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Bridge function for liquid Na

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Bridge function $B(r)$ for liquid Na is calculated in the referense hypernetted chain approximation from the pair distribution function obtained by means of MD simulations. A comparison with the bridge function obtained in a Mori-Hoshino-Watabe scheme is made. The influence of the cut-off radius and the MD sample size on the structure factor is investigated.

Key words: *static structure factor, bridge function, integral equation*

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1. Introduction

It has been proven in the recent years that the reference hypernetted chain approximation (RHNC) is the most successful approach among various liquid-state theories to the study of the structure and thermodynamics of liquids. It is based on the universality hypothesis of a bridge-functional [1] and has led to very satisfactory results for a large variety of liquid systems such as a one-component plasma [2] and Lennard-Jones liquids [3]. This technique was also applied in calculations of the structure factor of liquid alkali and polyvalent metals [4–7]. Recently, the RHNC theory has been generalized for the study of the partial structure factors of liquid binary alloys [8,9].

Following Rosenfeld and Ashcroft [10], the exact bridge function $B(r)$ in the closure of the Ornstein-Zernike (OZ) relation is replaced by the bridge function of a suitably chosen reference system. Usually, a hard-sphere system in the Percus-Yevic approximation is used as such a reference system. The effective hard-sphere diameter, which is the only parameter characterizing the hard-sphere system, is determined either from a thermodynamic self-consistency criterion [10] or from the Lado criterion derived from the extremum condition of free energy [2].

Another way to construct the bridge function was proposed by Mori-Hoshino-Watabe (MHW) [9]. It consists in choosing a system interacting via the repulsive part of the interatomic potential as a reference system. The bridge function of such a system obtained in the Percus-Yevic (PY) approximation is assumed to be nearly equal to the actual $B(r)$. This scheme is useful for practical calculations, since it contains no adjustable parameters.

In the recent years an approach based on a combination of computer simulation and integral equation techniques has been developed and applied to the description of the equilibrium properties of liquid systems [11,12]. The pair distribution function (PDF) obtained in molecular dynamics simulation with a relatively small number of particles, is extended to large r by means of integral equations. It is then possible to extract an 'exact' bridge function and to compare it with various model results.

In the present paper, the structure factor of liquid Na is calculated by means of a combined use of the RHNC theory and MD simulations. This system may be considered in the nearly-free-electron approximation and, therefore, the pseudopotential perturbation theory can be applied. This fact has stimulated an appreciable amount of theoretical work on liquid Na with diverse forms of the interacting potential: the Ashcroft [13] and Hasegawa [14] empty-core pseudopotentials, the potential implemented by Price, Singwi and Tosi [15]. Some first-principle calculations have also been carried out for this system [17]. Recently, the static structure in good agreement with the experimental data has been obtained in the RHNC theory for liquid Na interacting via an effective pair potential derived by means of the neutral-pseudoatom method [16].

The aim of this paper is to study in detail the behaviour of the bridge function extracted from MD simulations for metallic systems like liquid Na. The obtained bridge function was compared with the MHW model. The next section gives a brief summary of the theory. In section 3 we discuss the most significant results of the calculations.

2. The basic theory

In the integral equation theory the pair correlation function $g(r)$ can be obtained by solving the Ornstein-Zernike relation

$$h(r) = c(r) + \rho \int c(|\vec{r} - \vec{r}\,'|)h(r')\mathrm{d}\vec{r}\,', \tag{1}$$

where ρ is a number density of the liquid, $h(r) = g(r) - 1$ is a total correlation function and $c(r)$ – a direct correlation function. Equation (1) is supplemented by a closure between $h(r)$ and $c(r)$:

$$g(r) = \exp\left(\gamma(r) - \beta U(r) + B(r)\right). \tag{2}$$

Here $\beta = 1/k_{\mathrm{B}}T$ is inverse temperature , $U(r)$ is an interacting potential, $\gamma(r) = h(r) - c(r)$ and $B(r)$ is a bridge function. The detailed knowledge of the bridge function is necessary to solve this integral equation for a given potential. In order to extract the bridge function from the PDF calculated by MD simulation we extended $g^{\mathrm{MD}}(r)$ beyond the simulated box following the procedure proposed by

