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A new bridge function scheme in the modified hypernetted-chain approximation for liquid alloys

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Abstract. We propose a new choice of the reference bridge functions to be employed in the modified hypernetted-chain (MHNC) approximation for determining the structure of a liquid alloy. The reference system we choose is the one interacting with the repulsive part of the interatomic potentials. The new scheme is applied to a liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy and it is shown that the calculated radial distribution functions are in excellent agreement with those of the molecular dynamics simulation. The results are also compared with those of the HNC and PY approximations as well as those of the MHNC scheme in which the bridge functions of the additive hard-sphere mixture are used.

The modified hypernetted-chain (MHNC) approximation proposed by Rosenfeld and Ashcroft (1979) is known to yield excellent structural and thermodynamic properties for various one-component fluids such as the one-component plasma and the Lennard-Jones liquids. Recently we (Hoshino *et al* 1990, Mori *et al* 1990, Matsuda *et al* 1991) have investigated the structure of liquid alkali metals for a wide range of density along the liquid–vapour coexistence curve in the MHNC approximation and the molecular dynamics (MD) simulation, and shown that the MHNC approximation also yields reliable results for realistic liquid metals in the sense that the results of the MHNC approximation are in excellent agreement with those of the simulation.

In the MHNC approximation, which is based on a ‘universality *ansatz*’ of the ‘bridge function’, one may represent the bridge function of the system under study with the known bridge function of the hard-sphere system. The effective hard-sphere diameter, which is the only parameter characterizing the hard-sphere system, is determined either from a thermodynamic self-consistency (TSC) criterion (Rosenfeld and Ashcroft 1979) or from the Lado criterion derived from an extremum condition on the free energy (Lado 1982, Lado *et al* 1983). Some attempts have also been made to improve the hard-sphere bridge function (Foiles *et al* 1984, Iyetomi and Ichimaru 1982).

There have been some attempts (Rosenfeld 1980, Enciso *et al* 1987) to extend the MHNC approximation straightforwardly to mixtures by using the known bridge functions of the hard-sphere mixture with additive hard-sphere radii (Lebowitz 1964, Grundke and Henderson 1972, Lee and Levesque 1973), but the pair interactions in actual mixtures are generally not additive. Though several approaches have been proposed for specific systems such as molten salts (Caccamo *et al* 1984, Ballone *et al* 1984, Zerah and Hansen 1986), they are not suited to being applied to liquid alloys. In this paper we

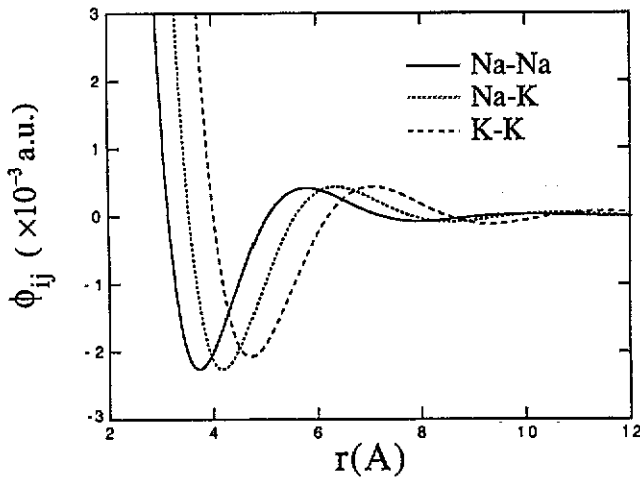


Figure 1. The effective pair potentials of the liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy at $T = 380$ K.

propose a new scheme of calculating the reference bridge functions appearing in the MHNC approximation and apply it to a liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy.

The Ornstein-Zernike relation for a two-component mixture is written as

$$h_{ij}(r) = c_{ij}(r) + \sum_{k=1}^2 n_k \int ds c_{ik}(s) h_{kj}(|r-s|) \quad (1)$$

where $h_{ij}(r)$ ($= g_{ij}(r) - 1$, $g_{ij}(r)$ being the partial radial distribution function) is the total correlation function, $c_{ij}(r)$ is the direct correlation function and n_k is the number density of the k th species. On the other hand, from the diagrammatic expansion, $g_{ij}(r)$ is exactly expressed by (Morita and Hiroike 1961)

$$g_{ij}(r) = \exp(-\beta\varphi_{ij}(r) + h_{ij}(r) - c_{ij}(r) + B_{ij}(r)) \quad (2)$$

where $\varphi_{ij}(r)$ is the interatomic potential, $B_{ij}(r)$ the bridge function and $\beta = 1/k_B T$.

In the MHNC approximation, we replace $B_{ij}(r)$ by the bridge function for some reference system. We propose here to choose the reference system interacting with the repulsive part of the interatomic potentials $\varphi_{ij}(r)$:

$$\varphi_{ij,\text{rep}}(r) = \begin{cases} \varphi_{ij}(r) - \varphi_{ij}(R_{ij}) & r < R_{ij} \\ 0 & r > R_{ij} \end{cases} \quad (3)$$

where the R_{ij} are the positions of the first minimum of $\varphi_{ij}(r)$. This choice is based on the assumption that the bridge functions $B_{ij,\text{rep}}(r)$ of this reference system are nearly equal to the real $B_{ij}(r)$. In our actual calculation we obtained $B_{ij,\text{rep}}(r)$ by solving the PY equations numerically. It is expected to be reasonable to assume that the PY approximation is good for this reference system, since the PY approximation is known to be good for one-component liquids with highly repulsive short-range forces. It should be noted that our new scheme can be used for non-additive as well as additive potentials. The scheme is also particularly useful for practical numerical calculations, since it contains no disposable parameter.

