PHYSICAL REVIEW A VOLUME 46, NUMBER 2 15 JULY 1992

Instability and phase separation of a binary mixture: The role of short-range repulsion and core-size ratio

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(Received 8 July 1991)

The integral equation of the fluid theory has been solved for the supercooled binary mixtures of fourth-, sixth-, ninth-, and twelfth-inverse-power potentials with a modified hypernetted-chain approximation recently proposed by us. In order to calculate zero-pressure thermodynamic and structural properties, we have incorporated an attractive potential of the Kac form. Using pair distribution functions obtained, we have calculated the concentration-concentration structure factor $S_{CC}(k)$ and partial coordination numbers, which are useful to investigate mixing properties depending on the softness of the potentials to which some groups of material are attributed. For the mixture of fourth-inverse-power potential with a core-size ratio of 1.2, $S_{CC}(0)$ and the partial coordination numbers show a remarkable tendency towards phase separation near the freezing temperature, which is in good agreement with experiments on inter-alkali-metallic alloys. For the potentials with $n \geq 6$, the mixtures are stable near freezing (even in a highly supercooled regime), which is typical of alloys of the rare-gas families. The interchange energy obtained is also in good agreement with experimental values.

PACS number(s): 64.75.+g, 64.70.Pf, 61.20.Gy

I. INTRODUCTION

The aim of this work is to study the thermodynamical stability of binary mixtures under normal and highly supercooled fluid conditions. Our particular interest is concerned with the phase separation of binary fluid mixtures which is a very common thermodynamic phenomenon in simple atomic and molecular systems, as well as metallic alloys. Segregation is usually believed to be induced by van der Waals attractions rather than short-range repulsions. Recent theoretical investigagtions, however, have revealed that phase separation also takes place even in mixtures of purely repulsive interactions such as the inverse power potential [1], repulsive α-exp-6 potentials [2], and hard-sphere potentials [3]. Especially the prediction of phase separation for hard-sphere mixtures [3] is contrary to the long-held belief [4] that they never encounter the segregation under possible choices of potential and thermodynamic parameters within the Percus-Yevick (PY) approximation [5]. In these circumstances, this work is mainly concerned with roles of the form (softness) of short-range repulsive interactions in mixtures by adopting a series of soft-sphere potentials with different softness.

Another interest in the discussion of the phase separation is the role of the atomic size ratio σ_2/σ_1. For example [6], in a NaCs ($\sigma_2/\sigma_1 \sim 1.43$) liquid solution a distinct tendency to phase separation has been observed, while in a NaK ($\sigma_2/\sigma_1 \sim 1.24$) liquid solution the tendency becomes much weaker. It is known that a KCs ($\sigma_2/\sigma_1 \sim 1.15$) mixture behaves almost like an ideal solution. There are at least two empirical relations related to the stability of a binary mixture against phase separation: A binary substitutional solid solution becomes unstable when the atomic sizes of constituent particles differ by more than 15%, known as the empirical Hume-Rothery rule [7, 8]. Careful analyses of glass-forming metallic alloys [9, 10] reveal that the ability or easiness of glass formation is related to the core-size ratio of constituent atoms, which is mostly satisfied when $\sigma_1/\sigma_2 < 0.85$.

The mixing stability of a binary mixture is described by concentration fluctuations of the system under consideration [11], which are directly related to the partial pair distribution functions (PDF's) of the mixture [12]. Especially, the concentration-concentration structure factor, $S_{CC}(k)$, is well suited for the investigation of stability mixtures, because its long-wavelength limit, i.e., $S_{CC}(0)$, is proportional to inverse of the second derivative of the Gibbs free energy with respect to the number concentration. Therefore, the phase separation of a fluid mixture is given by the equation $S_{CC}(0) = \infty$.

The partial PDF's can be obtained through either computer simulations or the integral equation based on the theory of liquids. The result of computer simulations provides numerically exact PDF's only for the range of the interparticle distance shorter than half the side length of a simulation cell. This causes an unavoidable difficulty for the determination of $S_{CC}(0)$, which is a Fourier transform of the PDF's. On the other hand, any known integral equations provide only approximate PDF's [11], the reliability of which depends on the approximate form of the bridge function used. Well-known classical hypernetted-chain (HNC) and PY approximations only work for specific volumes or temperatures far above the freezing point [11]. Recently we proposed a modified HNC approximation for supercooled soft-sphere fluids (MHNCS), which has successfully been tested for one- and two-component fluids [13, 14]. In the MHNCS approximation, the bridge function is approximated by a proper interpolation of bridge functions of the PY hard-sphere model and the leading elementary diagram. It has been obtained that the MHNCS approximation works excellently well above and below the freezing temperature, leading to a better agreement with the computer-simulation results over thermodynamically consistent approximations such as the Rogers-Young (RY) [15] approximation. Near and below the glass-transition temperature, the PDF's obtained from the MHNCS have been found to exhibit a splitting of the second peak of the PDF compatible with the results of the computer simulations.