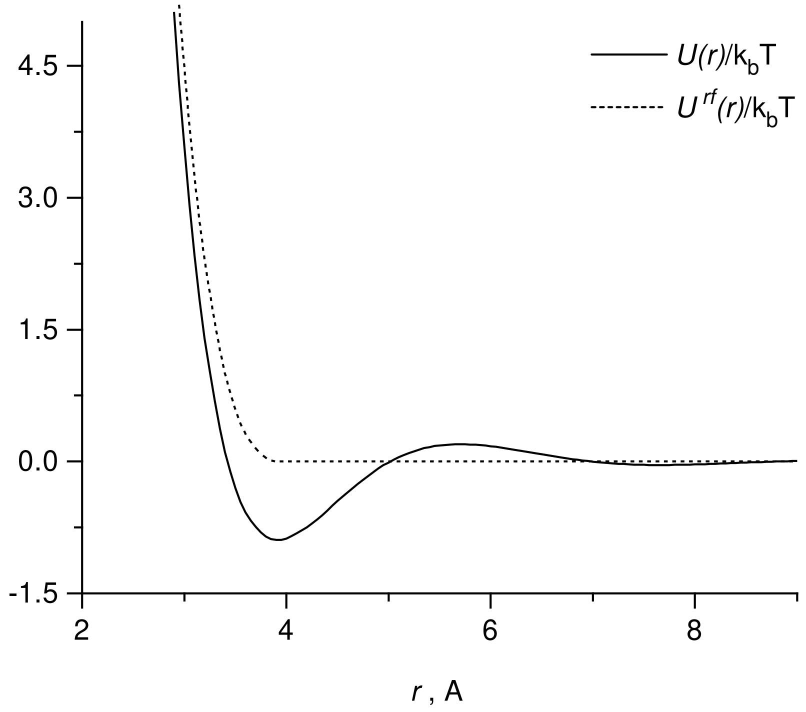

Figure 1. The interacting potential for liquid Na and the potential for the MHW reference system.

Galam and Hansen [18] which reduces to solving (1) coupled with the MSA closure:

$$c(r) = \begin{cases} g^{\mathrm{MD}}(r) - 1 - \gamma(r), & r < R_{\mathrm{c}} \\ -\beta U_{\mathrm{m}}(r), & r > R_{\mathrm{c}} \end{cases}, \tag{3}$$

where $g^{\mathrm{MD}}(r)$ is the simulated pair distribution function, R_{c} is a cut-off distance and $U_{\mathrm{m}}(R)$ is a cut potential used in the simulation. The cut-off radius R_{c} in fact is limited to half a simulation box length $L/2$. The bridge function can now be extracted from $g(r)$ and $\gamma(r)$ via the following relation:

$$B(r) = \gamma(r) - \ln g(r) - \beta U(r). \tag{4}$$

For completeness we also solved equations (1)–(2) by using the bridge function derived from the Mori-Hoshino-Watabe scheme. In the MHW approximation the system interacting via the repulsive part of the interatomic potential $U(r)$ is only chosen as a reference system:

$$U^{rs}(r) = \begin{cases} U(r) - U(r_{\mathrm{m}}), & r < r_{\mathrm{m}} \\ 0, & r > r_{\mathrm{m}} \end{cases}, \tag{5}$$

where r_{m} is the first minimum of $U(r)$.The bridge function of such a system is calculated in the PY approximation which is known to give good results for repulsive potentials. Obtained in this way $B(r)$ is assumed to be nearly equal to the real one [9].

