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# Application of the modified hypernetted-chain integral equation to supercooled and expanded liquid structures

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A previously reported modified hypernetted-chain theory is applied to study the structure of liquid metal in the liquid domain well above and below the freezing point. The former liquid domain permits a structural investigation of the metal-nonmetal transition for the expanded liquid metals, whereas the latter liquid domain permits a microscopic understanding of the dynamics of supercooled simple liquids. It was found in this work that the hard-sphere bridge function proposed by Malijevský and Labík [Mol. Phys. **60**, 663 (1987)] is currently the most reliable and accurate means for studying the structure of liquid metals over a fairly wide range of densities.

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In a recent paper [1] we reviewed the present status of theories in the study of liquid structure. It was concluded from our study that for a fluid such as a liquid metal near freezing the modified hypernetted-chain (MHNC) integral equation is the most accurate method presently available. This conclusion finds support in various applications of the theory such as the investigation of expanded liquid metals [2]. The basic structure of MHNC theory was reexamined later in other papers [3,4] within the context of variational MHNC. It appears from these latter works that an appropriate correction related to the widely used analytical Percus-Yevick hard-sphere bridge function $B(r)$ has to be considered seriously for reliably applying a fully self-consistent MHNC theory. In this paper we intend to assess the potential application of the MHNC theory to the problem of supercooled liquid dynamics. This idea was inspired from our recent calculation [5] on the liquid-glass transition using the mode-coupling theory.

The mode-coupling theory, which is based on the kinetic theory of a classical equilibrium liquid and the Zwanzig-Mori formulation, was extended a decade ago by Leutheusser [6] and Bengtzelius, Götze, and Sjölander [7] to a supercooled liquid region. Central to this kind of theory is the density-density correlation function describing the spatial and temporal evolution of particles. It can be shown that the density-density correlation function satisfies a certain self-consistent integral equation and that the latter in turn is expressed explicitly as a functional of the static structure factor $S(q)$, which is the sole input to the theory. Consequently, given $S(q)$ at each lowered temperature or increased pressure, an iterative self-consistent calculation would permit us to extract useful information such as the critical temperature in a supercooled liquid [7], to understand relaxation processes such as the $\alpha$ [8] and $\beta$ [9] dynamics, to deduce the mechanism of diffusive behavior [10], etc. In our previous works we have obtained these $S(q)$'s [or the Fourier-transformed of pair-correlation functions $g(r)$'s] from the molecular-dynamics (MD) simulation. It is our present interest to evaluate $S(q)$ for a monatomic liquid metal using the variational MHNC theory. To our knowledge neither the variational MHNC nor the MHNC has been applied to the metastable states of realistic systems in the literature (closely related works are the one-component soft-sphere fluid by Kambayashi and Hiwatari [11] and the hard-sphere fluid by Malijevský, Labík, and Smith [12] and Nezbeda and Smith [13]).

The study of $g(r)$ as a function of temperature and density begins with the Ornstein-Zernike relation

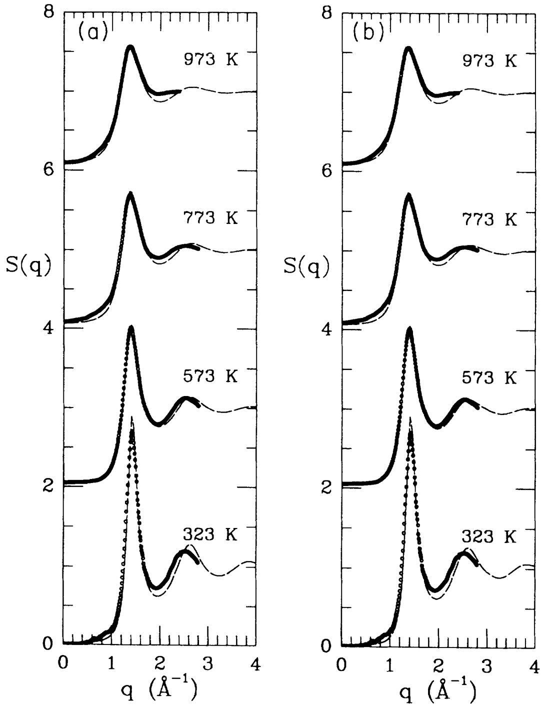

FIG. 1. (a) Static structure factor $S(q)$ (long-dashed curve) for the liquid metal Cs obtained by Fourier-transforming $g(r)$ and calculated using Eqs. (1)–(3) compared with experimental data (open circles) from [18]. (b) Static structure factor $S(q)$ (long-dashed curve) for the liquid metal Cs obtained by Fourier-transforming $g(r)$ and calculated using Eqs. (1), (2), and (4) compared with experimental data (open circles) from [18].