In this paper we discuss the mixing properties of binary soft-sphere mixtures of inverse-power potentials with various inverse-power (softness) parameters n from $n = 4$, 6, 9, to 12, and the MHNCS integral equation. The results are shown for each softness parameter near and below the freezing points estimated with an equivalent one-component fluid model. The core-size ratio was chosen to be 1.2 and 1.4. In order to take into account attractions between particles, we have used a generalized van der Waals model as in our previous papers [16–18]. In this model, the particles interact through the Kac potential [19] (attraction) as well as the soft-sphere potential (repulsion). We examine in detail the difference of short-range interactions (both softness and core-size ratio) effects on $S_{CC}(0)$ and a characteristic energy of mixing under a constant pressure condition. We also study the conformal-solution theory [11] for binary soft-sphere mixtures. These results are compared with the experimental data on inter-alkali-metallic binary alloys. It is found that the present model with $n = 4$ gives rise to a good agreement with the experiments.

II. PAIR STRUCTURE AND PHASE SEPARATION

The microscopic pair structure of binary mixtures is well described by the partial PDF's $g_{ij}(r)$ and structure factors $S_{ij}(k)$, where the subscripts denote the species indices. The PDF's and structure factors are related to each other through the Fourier transforms as [11]

$$S_{ij}(k) = x_i\delta_{ij} + x_i x_j \rho \int e^{-i\mathbf{k}\cdot\mathbf{r}}[g_{ij}(r) - 1]d\mathbf{r}\ , \qquad (1)$$

where δ_{ij} is the Kronecker δ symbol and x_i the number concentration of the ith species. Knowledge of the PDF's or structure factors allows us to calculate equilibrium thermodynamic properties of mixtures, such as the excess internal energy, equation of state, and isothermal compressiblity. The concentration-concentration structure factor $S_{CC}(k)$, which is a measure of concentration fluctuation in a mixture [12], is simply a linear combination of the partial structure factors [11];

$$\begin{aligned} S_{CC}(k) &= x_2^2 S_{11}(k) - 2x_1x_2S_{12}(k) + x_1^2 S_{22}(k) \\ &= x_1x_2 + (x_1x_2)^2\rho \\ &\quad \times \int e^{-i\mathbf{k}\cdot\mathbf{r}}[g_{11}(r) + g_{22}(r) - 2g_{12}(r)]d\mathbf{r}\ . \end{aligned} \qquad (2)$$

The long-wavelength limit of $S_{CC}(k)$ is related to the second derivative of the Gibbs free energy G with respect to the number concentration x_1 [12],

$$\lim_{k\to 0} S_{CC}(k) = \frac{N}{\beta(\partial^2 G/\partial x_1^2)_{T,P,N}}\ , \qquad (3)$$

where β is the inverse temperature $(k_{\rm B}T)^{-1}$ and N the total number of particles.

To illustrate ideal-mixing and -demixing behaviors of $S_{CC}(0)$, we recall a simple expression for G in binary mixtures as follows [11, 12]:

$$\begin{aligned} G = {} & N(x_1\mu_1^0 + x_2\mu_2^0) \\ & + Nk_{\rm B}T(x_1\ln x_1 + x_2 \ln x_2) + Nwp(x_1)\ , \end{aligned} \qquad (4)$$

where μ_i^0 are the chemical potential of a purely ith species, w a so-called "interchange energy," and $p(x_1)$ an upper convex function with a boundary condition of $p(0) = p(1) = 0$; the simplest model for the form of $p(x_1)$ is given by a quadratic function of the composition

$$p(x_1) = x_1x_2\ . \qquad (5)$$

The second term of Eq. (4) represents the entropy of mixing originated by the labeling of particles. An ideal mixture is represented by setting $w = 0$ in Eq. (4), using Eqs. (3) and (4), which leads to

$$\frac{x_1x_2}{S_{CC}(0)} = 1 + x_1x_2\beta w p''(x_1)\ . \qquad (6)$$

Here primes denote differentiation with respect to the argument. When w is positive and temperature independent, it is clear from Eq. (6) that $S_{CC}(0)$ diverges at a concentration-dependent critical temperature $T_c(x_1)$

$$\begin{aligned} T_c(x_1) &= -\frac{x_1x_2wp''(x_1)}{k_{\rm B}} \\ &= T\left(1 - \frac{x_1x_2}{S_{CC}(0)}\right)\ . \end{aligned} \qquad (7)$$

Below T_c, the mixture separates into two fluid phases. Henceforth the ratio $x_1x_2/S_{CC}(0)$ plays an important role interpreted as a stability parameter for the phase separation; it is unity for an ideal mixture, while it becomes zero when the phase separation takes place at T_c [20].