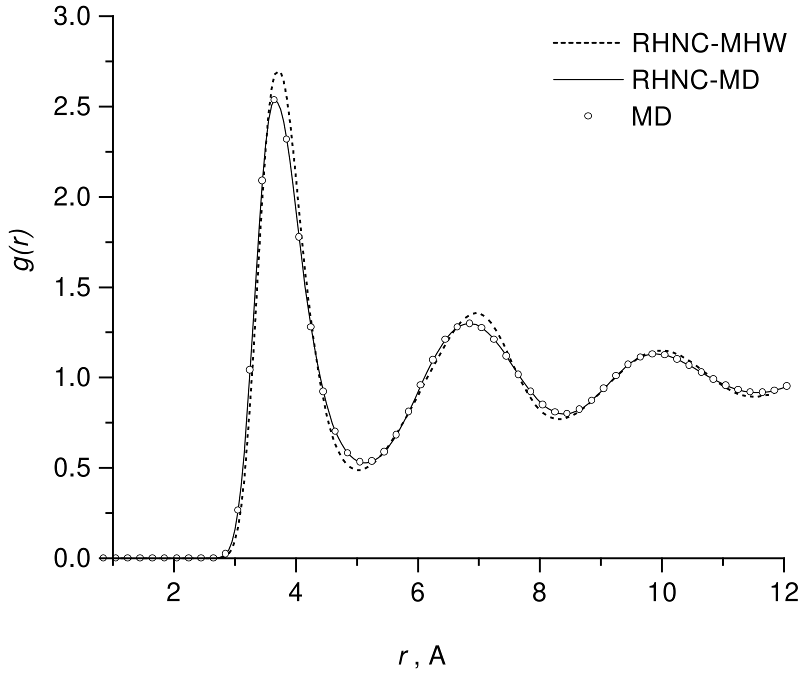

Figure 2. The sample II MD pair distribution function $g(r)$ for liquid Na together with the PDFs from the RHNC equation with two bridge functions: extracted from the MD data (RHNC-MD), and from the MHW reference system (RHNC-MHW)

3. Results

We have investigated liquid Na at the numerical density $\rho = 0.024217$ Å^{-3} and temperature T=373 K. The interatomic potential was calculated from the local Ashcroft empty-core pseudopotential. Although nowadays more sophisticated methods exist to construct effective interatomic potential in liquids, we stick to this rather simple model potential as it is able to produce excellent results for the static structure of liquid metals (for an overview see Hafner [20]). The only parameter of the potential is the core-radius r_c, which is chosen to be 1.78 a.u., that guarantees a zero-pressure condition for the solid state at T=0 K and gives good agreement with an experiment for the static structure factor over a large temperature range [13]. A dielectric screening function is used with the local-field correction proposed by Ishimaru and Utsumi. The function $\beta U(r)$ for liquid Na, together with that used for the MHW reference system, is plotted in figure 1. The molecular dynamics simulations were performed in the usual (NVE) ensemble for two different system sizes. Sample I contains 864 particles and sample II has 2048 particles. Integration of the equations of motion was done by a 4th-order predictor-corrector Gear algorithm with the time step 4×10^{-14} s. The initial configuration of particles was a face-centred cubic lattice, and their initial velocities were randomly put into a Maxwellian distribution. In the first stage of the simulations the system was molten at 900 K to break the lattice. In the second run temperature was