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$$h(r)=c(r)+\rho\int d\mathbf{r}'h(|\mathbf{r}-\mathbf{r}'|)c(r') , \qquad (1)$$

where $\rho$ is the number density, $h(r)=g(r)-1$ and $c(r)$ are the total and direct correlation functions, respectively. To solve this equation one must supplement it with a closure. The most frequently used form is

$$g(r)=\exp[h(r)-c(r)-\beta\phi(r)-B(r)] , \qquad (2)$$

where $\phi(r)$ is the pair potential and $\beta=(k_BT)^{-1}$ is the inverse temperature. Given $\phi(r)$ the pair-correlation function can be obtained by solving Eqs. (1) and (2) iteratively for a prescription of bridge function $B(r)$ [the usual hypernetted-chain approximation corresponds to setting $B(r)=0$]. There are two alternatives to the choice of $B(r)$ according to the variational MHNC [4]. One can take advantage of the analytic Percus-Yevick hard-sphere $B_{\mathrm{PYHS}}(r;\eta)$, $\eta$ being the packing ratio, but as demonstrated in [4] a correction

$$\delta_{\mathrm{HS}}(\eta)=(4\eta-3\eta^2)(1-\eta)^{-2}-6\eta(1-\eta)^{-1}-2\ln(1-\eta)$$

has to be augmented. In this case $\eta$ is fixed by (to be called method *C* below)

$$\partial\delta_{\mathrm{HS}}(\eta)/\partial\eta+\tfrac{1}{2}\rho\int d\mathbf{r}[g^{\mathrm{MHNC}}_{\phi,\mathrm{PYHS}}(r;\eta)-g_{\mathrm{PYHS}}(r;\eta)] \times\frac{\partial B_{\mathrm{PYHS}}(r;\eta)}{\partial\eta}=0 . \qquad (3)$$

Here $g^{\mathrm{MHNC}}_{\phi,\mathrm{PYHS}}(r;\eta)$ and $g_{\mathrm{PYHS}}(r;\eta)$ are the pair-correlation functions in the MHNC theory associated with the $\phi(r)$ and "PYHS"-type potentials, respectively. On the other hand, one can use the "exact" Verlet-Weis-Henderson-Grundke parametric $g_{\mathrm{VWHS}}(r;\eta)$ and $B_{\mathrm{VWHS}}(r;\eta)$ [14,15], in which case the criterion for fixing $\eta$ is (to be called method *D* below)

$$\tfrac{1}{2}\rho\int d\mathbf{r}[g^{\mathrm{MHNC}}_{\phi,\mathrm{VWHS}}(r;\eta)-g_{\mathrm{VWHS}}(r;\eta)]\frac{\partial B_{\mathrm{VWHS}}(r;\eta)}{\partial\eta}=0 . \qquad (4)$$

Employing a highly reliable $\phi(r)$ [16,17], Eqs. (3) and (4) have been applied previously [4] to the calculation of $S(q)$ for liquid metals Na, K, Rb, and Cs near freezing. Both criteria yield similar liquid structure factors that are in reasonably good agreement with measured data. To test further the usefulness of the variational MHNC theory, it is perhaps more instructive to extend our calculation to the liquid domain away from the melting temperature. To this end we first perform an iterative calculation for the liquid metal Cs at elevated temperatures. Figures 1(a) and 1(b) compare observed values [18] with $S(q)$'s calculated respectively from Eqs. (1)–(3) and Eqs. (1), (2), and (4). It can be inferred from the comparison that the theoretical $S(q)$'s well above freezing are of equally good quality with what we found for liquid alkali metals near freezing and with those reported by others [2,3] for the expanded liquid metals. With these encouraging results we proceed next with our variational MHNC calculation focusing now on temperatures below