Let us make a brief consideration of $S_{CC}(0)$ based on the conformal-solution theory or so-called "one-fluid" approximation [11], which assumes that the partial PDF's of a mixture can be represented by that of an "equivalent one-component fluid." Then, the crudest example is given by the random-mixing approximation assuming that all partial PDF's are identical. It is clear from Eqs. (2) and (6) that this approximation leads to an ideal-mixing for any concentration and core-size ratio. Another useful one-fluid approximation is to assume that

$$g_{ij}(r/\sigma_{ij}) = g_e(r/\sigma_e) \ , \tag{8}$$

$$\sigma_e^3 = \sum_i^2 \sum_j^2 x_i x_j \sigma_{ij}^3 \ , \tag{9}$$

where the subscript e represents the equivalent one-component fluid. Substituting Eq. (8) for Eq. (2), we obtain an approximate form for the stability parameter as

$$\frac{x_1 x_2}{S_{CC}(0)} = \left[1 - x_1 x_2 \left(1 - \frac{\rho \chi_{T,e}}{\beta} \right) \times \frac{\sigma_{11}^3 + \sigma_{22}^3 - 2\sigma_{12}^3}{\sigma_e^3} \right]^{-1} , \tag{10}$$

where $\chi_{T,e}$ is the isothermal compressiblity of the equivalent one-component fluid. This is no more ideal mixing, which allows us to estimate an approximate temperature of the phase separation $T_c(x_1)$. We note that the conformal solution theory should be restricted to mixtures for which the differences of pair potentials are simply in the characteristic energy and length scales but the form of the potentials is given by an identical function.

III. THE MODEL

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

$$u_{ij}(r) = \varepsilon \left(\frac{\sigma_{ij}}{r} \right)^n \ , \tag{11}$$

where n (> 3) is the softness parameter of the potential and the diameters are assumed to be additive, i.e.,

$$\sigma_{ij} = \tfrac{1}{2}(\sigma_i + \sigma_j) \ . \tag{12}$$

In the present calculations, the softness parameter was chosen to be $n = 4$, 6, 9, and 12. 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

$$\Gamma = \rho \sigma_1^3 (\varepsilon \beta)^{3/n} \ . \tag{13}$$

With the conformal-solution theory described in Sec. II, the equivalent one-component soft-sphere fluid is introduced by choosing the effective diameter following Eq. (9). The corresponding effective coupling constant becomes

$$\Gamma_e = \Gamma \left(\frac{\sigma_e}{\sigma_1} \right)^3 \ . \tag{14}$$

Hereafter, we use a set of three parameters, i.e., Γ_e, x_1, and σ_2/σ_1, to assign each thermodynamic state for a binary soft-sphere mixture. The freezing points of one-component soft-sphere fluids with $n = 4$, 6, 9, and 12 are 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 [21].

The inverse-power potential works very well for high-density liquids in which the short-range repulsive force is dominant. The pure repulsive nature of the inverse-power potential, however, yields an unphysically high pressure. In order to investigate thermodynamic and structural properties at more realistic conditions, we take into account the effect of attractive interactions between particles within a standard van der Waals mean-field approximation [22]. This approximation turns out to be exact for the limit of an infinitely weak and long-range attractive potential of the Kac form [19],

$$v_{ij}(r) = -a_{ij} \gamma^3 \exp(-\gamma r) \ , \tag{15}$$

where $\gamma \to 0$ after a thermodynamic limit ($N \to \infty, V \to \infty$) under a constant density (N/V); the Helmholtz free energy of the system can be obtained by adding a correction term to the free energy of the inverse-power potentials, that is,

$$F = F_0 - 4\pi \rho N \sum_i^2 \sum_j^2 x_i x_j a_{ij} \ , \tag{16}$$

where F_0 is the free energy for $a_{ij} = 0$ and N the total number of particles. In our study, we make a simple assumption as

$$a_{ij} = \varepsilon \sigma_{ij}^3 \ , \tag{17}$$

where ε is the same energy scale as in Eq. (11). Therefore, the equation of state takes a simple form of the van der Waals type,

$$\frac{P\beta}{\rho} = P_0^* - 4\pi \Gamma_e (T^*)^{-(n-3)/n} \ , \tag{18}$$

where P_0^* is the compressibility factor for the purely inverse-power potential and T^* the reduced temperature $k_B T/\varepsilon$. The condition of zero pressure ($P = 0$) yields then the following simple relation between the effective coupling constant Γ_e and the reduced temperature T^*:

