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A nearly free-electron model of the pair potential in molten copper

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Abstract. An effective interionic pair potential in liquid copper at 1393 K was extracted from the neutron-diffraction data using an iterative fitting procedure based on the modified *hypernetted-chain approach*. The procedure involved extensive molecular-dynamics simulation using a system of 16 384 particles. The potential, constructed within the framework of the nearly-free-electron approximation, is based on the Dagens–Rasolt–Taylor model, and it is repulsive and positive around the first-neighbour distance. The proposed potential when used in molecular-dynamics calculations reproduces, within the limit of experimental accuracy, the structure factor measured by neutron diffraction, including the long-wavelength region of the structure factor and the isothermal compressibility limit, as well as the experimental value of the self-diffusion coefficient. The bridge function of liquid copper derived from the simulation data is compared with a hard-sphere fluid bridge function obtained in the context of the modified hypernetted-chain approximation.

1. Introduction

Ion–ion interactions in metallic systems, in the simplest approximation, can be treated as a superposition of spherically symmetric effective pair potentials. In the past two decades, this approximation has been successfully used in computer simulations to reproduce the structure of a wide range of liquid metals, demonstrating that n -particle interactions ($n \geq 3$) in those systems are either negligible or can be easily incorporated into the effective pair interaction. First-principles calculations of effective interionic pair potentials had a remarkable success for a number of simple metals [1], but quantitatively reliable results for non-simple metals are still beyond the reach of these theories. In the case of d-band metals, the complexity of the interactions within the core invalidates those approximations that assume decoupling of valence and core electrons. Therefore, the development of a reliable *ab initio* pseudopotential for these systems remains an open problem, and thus one must make use of models which are of empirical or semi-empirical nature.

Two attempts to derive effective interionic pair potentials in liquid copper have been published in recent years [2, 3], but the results of these studies show considerable disparity. Lam *et al* [2] proposed a first-principles pair potential that, when tested in molecular-dynamics (MD) simulations, failed to reproduce the experimental structure factor and self-diffusion coefficient. In another attempt, Arai *et al* [3] fitted a purely empirical potential,

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in order to reproduce the x-ray structure factor data of Waseda and Ueno [4], paying special attention to the small- Q region. The two potentials show striking discrepancies in the significant area around the estimated nearest-neighbour distance. Besides that, another source of confusion is the disagreement between the x-ray measurements of the liquid Cu structure factor used by Arai and Yokoyama and data obtained by neutron diffraction, especially in the small- Q region [5]. Therefore the problem of developing an adequate potential model for liquid Cu is far from being closed.

In this study, a nearly-free-electron (NFE) pseudopotential model proposed by Dagens, Rasolt and Taylor (DRT) [6, 7] is used to build a functional form of pair potential with adjustable parameters, that are optimized to fit the structure factor of liquid Cu measured by neutron diffraction. The optimization procedure, based on the modified hypernetted-chain (MHNC) equation [8, 9], involves extensive MD simulations of the structure factor. It will be shown that this procedure provides a rapid convergence of the simulated structure factor, $S(Q)$, to the experimental data given by Eder *et al* [5]. We will also show that this potential is adequate to reproduce the self-diffusion coefficient in liquid copper.

The rest of the paper is organized as follows. A brief description of the DRT model potential is given in section 2. In section 3, we summarize computational aspects of the effective pair potential fitting. Section 4 is devoted to the details of our MD simulations. Finally, in sections 5 and 6 we discuss the most relevant results and present the main conclusions derived from this study.

2. NFE Rasolt–Taylor model

An effective interionic pair potential developed within the framework of the NFE approximation has been employed in the description of ion–ion interactions in liquid Cu. This model was derived from first principles by Dagens, Rasolt and Taylor [6, 7] to study disordered simple metals. Nevertheless, we have used this potential as a semi-phenomenological approximation, in the sense that the potential parameters are here considered as adjustable parameters in an optimization process.