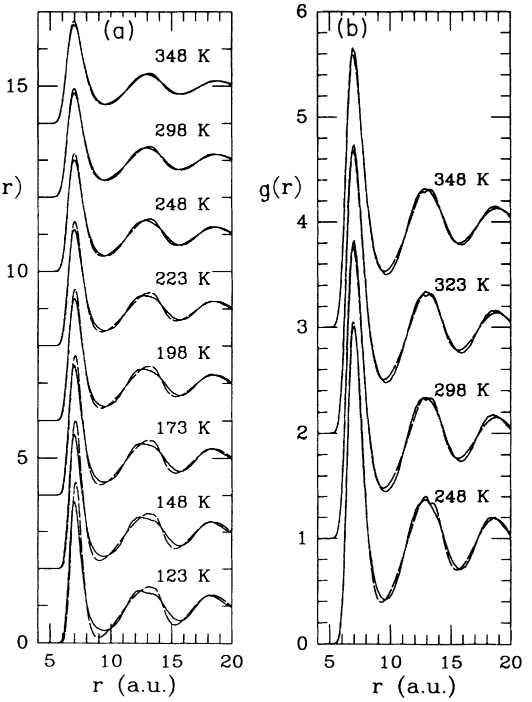

FIG. 2. (a) Pair-correlation function $g(r)$ (long-dashed curve) for the liquid metal Na calculated using Eqs. (1)–(3) compared with molecular-dynamics data (full curve) from [5]. (b) Pair-correlation function $g(r)$ (long-dashed curve) for the liquid metal Na calculated using Eqs. (1), (2), and (4) compared with molecular-dynamics data (full curve) from [5].

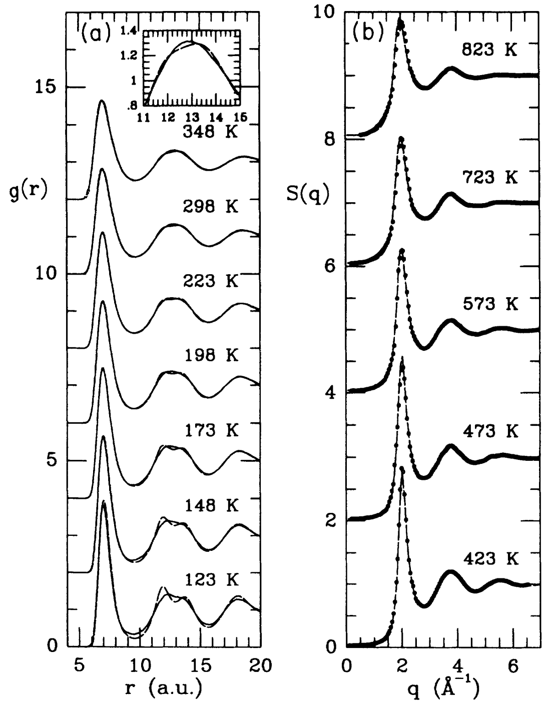

FIG. 3. (a) Pair-correlation function $g(r)$ (long-dashed curve) for the liquid metal Na calculated using Eqs. (1), (2), and (5) compared with molecular-dynamics data (full curve) from [5]. The inset corresponds to the second peak region of $g(r)$ at $T=348$ K. (b) Static structure factor $S(q)$ (long-dashed curve) for the liquid metal Na by Fourier-transforming $g(r)$ and calculated using Eqs. (1), (2), and (5) compared with experimental data (open circles) from [21] for $T=423$ K and from [22] for others.

freezing. The liquid metal Na was taken as our prototype system of investigation. There are two reasons. One is the fact that realistic $\rho$ vs $T$ data for the Na system are available [5] and the other is because of the unavailability of experimental data for Cs $S(q)$'s below freezing, while the MD simulation for the Na system has been performed previously [5]. In Figs. 2(a) and 2(b) we present the calculated $g(r)$'s obtained using the above-mentioned two criteria and they are compared separately with the same MD $g(r)$'s. There are several discernible features that merit emphasis.