$$T^* = \left(\frac{P_0^*}{4\pi \Gamma_e} \right)^{-n/(n-3)} \ . \tag{19}$$

With this equation, all zero-pressure thermodynamic and structural quantities can be calculated as a function of temperature. Equation (16) is useful because the repulsive and attractive terms of the total potential can be treated separately. This model has been found to work well for various simple classical liquids; for example, the case $n = 15$ works for liquefied inert gases and the case $n = 5$ for liquid alkali metals [16, 17]. Note that the Kac potential gives no influence on the properties of the structures (both static and dynamic).

IV. THE INTEGRAL EQUATION

A. The MHNCS approximation

The integral equation of the fluid theory plays an important role in the study of structural and thermodynamic properties of liquids [11]. The integral equation results from the combination of two relations. One is the Ornstein-Zernike relation

$$h_{ij}(r) = c_{ij}(r) + \rho \sum_{k}^{2} x_k \int d\mathbf{r}' h_{ik}(r') c_{kj}(|\mathbf{r} - \mathbf{r}'|) , \tag{20}$$

where $c(r)$ is the direct correlation function and $h(r) = g(r) - 1$ the pair-correlation function. The other is a closure relation

$$g_{ij}(r) = e^{-\beta u_{ij}(r) + \gamma_{ij}(r) + B_{ij}(r)} , \tag{21}$$

where $\gamma(r) = h(r) - c(r)$ is the so-called sum of the nodal diagrams and $B(r)$ the bridge function. It is well known that $B(r)$ can be expanded in terms of h-bond elementary diagrams as [11]

$$B_{ij}(r) = \sum_{n=4}^{\infty} [\varepsilon_{n;ij}(r)] , \tag{22}$$

where $[\varepsilon_{n;ij}(r)]$ represents a set of n points elementary diagrams. However, the convergence of Eq. (22) 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 [11, 15, 23–30].

Recently, we proposed the MHNCS approximation which reproduces the correct behavior of the PDF in both stable and supercooled liquids for one-component soft-sphere fluids and their mixtures [13, 14]. 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. This approximation is based on the idea of a universality of the short-range part of $B(r)$, suggested by Rosenfeld and Ashcroft [23], and the relevant work for the one-component plasmas (OCP's) by Iyetomi and Ichimaru [27]. 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., $B_H^{\rm PY}(r,d)$, irrespective of the choice of potentials for repulsive cores. Iyetomi and Ichimaru, on the other hand, have shown that an approximate $B(r)$ based on the leading term of Eq. (22), $\varepsilon_4(r)$, together with a rescaling assumption [31] 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 [28]. Based on these findings we proposed an empirical bridge function of the form of a linear combination of the short-range-distance part $B_H^{\rm PY}(r,d)$ and the long-range-distance part $\varepsilon_4(r)$ [13, 14]:

$$B_{ij}(r) = [1 - f(r,d_{ij})] B_{H;ij}^{\rm PY}(r,d_1) + f(r,d_{ij}) \varepsilon_{4;ij}(r) , \tag{23}$$

where d_1 is an adjustable hard-sphere diameter, $0 \leq f(r,d_{ij}) \leq 1$ a continuous mixing function, and d_{ij} are defined as [14]

$$d_{ij} = \frac{d_1(\sigma_i + \sigma_j)}{2\sigma_1} . \tag{24}$$

The mixing function is simply taken of the form [13, 14, 30]

$$f(r,d) = \frac{1}{2}\left[1 + \tanh\left(\frac{r-d}{W}\right)\right] , \tag{25}$$

where W is a dumping parameter that could be determined from the magnitude of thermal vibration of particles (root-mean-square amplitude) or the width of the first peak of the PDF. The adjustable parameter d_1 in Eq. (23) is determined using the property of the screening potential $H(r) = -\gamma(r) - B(r)$ at $r = 0$ given by [14, 23]

$$H(0) = 2(\beta u^{\rm ex} - \tfrac{3}{2})(1 - 2^{(n-2)/3}) , \tag{26}$$

where $u^{\rm ex}$ is the excess internal energy per particle.