The interionic pair potential can be presented in the following form:

$$u(r) = \frac{(Ze)^2}{r} - \frac{1}{(2\pi)^3} \int \frac{4\pi(Ze)^2}{Q^2} F(Q) \exp(-i\mathbf{Q} \cdot \mathbf{r}) d\mathbf{Q} \quad (1)$$

where Z is the valence and e the electron charge. The energy-wave-number characteristic function, $F(Q)$, according to Rasolt and Taylor, is a functional of the non-local pseudopotential $v_p(r)$ (see (1)–(26) in [6]), which formally represents the full ionic potential. In the variable-phase method, adopted in [6], the pseudopotential is described by

$$v_p(r) = \sum_{l=0}^L \left[A_l \Theta(R_l - r) - \frac{Ze^2}{r} \Theta(r - R_l) \right] \hat{P}_l. \quad (2)$$

Here $\Theta(x)$ is the step function, \hat{P}_l the angular momentum projection operator and $L = 2$ in most cases. Thus, the variable-phase pseudopotential consists, for each angular-momentum l value, of a square well of constant depth, A_l , for $r < R_l$, and for $r > R_l$ is the ionic Coulomb contribution. Even though the mathematical formulation of the DRT model is rather cumbersome (details are given in both [6] and the appendix of [10]), eventually the evaluation of the interionic potential, $u(r)$, depends only on the quantities A_0, A_2, R_0

and R_1 , via $F(Q)$. Within the original DRT formulation, these system-specific parameters are adjusted so that the linear-response charge density coincides with the non-linear self-consistent results for all $r > R_L$, i.e. for all values outside the ionic core region (for details, see section 2 of [7]). However, in our semi-phenomenological approach, these quantities are regarded as free parameters to be adjusted in an optimization procedure to fit the experimental $S(Q)$ of liquid Cu as described in the following section.

3. Determination of the effective pair potential: optimization procedure

Diagrammatic analysis leads to the following general closure relating the pair potential $u(r)$ and the structure of a liquid:

$$g(r) = \exp[-\beta u(r) + g(r) - 1 - c(r) - B(r)] \quad (3)$$

where $\beta = (k_B T)^{-1}$. $B(r)$ is the bridge function which formally incorporates all the higher-order terms in the diagrammatic expansion. This expression forms a closed set together with the Ornstein–Zernike (OZ) equation which, in the wave-vector space, can be expressed as

$$\tilde{c}(Q) = \frac{S(Q) - 1}{\rho S(Q)} \quad (4)$$

where $\tilde{c}(Q)$ is the Fourier transform of the direct correlation function and ρ the number density.

The MHNC approximation is based on the well documented idea, first suggested by Lado [11] and further developed by Rosenfeld and Ashcroft [12], that the bridge function in simple monoatomic liquids can be reduced to a universal family of curves, which can, therefore, be conveniently approximated by the hard-sphere bridge, $B_{HS}(r; \sigma)$. Here σ is the hard-sphere diameter regarded as a free parameter to be optimized. However, direct calculation of the pair potential from the structure using this approximation was found to be inadequate [8].

The hard-sphere approximation, however, can be further elaborated using an iterative predictor–corrector method involving MD simulation suggested by Levesque *et al* [9]. At every iteration step, an MD simulation with a trial potential produces structure functions $g_i(R)$ and $c_i(r)$ which are then used to calculate the correction to the pair potential, $\Delta u_{i+1}(r)$, as follows from the closure equations (3), (4),

$$\frac{\Delta u_{i+1}(r)}{k_B T} = [g(r) - g_i(r)] - [c(r) - c_i(r)] - \ln[g(r)/g_i(r)] \quad (5)$$

where $g(r)$ and $c(r)$ represent the experimental correlation functions. This procedure, which earlier proved to be successful in deriving the pair potential of liquid Pb from the structure data [8], is employed in this study. For each step, a parametrized form of DRT potential is fitted to the corrected output, $u_{i+1}(r) = u_i(r) + \Delta u_{i+1}(r)$. Although using an analytical form of potential at every step is not necessary in the general formulation of the method, it provides a convenient way to calculate the derivative of the corrected potential, thus avoiding the noise arising from simulation. This is not expected to affect the result of the fitting provided the potential form chosen is flexible enough to reproduce it.