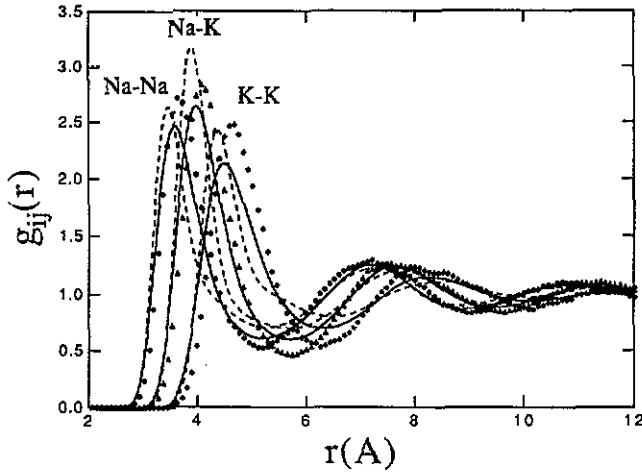


Figure 2. The pair correlation functions of the liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy obtained by the HNC (full curves) and the PY (dashed curves) approximations are compared with MD simulation (points).

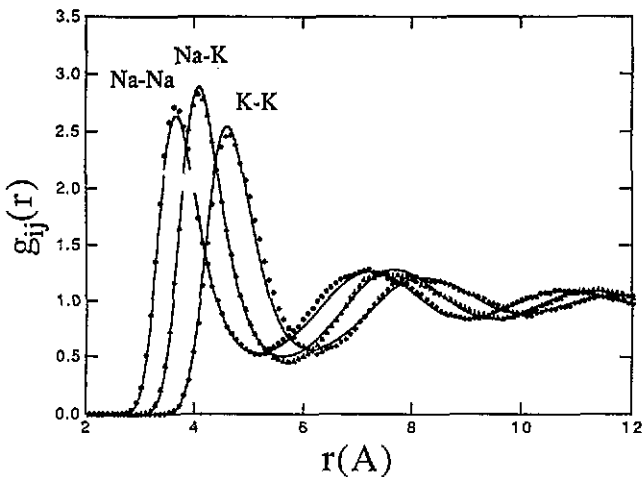


Figure 3. The same as figure 2, but the full curves are the results of the MHNC approximation with the bridge function $B_{ij,rep}(r)$ mentioned in the text.

We show here the results for the liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy at $T = 380$ K. In our calculation we obtain the effective pair potentials $\varphi_{ij}(r)$ in the pseudopotential theory, in which we use the local empty-core pseudopotential due to Hasegawa *et al* (1990) and the dielectric function with the local field correction due to Ichimaru and Utsumi (1981). We use the observed density of 0.866 g cm^{-3} . The pair potentials thus obtained are nearly additive as shown in figure 1. Using these pair potentials we calculated the structure functions of the liquid $\text{Na}_{0.5}\text{K}_{0.5}$ by the HNC, PY and MHNC approximations with the bridge functions both for the additive hard-sphere mixture and for the repulsive-potential reference

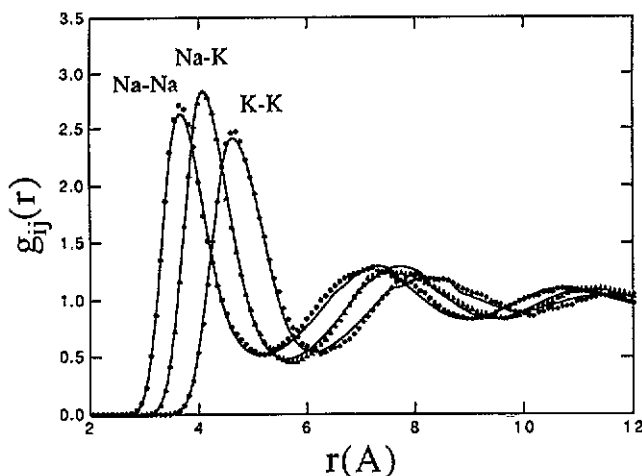


Figure 4. The same as figure 2, but the full curves are the results of the MHNC approximation with the additive hard-sphere bridge functions determined by the extended Lado criterion.

system proposed here. We also performed a standard MD simulation for the same system (consisting of 1000 atoms) using the same pair potentials.

Firstly, the radial distribution functions obtained by the HNC and PY approximations are compared, in figure 2, with those of the MD simulation—the agreement between them is poor.

In figure 3, the results obtained in the MHNC approximation by employing the bridge function, $B_{ij,rep}(r)$, are shown. Overall agreement of these with the MD results is much improved in comparison with the HNC and PY results shown in figure 2 and may be said to be excellent.

Since the pair potentials of the liquid Na–K alloy are nearly additive, it is expected that the MHNC approximation, by employing the bridge function of the additive hard-sphere mixture, gives rise to reasonable results for the structural functions of this alloy. In fact, as is shown in figure 4, the results are in excellent agreement with the MD results.

In conclusion, our new bridge function scheme in the MHNC approximation yields excellent results for the liquid $\text{Na}_{0.5}\text{K}_{0.5}$ alloy and is a promising method for the study of the structure of liquid alloys. The application of this scheme to strongly non-additive cases, to which the additive hard-sphere mixture is not expected to be an appropriate reference system, is now in progress.

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