As we have shown in our previous papers, $\varepsilon_4(r)$ yields a significant oscillatory behavior around zero value at an intermediate distance range for a highly supercooled regime, which is responsible to the splitting of the second peak of the PDF. On the other hand, the oscillatory behavior disappears for stable liquid states. In this case, $\varepsilon_4(r)$ at intemediate distances can be expressed as [25]

$$\varepsilon_4(r) \simeq -\tfrac{1}{2} x_i x_j \rho^2 \left[\sum_{k}^{2} \int d\mathbf{r}' h_{ik}(r') h_{kj}(|\mathbf{r} - \mathbf{r}'|)\right]^2 . \tag{27}$$

The right-hand side of Eq. (27) always gives a negative value in a qualitative agreement with a property of the respective bridge functions for the PY or RY approximation [13].

B. Numerical procedures

The MHNCS integral equation has been solved on a FACOM VP-2600 vector processor at Computing and Information Systems Center of Japan Atomic Energy Research Institute. The method used here to solve the integral equation is an iterative procedure proposed by Ng [32]. A number of iterations were made so that the following self-consistent measure Δ is minimized:

$$\Delta^2 = \sum_{i}^{2} \sum_{j}^{2} \int |c_{ij}^{\rm in}(r) - c_{ij}^{\rm out}(r)|^2 r^2 dr . \tag{28}$$

The superscripts "in" and "out" denote the input and output functions, respectively. It took about 100 iterations within about 1 sec 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. $B_H^{\mathrm{PY}}(r,d)$ in Eq. (23) has been calculated with the analytical solution of the PY approximation for the hard-sphere model given by Lebowitz [5]. To solve the integral equation, we used dimensionless length $x = r\rho^{1/3}$. The number of grid points and the 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.

The numerical integration to calculate $\varepsilon_4(r)$ has been carried out using the Legendre expansion of $h(r)$ obtained from the simple HNC equation, as discussed in detail in Refs. [27], [29], and [33], which was originally used for the calculation of the virial coefficients by Barker and Monaghan [34]. In our calculation we have taken the first 11 terms of this expansion, which give an error to be smaller than about 1%, and it takes about 150 seconds for this calculation. A dumping parameter W in Eq. (23) is taken to be $0.2\rho^{-1/3}$ 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 [13, 18, 35].

V. RESULTS

The MHNCS integral equation that has been solved for the binary soft-sphere mixtures in various concentration x_1's ranged from 0.1 to 0.9 by a step size of 0.1. In Table I, both the coupling constant Γ_e and core-size ratio σ_2/σ_1 for which we have studied are summarized together with the values of $P\beta/\rho$, reduced isothermal compressiblity $\rho\chi_T/\beta$, and total coordination number N_e, where

$$N_e = \sum_i^2 \sum_j^2 x_i x_j N_{ij} \ , \tag{29}$$

$$N_{ij} = 4\pi\rho \int_0^{r_{m;ij}} g_{ij}(r) r^2 dr \ . \tag{30}$$

N_{ij} are partial coordination numbers and r_m is the position of the first minimum of each partial PDF. In the calculations, the coupling constant was initially set to the value of the freezing point corresponding to each n and then increased to the supercooled regime. For both fourth- and sixth-inverse power potentials with $\sigma_2/\sigma_1 = 1.4$, a reasonable convergence in the numerical integral equations was not obtained in the supercooled regime. Otherwise a good convergence was attained and the partial PDF's obtained from the MHNCS integral equation exhibit a clear splitting of their second peak in a highly supercooled regime except for $n = 4$.

The equation of state, reduced compressibility, and total coordination number depend only weakly on the number concentration x_1 and the core-size ratio σ_2/σ_1 for a given coupling constant Γ_e as seen from Table I. This means that the equivalent one-fluid approximation, Eq. (8), works well at least for these quantities. We have examined the validity of the conformal solution theory by using partial coordination numbers. The equivalent one-fluid approximation, Eq. (8), together with Eqs. (29) and (30), leads to a simple relation

$$\frac{N_{ij}}{N_e} = \frac{\sigma_{ij}^3}{\sigma_e^3} \ , \tag{31}$$

and therefore

$$N_{11} \le N_{12} \le N_{22} \ . \tag{32}$$

It becomes evident from Fig. 1 that the one-fluid approximation, Eq. (31), is no longer valid, and the deviation becomes more remarkable for softer potentials like fourth- and sixth-inverse-power potentials. In the case of the fourth-inverse-power potential, the inequality, Eq. (32), fails and instead it holds $N_{11} > N_{12}$, indicating that the system favors homocoordination over heterocoordination or a tendency of phase separation. Note that when $x_1 \simeq 0$ or $x_1 \simeq 1$, the partial coordination number for a dominant species tends to its ideal value consistent with the conformal solution theory.