4. MD simulation

Convergence of the optimization procedure and adequacy of the resulting pair potential both depend crucially on a reliable calculation of the structure factor in the MD simulation; this was facilitated by using a system of 16384 particles. The advantages of a large-scale MD simulation are the following.

(i) It allows us to explore the small- Q region, including the compressibility limit, which is sensitively dependent on the long-range tail of the pair potential.

(ii) Periodic boundary conditions employed in MD simulations impose constraints on the configurational space and trajectories of the constituent particles. This effect is strongly size dependent: while a liquid system of 10^2 particles contains considerable anisotropic distortion [14], the system employed here provides adequate simulation of structure [13, 15].

(iii) This large system size makes feasible the calculation of $S(Q)$ by direct Fourier transformation of $g(r)$ [13]. This ensures consistency of the structural functions involved in the basic equations of the MHNC inversion scheme.

The microcanonical NVE ensemble MD model of liquid Cu was equilibrated at 1393 K (the melting point for Cu is 1363 K); the number density was fixed at $\rho = 0.0753 \text{ \AA}^{-3}$, which corresponds to the observed density in liquid copper at this thermodynamic condition. In order to avoid ensemble-related distortions, many researchers resort to using constant-pressure or constant-temperature simulations which are assumed to be more realistic. Our previous experience with simulation of a liquid metal [8] has demonstrated that such distortions must be negligible in this case due to the size of the system.

5. Results and discussion

The simulation reported here combines the DRT parametrized model of pseudopotential described in section 2 with the MHNC optimization routine to invert the structure of liquid Cu measured by neutron diffraction [5]. The iterative procedure was initiated by assuming as a first approximation the pair potential derived from MHNC closure (equations (3), (4)) using the hard-sphere model for the bridge function. For that purpose, we have computed the hard-sphere bridge function $B_{HS}(r; \sigma)$ by using the Verlet–Weis (vw) parametrization [16] of the pair distribution function and the Henderson–Grundke (HG) [17] parametrization of $y(r) = g(r) \exp(\beta u(r))$. In this way, the hard-sphere fluid constitutes a reference system for the system under investigation. In this computation, the hard-sphere diameter, σ , has been determined in a thermodynamically consistent way, as is done in common perturbation theory. An efficient criterion for this purpose was introduced by Lado *et al* [18]; they suggested that the hard-sphere diameter chosen should minimize the free energy. To satisfy this condition, σ has to fulfil the following equation involving the bridge function:

$$4\pi \int_0^\infty [g(r) - g_{HS}(r; \sigma)] \frac{\partial B_{HS}(r; \sigma)}{\partial \sigma} r^2 dr = 0. \quad (6)$$

Starting from the hard-sphere approximation described, the inversion procedure has led to a successful and rapid convergence of the simulated structure factor to the experimental one. The final pair potential for liquid Cu at which we arrived is presented in figure 1. The corresponding set of adjustable potential parameters is given in table 1. It is interesting to compare these values with those obtained in a first-principles calculation of interionic

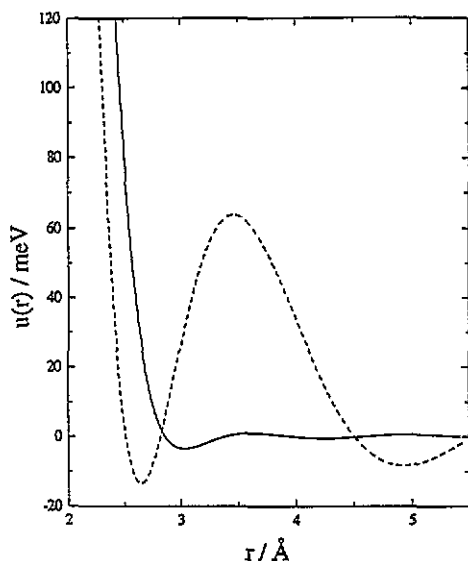


Figure 1. Effective interionic pair potential in liquid Cu at 1393 K derived in this study (solid line) compared with the analytical potential of Lam *et al* [2] (dashed line).

potentials for a number of simple metals [7]. The results obtained in the present study lie well within the range of variation of the corresponding parameters in [7]. This indicates that an NFE model, constructed to be used in the study of simple metals, remains valid in the case of copper where ionic core electrons are not so tightly bound. A possibility suggested by this observation is that the approach used here can be extended to describe the interactions in other non-simple metals.