First of all we see that the overall agreement between MD $g(r)$'s and those calculated in methods $C$ and $D$ is qualitatively satisfactory. Quantitatively method $C$ is capable of yielding $g(r)$'s at sufficiently low $T$, but the computed principal peak of $g(r)$ is overestimated somewhat; this overestimation is seen to be more pronounced as $T$ is decreased. On the other hand, for $g(r)$'s calculated in method $D$, we obtain quite different behavior. Here we notice that the iterative calculation fails at $T=223$ K (no solution) and, for the successful ones above this $T$, the calculated first peak of $g(r)$ relative to MD's is seen to be slightly underestimated from near freezing to $T$ below. For both methods $C$ and $D$, a relative shift in phase at the first minimum and beyond is clearly noticeable. These discrepancies between the MHNC theory and the MD simulation suggest the inadequacies of the methods and can be physically traced back to the use of the hard-sphere $B(r)$. In method $C$ the Percus-Yevick hard-sphere approximation is surely not accurate enough for a fluid at high densities. This argument applies partly also to the Verlet-Weis-Henderson-Grundke approximation, for $B_{\mathrm{VWHS}}(r;\eta)$ may be subject to numerical uncertainties due to inverse Fourier transformation (see the comments in Ref. [19]). Accordingly, despite the fact that method $D$ is quantitatively preferable for obtaining a reasonable $g(r)$, it is nevertheless not a good starting approach for the study of the liquid$\rightarrow$glass transition problem.

The above deficiencies imply a need to seek a more accurate hard-sphere $B(r)$. A guide toward this goal is to adopt a theory such that for any proposed $B(r)$ it should ensure agreement with the computer simulation data of hard spheres. Malijevský and co-workers [12,19,20] have in fact made a very successful attempt. In their original work [19] these authors assumed an empirical analytic expression for the bridge function $B_{\mathrm{MLHS}}(r)=b^2(r)$ where

$$b(r)=\begin{cases}[a_1+a_2(r/\sigma-1)][r/\sigma-1-a_3][r/\sigma-1-a_4]/(a_3a_4), & r\le a_4\sigma\\ A_1\exp[-a_5(r/\sigma-1-a_4)]\sin[A_2(r/\sigma-1-a_4)]/r, & r\ge a_4\sigma\end{cases} \tag{5}$$

$\sigma$ being the hard-sphere diameter and the parameters $A_i$ and $a_i$ are determined, respectively, by continuity conditions and by fitting to all known structural and thermodynamic computer simulation data of hard spheres over the entire fluid range up to the density of freezing. We have substituted Eq. (5) and its associated $g_{\mathrm{MLHS}}(r;\eta)$ [obtained by solving Eqs. (1) and (2) for a hard-sphere system with $B_{\mathrm{MLHS}}(r;\eta)$] into Eq. (4). An iterative calculation with Eqs. (1) and (2) is then repeated. The results of computations are depicted in (a) Fig. 3(a) along with the MD $g(r)$'s from [5] for $T$ below freezing and (b) Fig. 3(b) along with the experimental $S(q)$'s [21,22] for $T$ above freezing. It is interesting to note two points. First, for $T>373$ K, the calculated $S(q)$'s agree excellently with the measured $S(q)$'s throughout a wide range of $q$ values notably at different positions of peaks and valleys; this quality of the liquid structure persists below $T=373$ K down to $T=173$ K where the $g(r)$'s obtained compare very well also with the MD $g(r)$'s. Second, there appears a distinct shoulder near the second maximum at a lower $T$ near freezing and the subsequent change of it into a double-peak structure at a much lower $T$. The first point is clearly due to our choice of $B_{\mathrm{MLHS}}(r;\eta)$, which has been assessed critically by Malijevský and co-workers [12,20]. As for the occurrence of a shoulder or subpeaks, its existence is theoretically unknown, but it is believed to be a characteristic feature of the hard-sphere system having a density that is greater than the freezing density ($\eta\approx0.49$, Ref. [12]). Recent Monte Carlo simulation of hard spheres seems to substantiate this point (see Fig. 1 in Ref. [20]).

In conclusion we have examined the MHNC integral equation theory and confirmed positively the possibility of extending it to the study of liquid structure factors of metals at $T$ well above and below freezing. Our results of calculations show that the hard-sphere $B(r)$ proposed by Malijevský and Labík is capable of yielding reasonably accurate structural data; the theory is sufficiently quantitative also for making realistic the structural study of expanded liquid metals and the dynamics of supercooled liquids.

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