The phase-separation condition was examined with

TABLE I. Summary of calculations with the MHNCS integral equation. Values of the equation of state $P\beta/\rho$, reduced compressibility $\rho\chi_T/\beta$, and total coordination number N_e are those obtained by averaging over the number concentration x_1. Each second column denotes a mean deviation over different x_1's.

n	Γ_e	σ_2/σ_1	$P\beta/\rho$		$\rho\chi_T/\beta$ (units of 10^2)		N_e	
4	5.54	1.2	109.45	± 0.05	0.4637	± 0.0002	13.47	± 0.05
6	2.18	1.2	40.35	± 0.03	1.064	± 0.007	12.92	± 0.03
6	2.8	1.2	63.48	± 0.06	0.671	± 0.004	12.98	± 0.05
6	3.6	1.2	101.2	± 0.1	0.417	± 0.002	12.95	± 0.03
9	1.33	1.2	23.14	± 0.02	1.62	± 0.02	12.62	± 0.02
9	1.7	1.2	41.73	± 0.06	0.879	± 0.007	12.74	± 0.04
9	2.1	1.2	71.6	± 0.1	0.504	± 0.004	12.72	± 0.02
12	1.15	1.2	19.87	± 0.01	1.73	± 0.02	12.46	± 0.04
12	1.3	1.2	28.01	± 0.03	1.213	± 0.009	12.56	± 0.03
12	1.5	1.2	42.96	± 0.08	0.779	± 0.006	12.61	± 0.03
9	1.33	1.4	23.6	± 0.2	1.58	± 0.03	12.53	± 0.04
12	1.15	1.4	20.4	± 0.2	1.68	± 0.03	12.39	± 0.05

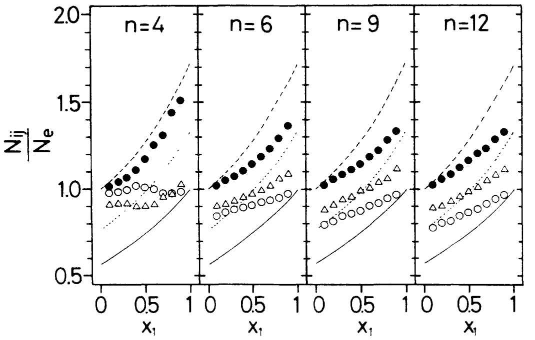

FIG. 1. N_{ij}/N_e calculated with the MHNCS approximation near the freezing point for the core-size ratio $\sigma_2/\sigma_1 = 1.2$. Points marked by ○, △, and ● are those of N_{11}, N_{12}, and N_{22}, respectively. Respective predictions with the one-fluid approximation, Eq. (31), are plotted by solid, dotted, and dashed curves.

the stability parameter $x_1x_2/S_{CC}(0)$ (Fig. 2). As already noted with Eq. (10), the approximate form of $x_1x_2/S_{CC}(0)$, based on the conformal-solution theory, involves the reduced compressibility $\rho\chi_T/\beta$. With this approximation, Eq. (10), and the values of $\rho\chi_T/\beta$ in Table I, no phase separation can be predicted to occur. The correct values of the stability parameter, however, indicate a demixing tendency, which becomes remarkable for softer potentials. Especially for the fourth-inverse-power potential, $x_1x_2/S_{CC}(0)$ yields no positive value in the concentration range of $0.4 \lesssim x_1 \lesssim 0.8$, which means that the system is no longer forming a stable mixture in this regime, i.e., the phase separation is predicted. We should note that the dependency of $x_1x_2/S_{CC}(0)$ on the number concentration is not symmetric about the equimolar line, $x_1 = 0.5$, suggesting a breakdown of the quadratic form in the excess mixing energy, Eq. (5). Similar results are reported for the hard-sphere mixtures [8].

To obtain a dependence of the characteristic energy of mixing on the softness parameter, we have calculated the interchange energy with Eq. (4). The interchange energy w has been determined using the following equation obtained by integrating Eq. (6):

$$2\beta w \int_0^1 p(x_1)dx_1 = \int_0^1 \left[1 - \frac{x_1x_2}{S_{CC}(0)}\right] dx_1 \, . \qquad (33)$$

Here, we assume the quadratic form of $P(x_1)$ [Eq. (5)] for the sake of simplicity. The zero-pressure condition, Eq. (19), was also applied. In Fig. 3, the reduced interchange energy $w^* = w/\varepsilon$ is shown together with the freezing temperature and the stability limit point of one-component soft-sphere fluid [18], which can be interpreted as a lower limit of the glass-transition temperature. It is clearly seen that w^* is much smaller than the freezing temperature for the ninth- and twelfth-inverse-power potentials. This indicates that these mixtures can be easily supercooled without causing a phase separation. Since as the core-size ratio increases the interchange energy substantially increases, a mixture with a larger core-size ratio will presumably lead to a phase separation even in a normal liquid state for the softness $n = 9$ and 12 [1]. For $\sigma_2/\sigma_1 = 1.2$, a ratio of the interchange energy to the excess-internal energy due to the repulsive part of potentials yields an almost constant value irrespective to the value of the softness parameter (Table II). On the other hand, for the larger core-size ratio, $\sigma_2/\sigma_1 = 1.4$, w seems to be sensitive to the softness of the repulsive core potential.