Table 1. The model potential parameters entering (1) obtained in the optimization routine by fitting to the structure of molten Cu at 1393 K. All the values are in au.

A_0	A_2	R_0	R_1
-1.0427	-3.82182	1.4566	1.46181

Figure 2(a) compares the structure factor simulated by MD using the derived pair potential with the experimental $S(Q)$. The agreement is very good over the entire range of Q covered by the measurements as compared with experimental accuracy (the error bars corresponding to the experimental points can be seen in figure 2 of [5]).

It is of special interest to note the perfect congruence of the two sets of data in the small- Q region including the compressibility limit; this is shown in figure 2(b). The behaviour of the structure factor in this Q -region is known to be sensitively dependent on the long-range part of the pair potential.

Atomic transport is another property to test the adequacy of our MD model of liquid Cu; its sensitivity to the detailed shape of the pair potential has already been discussed [8]. The self-diffusion coefficient evaluated from the behaviour of $\langle r^2 \rangle$ comes out as $D = 4.01 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$, which is in perfect agreement with the experimental value [19], $D_{\text{exp}} = 3.95 \times 10^5 \text{ cm}^2 \text{ s}^{-1}$.

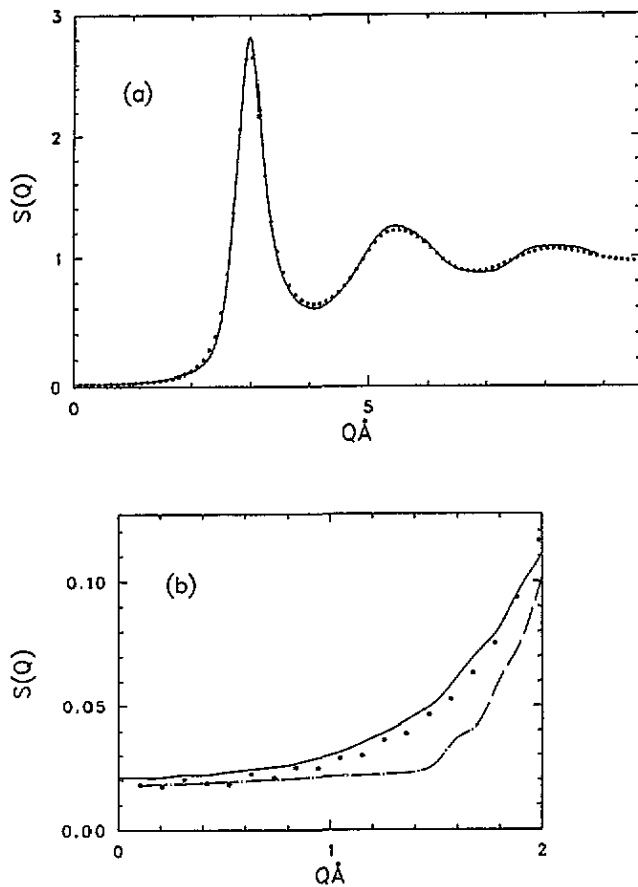


Figure 2. Structure factors in molten Cu. (a) General view, (b) the low- Q region. Solid line, neutron diffraction data of Eder *et al* [5] measured at 1393 K; points, MD results simulated in the present study; dashed-dotted line, x-ray measurements by Waseda and Ueno [4].

The apparent success of the inversion of $S(Q)$ implies that the MD calculation of the structure functions entering equations (3), (4) is both accurate and numerically consistent. Another important conclusion is that the parametrized DRT form of the pseudopotential provides sufficient flexibility to reproduce the variation in the pair potential suggested by equation (5).