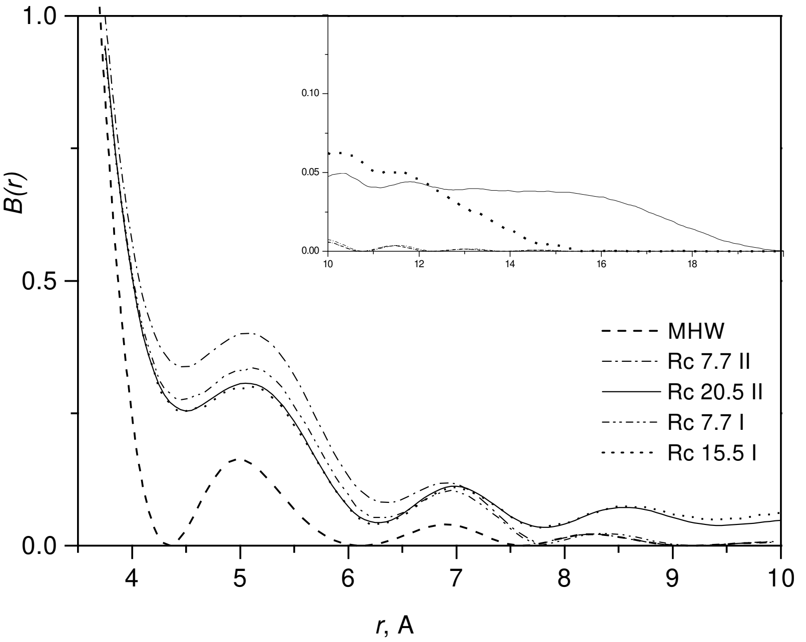

Figure 3. The extracted from MD simulations bridge functions at different cut-off radii and $B(r)$ of the MHW reference system. Sample I consists of 864 particles and sample II – of 2048 particles.

lowered by a slow cooling process down to 373 K and another 2000 steps were taken to equilibrate the system at the new temperature. The productional run in the equilibrium state was of 100 000 time steps for system I and 50 000 for system II. The total energy was conserved during the MD runs within 0.05% and may be regarded constant. Every tenth configuration was taken into account in the computation of the static equilibrium averages.

The pair distribution function obtained in MD simulations was used to generate the bridge function following the procedure described in section 2. The integral equations (1)–(3) were solved numerically by means of a Newton-Raphson method [21] with the accuracy of 1.0×10^{-6}. In figure 2, we show the pair correlation functions obtained with the bridge function extracted from the MD data (RHNC-MD) and that calculated by using the MHW scheme (RHNC-MHW). We also depict the pair distribution function obtained directly from MD simulation for a larger system. An agreement between the RHNC-MD and the simulation is excellent even beyond R_c, whereas the RHNC-MHW shows some discrepancies in the magnitude of the first and second peaks. Some further suggestions as to these discrepancies will be made later.

In order to assess the cut-off radius dependence in the MD-data extension procedure we used several values of R_c. The bridge functions for the two sample sizes calculated with the smallest ($R_c = 7.7$ Å) and the largest (equal to half the cell length) PDF cut-off radii are presented in figure 3 together with the bridge function from the MHW approximation. The rest of $B(r)$ fall between these two extreme cases. The results for $B(r)$ at large values of r are plotted in the inset of

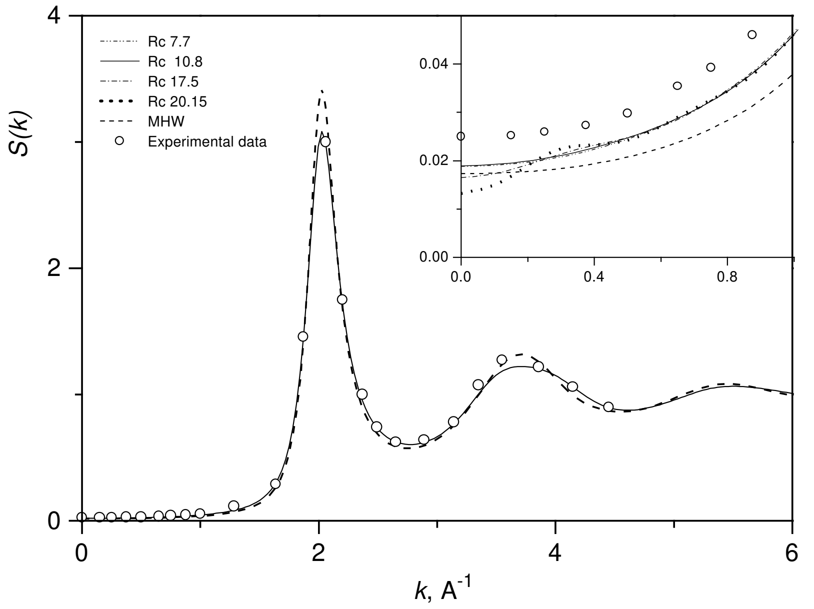

Figure 4. A structure factor for liquid Na calculated from the RHNC equation with different bridge functions for sample II.

