the same height irrespective of the value of core-size ratio. However, the first peak of $g_{22}(r)$ becomes very sharp and higher as x_1 and σ_2/σ_1 increase [Fig. 2(b)]. This behavior suggests a phase separation to be predicted.

The concentration-concentration structure factor at $q=0$, $S_{c\text{-}c}(0)$, measures mixing or demixing properties of the binary mixtures: The ratio $x_1x_2/S_{c\text{-}c}(0)$ is equal to unity for the random mixing (ideal mixing); otherwise it deviates from unity. Figure 4 shows dependencies of $x_1x_2/S_{c\text{-}c}(0)$ on the thermodynamic state

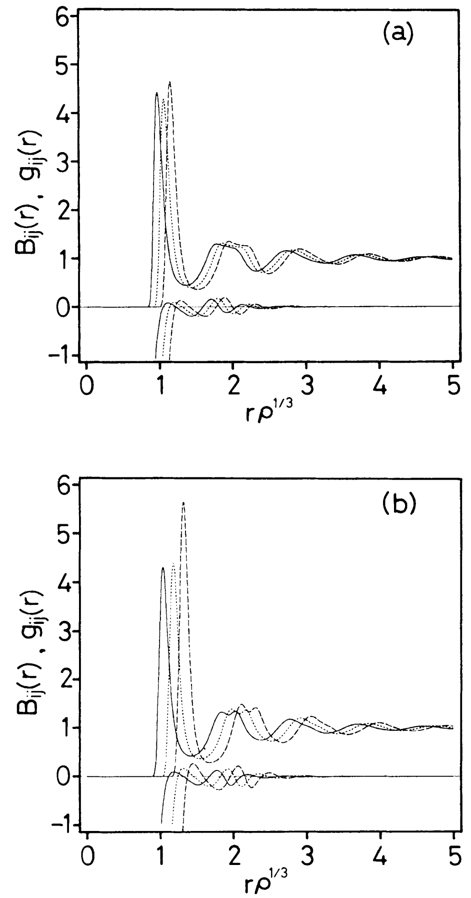

FIG. 2. Partial PDF's and the bridge functions calculated with the MHNCS integral equation in a highly supercooled regime (g_{11} and B_{11}, solid curve; g_{12} and B_{12}, dotted curve; g_{22} and B_{22}, dashed curve). The thermodynamic state is (a) $\{1.5,0.5,1.2\}$ and (b) $\{1.5,0.9,1.3\}$.

TABLE III. Thermodynamic properties calculated from the MHNC equation and molecular-dynamics (MD) simulations (Refs. 7 and 29) with the twelfth-inverse-power potential at $\Gamma_{\text{eff}}=1.5$. The values in parentheses are the hard-sphere parameters d_1/l for the MHNCS integral equation. The first line of each pair of x_1 and σ_2/σ_1 shows the equation of state $P\beta/\rho$ and the second line the reduced inverse compressibility $(\chi_T^*)^{-1}$. The MD data for $\sigma_2/\sigma_1=1.4$ were taken from a numerical interpolation of the simulation data in Ref. 7.

x_1	σ_2/σ_1	MHNCS		MD
0.1	1.1	42.690	(0.9298)	
		126.734		
0.1	1.2	42.824	(0.8576)	
		126.759		
0.1	1.3	42.990	(0.7954)	
		127.373		
0.1	1.4	43.195	(0.7414)	
		128.307		
0.5	1.1	42.608	(0.9290)	
		128.179		
0.5	1.2	43.036	(0.9182)	42.806
		129.200		
0.5	1.3	43.748	(0.8723)	
		131.173		
0.5	1.4	44.650	(0.8296)	44.76
		134.540		
0.9	1.1	42.679	(1.0036)	
		127.040		
0.9	1.2	42.876	(0.9921)	
		128.300		
0.9	1.3	43.302	(0.9793)	
		130.326		
0.9	1.4	43.915	(0.9657)	
		132.903		