Comparison of the present results of w with the experimental values for inter-alkali-metallic alloys [6] is found to be in a good agreement. The interchange energy has been found to be $w = 0.145k_BT$ and $0.94k_BT$ for KCs and NaK liquid alloys, respectively, at 373 K. Taking the potential parameter ε shown in Table III and assuming for ε_{ij} the average of each combination, w/ε is found to be 0.053 and 0.39 for KCs ($\sigma_2/\sigma_1 \sim 1.15$) and NaK

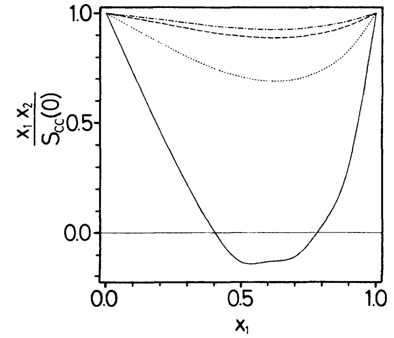

FIG. 2. $x_1x_2/S_{CC}(0)$ vs the number concentration x_1 for the soft-sphere mixtures near the freezing points with the core-size ratio $\sigma_2/\sigma_1 = 1.2$; the softness parameters are $n = 4$ (solid curve), 6 (dotted curve), 9 (dashed curve), and 12 (dotted-dashed curve), respectively.

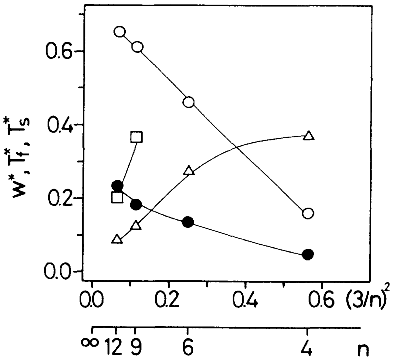

FIG. 3. Softness (n) dependence of the reduced interchange energy $w^* = w/\varepsilon$ for the soft-sphere mixtures obtained from the MHNCS equation near the freezing points. Points marked by △ and □ are for the core-size ratio $\sigma_2/\sigma_1 = 1.2$ and 1.4, respectively. The freezing temperature T_f (○) and the temperature of the stability limit point T_s (●) for the one-component soft-sphere fluids are also plotted in the reduced units, i.e., k_BT_f/ε and k_BT_s/ε, respectively. Curves attached are only for visual clarity.

TABLE II. Ratios of the interchange energy w to the excess repulsive internal energy $U_{\rm rep}^{\rm ex}$ for the soft-sphere mixtures near the freezing point.

n	σ_2/σ_1	$w/U_{\rm rep}^{\rm ex}(\%)$
4	1.2	2.81
6	1.2	3.04
9	1.2	2.85
12	1.2	2.91
9	1.4	8.11
12	1.4	6.52

($\sigma_2/\sigma_1 \sim 1.24$) liquid alloys, respectively. Those values are close to our result for $\sigma_2/\sigma_1 = 1.2$, as seen from Fig. 3. We also examined a similar caluculation for the AKr ($\sigma_2/\sigma_1 \sim 1.07$) mixture. By taking the result of a MC simulation by McDonald [36], $w = 0.19 \pm 0.03 k_{\rm B}T$ at 116 K, and potential parameters shown in Table III, w/ε is estimated to be 0.17 ± 0.03. This value is somewhat larger than our result. This discrepancy suggests that the mixing properties depend on the energy scales of interatomic potentials as well as the atomic size ratio.

For $n = 9$ and 12, the gross feature of $T_c(x_1)$ turns out to be insensitive to the temperature T. For $n = 6$, in the highly supercooled regime, however, the concentration dependence of $T_c(x_1)$ exhibits an anomalous behavior at $\Gamma_e = 3.6$ around $x_1 \simeq 0.7$ as shown in Fig. 4. This anomaly may reasonably be interpreted as a suppression of the long-ranged concentration fluctuation. The first-order approximation of $x_1x_2/S_{CC}(0)$ can be written with the partial coordination numbers as

$$\frac{x_1x_2}{S_{CC}(0)} = \frac{1}{1 + x_1x_2(N_{11} + N_{22} - 2N_{12})} \, . \tag{34}$$

This equation is exact only when the partial pair distribution functions are dumped within a distance characterized by the first coordination shell. It is found that T_c nearly agrees with values estimated from Eq. (34) around $x_1 \simeq 0.7$ where the anomaly occurs, and the partial coordination numbers also turn out to be $N_{11} > N_{12}$ below $x_1 \simeq 0.7$, instead of $N_{11} < N_{12}$ which holds above $x_1 \simeq 0.7$. In such a highly supercooled state, $\varepsilon_4(r)$ in Eq. (23) is responsible for the characteristic feature (such as second peak splitting) of the PDF at the intermediate distance effects on such an anomal behavior of $T_c(x_1)$.