figure 3. One readily sees that all the curves exhibit the same qualitative behaviour. For short distances, which correspond to the first and second coordination shells, the cut-off and sample size dependencies of the MD bridge functions are almost negligible and all $B(r)$ are remarkably close to each other. At larger values of r the influence of the sample size becomes more noticeable. It is clearly seen that the bridge function for sample II reaches a plateau near $13-14$ Å which smoothly tends to zero at $r = R_c$. It is difficult to find such a plateau for sample I because the simulation cell is too small. A similar plateau is reported in [22], where MD simulations were performed for 4000- and 32000-particle systems. It is found there that this plateau only results from statistical errors in PDF, and its amplitude is almost inversely proportional to the square root of the number of samples used in evaluating the PDF. The plateau can be reduced to zero by increasing either the number of particles or the number of PDF samplings.

The MHW bridge function exhibits a correct behaviour at short distances where it reproduces the positions of maxima and minima of the "experimental" bridge function. At larger r, it merges with the MD $B(r)$ of the smallest cut-off radius. The magnitudes of these two functions, however, are rather different. In purely metallic systems, where the interatomic potential has a long-range oscillatory character, one cannot safely neglect the potential's attractive tail without having grave consequences in $B(r)$ and, as a result, in $g(r)$ as shown in figure 2.

Finally, we investigated the cut-off and sample size dependence of the static structure factor $S(k)$. In figure 4 we plotted the structure factors calculated by using various sets of bridge functions for sample II. We found that $S(k)$ practically does not depend on the sample size. The small-k behaviour of the structure factors is shown in the inset of figure 4. For comparison we also depicted the experimental x-ray data of Waseda [23]. The value of $S(k)$ at $k = 0$ was calculated from the compressibility data. It should be noted that all structure factors with the MD bridge functions are hardly distinguishable from each other and merge into one curve. In a small-k region all $S(k)$ calculated with R_c up to the plateau coincide. For those cut-off radii belonging to the plateau (R_c=17.5 and 20.15) the statistical errors become large enough to distort the shape of the structure factor at $k \to 0$. The static structure factor calculated with the MHW bridge function reproduces the MD results quite accurately, with small discrepancies in the magnitudes of the main and second peaks.

Two conclusions can be drawn concerning the investigation of the bridge function for liquid metals considered here. Firstly, the bridge function and the static structure factor slightly depend on the cut-off radii and practically do not depend on the sample size. As a result, the combined use of MD simulations for a relatively small number of particles with the RHNC-type integral equations provides a powerful tool for the description of the microscopic structure of liquid metals. Such a combination is especially useful in *ab initio* calculations that deal with small sample sizes. Secondly, the reference system proposed by Mori, Hoshino and Watabe, described by the repulsive part of the pair potential and involving no adjustable parameters, gives a good account of the static structure of liquid metals.

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Елементарні діаграми для рідкого Na

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Елементарні діаграми $B(r)$ для рідкого Na розраховані в базисному гіперланцюговому наближенні з парних функцій розподілу отриманих методом МД. Проведено порівняння з $B(r)$ в наближенні Морі-Хошино-Ватабе. Досліджено залежність статичного структурного фактора від радіуса обрізання базисної парної функції розподілу.

Ключові слова: *статичний структурний фактор, елементарні діаграми, інтегральні рівняння*

PACS: *61.25.Mv, 65.50.+m, 61.20.Gy*