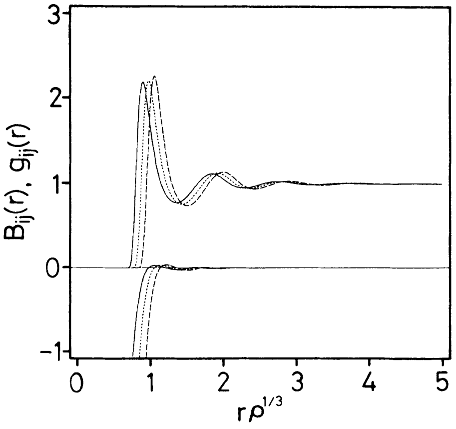

FIG. 3. Partial PDF's and the bridge functions calculated with the MHNCS integral equation in a stable liquid regime (g_{11} and B_{11}, solid curve; g_{12} and B_{12}, dotted curve; g_{22} and B_{22}, dashed curve). The thermodynamic state is $\{0.8,0.5,1.2\}$.

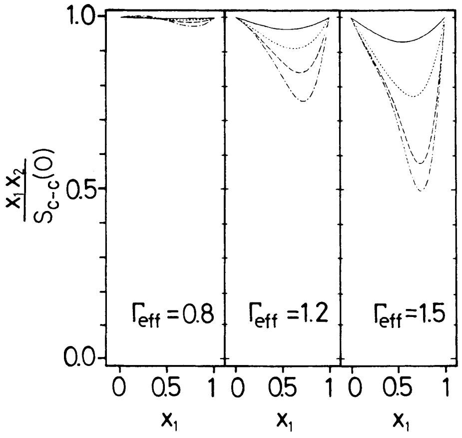

FIG. 4. $x_1x_2/S_{c\text{-}c}(0)$ vs the concentration x_1 for $\sigma_2/\sigma_1=1.1$ (solid curve), 1.2 (dotted curve), 1.3 (dashed curve), and 1.4 (dotted-dashed curve). The curves are obtained using a spline interpolation of the data.

$\{\Gamma_{\text{eff}}, x_1, \sigma_2/\sigma_1\}$. It is clearly seen that the demixing tendency becomes remarkable as the core-size ratio exceeds about $\sigma_2/\sigma_1 = 1.3$ for the highly supercooled state ($\Gamma_{\text{eff}} = 1.5$). This tendency is consistent with the behavior of $g_{22}(r)$ in the highly supercooled regime mentioned above (Fig. 2). The dependency of $x_1 x_2 / S_{c\text{-}c}(0)$ on the number concentration x_1 is not symmetric about the equimolar mixture ($x_1 = 0.5$). Similar results are obtained for the hard-sphere mixtures by Barrat *et al.*[30]

VI. DISCUSSION

We have made a crucial test of the MHNCS integral equation with the binary soft-sphere fluid up to a highly supercooled liquid regime. The MHNCS solutions result in an excellent agreement of the equation of state with that of the computer simulations. 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 an overly short 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 term of elementary diagrams, $\epsilon_4(r)$, which is responsible for the characteristic feature (second peak splitting) of the PDF at intermediate distances for highly supercooled liquids. Since $\epsilon_4(r)$ has almost no contribution for stable liquids, the MHNCS integral equation is equivalent to the RHNC or RY approximation above the freezing temperature. On the other hand, for highly supercooled liquids, $\epsilon_4(r)$, 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 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 for both one- and two-component fluids.

Another important conclusion of the present paper concerns thermodynamic and structural properties depending on the number concentration and core-size ratio in the supercooled regime, especially for $\Gamma_{\text{eff}} = 1.5$. As the number concentration and core-size ratio increase, we observed that the first peak of the partial PDF, $g_{22}(r)$, becomes sharper and higher, and the demixing tendency of binary mixtures becomes remarkable. With these results, the theory predicts a phase separation under suitable choices of $\{\Gamma_{\text{eff}}, x_1, \sigma_2/\sigma_1\}$.

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