TABLE III. Potential parameters for the generalized van der Waals model, n, σ, and ε [16].

Substance	n	σ (Å)	ε (10^{-15}erg)
A	15	3.64	15.1
Kr	15	3.89	21.0
Na	4.8	3.74	146
K	4.8	4.62	133
Cs	4.8	5.33	121

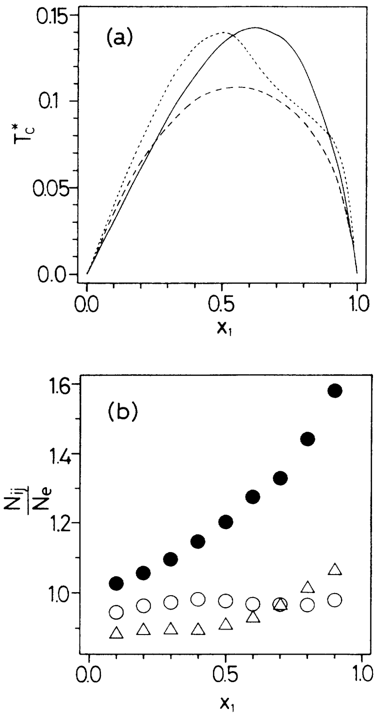

FIG. 4. (a) x_1 dependence of the temperature of the phase separation for the soft-sphere mixtures of the sixth-inverse-power potential with the core-size ratio $\sigma_2/\sigma_1 = 1.2$; coupling constants are Γ_e =2.18 (solid curve) and 3.6 (dotted curve), respectively. The dashed curve is obtained from Eq. (34) for Γ_e =3.6. (b) N_{ij}/N_e obtained from the MHNCS solutions for the sixth-inverse-power potential with Γ_e =3.6 and the core-size ratio $\sigma_2/\sigma_1 = 1.2$. Points marked by ○, △, and ● are those of N_{11}, N_{12}, and N_{22}, respectively.

VI. DISCUSSION

We have studied the mixing properties of the generalized van der Waals supercooled binary mixtures based on the integral equation with the MHNCS approximation. The conformal-solution theory holds well at least for the averaged thermodynamic and structural properties such as the equation of state, isothermal compressiblity, and total coordination number. The long-wavelength limit of $S_{CC}(k)$ significantly depends on the softness parameter of the repulsive potentials and the one-fluid approximation no longer gives correct predictions. As the softness n decreases, a mixture tends to separate into two phases because of a remarkable increase of the interchange energy of mixing. Especially in the case of the fourth-inverse-power potential, the mixture yields a phase separation already near the freezing temperature. In this regime, the partial coordination numbers violate a regular order of magnitudes represented by Eq. (32). The interchange energy depends on the core-size ratio as well as the softness of repulsive core potentials. A mixture with a larger core-size ratio yields a phase separation at a higher temperature. The calculated values of w/ε are in good agreement with the experimental values for inter-alkali-metallic alloys.

T_c (the temperature of phase separation) exhibits an anomalous x_1 (number-concentration) dependence at large x_1 in a supercooled state for the softness $n = 6$. This anomaly is possibly understood as a partial suppression of the long-ranged concentration fluctuation and the characteristic feature (second peak splitting) of the PDF at intermediate distances for highly supercooled liquids, for the latter of which the leading term of elementary diagrams, $\varepsilon_4(r)$, is essential.

In our model mixtures, the temperature dependence of the interchange energy is relatively weak. This suggests that the heat of mixing, e.g., the mixing enthalpy, can be approximated by the Gibbs free energy of the mixing. Thus, it is suggested that a mixture of a softer potential is more difficult to be in a stable amorphous phase than that of a harder potential and therefore possible core-size ratios for a stable amorphous phase are much more strongly restricted for the former than the latter.

ACKNOWLEDGMENTS

This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture (Japan), and the Österreichische Forschungsfonds under Project No. P7618-TEC. Most of the computations were carried out at the Computing and Information Systems Center of Japan Atomic Energy Research Institute and the Institute of Molecular Science.

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