It is of interest to compare the present results with another potential derived by Lam *et al* [2] from *ab initio* calculations, which is also shown in figure 1. These authors suggested a physically motivated analytical functional form of effective pair potential, which approximates the potential calculated by Dagens [20] from first principles. The latter takes into account contributions associated with d electrons. When tested in MD simulation, this potential failed to reproduce with sufficient accuracy either the experimental structure or the diffusion coefficient [3]. The two potentials compared in figure 1 disagree appreciably in all the relevant range of r . In particular, the potential derived in this study is positive and repulsive at the average nearest-neighbour distance ($\simeq 2.60$ Å), whereas the potential of Lam *et al* has a pronounced minimum in the same range of r . This discrepancy is expected to affect the low- Q region of $S(Q)$, including the compressibility limit. It is worthwhile mentioning that pronounced repulsion at the first-neighbour distance was found in liquid

Pb and Bi [13,21], and is regarded as a generic feature of interionic pair potentials in polyvalent metals, which exhibit an anomalously small value of the compressibility limit ($S(0) < 0.02$). It might also influence the pattern of collective dynamics in these metals [22, 23]. For longer distances, both the amplitude and the frequency of Friedel oscillations in the two potentials compared disagree dramatically. In this respect, it is worthwhile to note that in the case of the present potential, both the phase and the frequency of the observed long-range oscillations follow Friedel's asymptotic behaviour, $\cos(2k_{\text{F}}r)$.

Another interionic pair potential for liquid Cu, reported recently by Arai *et al* [3], is repulsive at the first-neighbour distance, but this region belongs to a negative well, the depth of which exceeds that of the potential derived in the present study by two orders of magnitude.

Recently, there have been attempts to analyse the shape of $S(Q)$ of liquid metals in the small- Q region by approximating it analytically as a series expansion in powers of Q/Q_0 . In this region, the two sets of diffraction data on liquid Cu shown in figure 2(b), the neutron measurements by Eder *et al* [5] which were used in this study, and the x-ray data of Waseda and Ueno [4], show strikingly different behaviour. Moreover, the latter contains a considerable linear term in its Q -expansion [24], which was found to be negligible in most liquid metals. In this respect, the fact that the present simulation is compatible with neutron-scattering data indicates that the problem of x-ray diffraction in liquid copper deserves to be revisited, at least as far as the small- Q region is concerned.

The large scale of the MD simulation employed ensures the production of numerically consistent $S(Q)$ and $g(r)$, which are directly connected by Fourier inversion, avoiding size-dependent distortions induced by periodic boundary conditions [13]. Therefore, the simulated bridge function can be extracted making use of (3), that can be rewritten as follows,

$$B(r) = \gamma(r) - \ln[g(r)] - \beta u(r) \quad (7)$$

where $\gamma(r) = g(r) - 1 - c(r)$. The direct correlation function, $c(r)$, is obtained by Fourier inversion of $\tilde{c}(Q)$, which in turn is obtainable from the simulated $S(Q)$ via (4). The extracted $B(r)$ is presented in figure 3 together with the hard-sphere bridge function, calculated following the prescription sketched at the beginning of this section. This plot shows a quite considerable difference between the two bridge functions which seems to be a clear indication of strong correlations between bridge functions and effective interionic pair potentials. It is worth mentioning that the fact that the simulated $B(r)$ stays mostly positive through the range of r up to 4 Å, well beyond the nearest-neighbour distance (contrary to the behaviour of the hard-sphere one and what is known to happen in Lennard-Jones fluids [25]); this was also recently found in a DRT model for molten Li [26]. Curiously, this sort of behaviour is characteristic of the bridge functions in the Percus-Yevick approximation. Pair distribution functions from the theory (MHNC with hard-sphere bridge function optimized using the VW-HG approach as described earlier in this section) and the simulated one are plotted in figure 4. Although the theory is in very good agreement with simulation results, still there are some small discrepancies in the amplitude, as well as in the positions of the minima and maxima. Once again, this fact supports the idea that the bridge function plays an important role in determining the relationship between the microscopic structure of a liquid metal and the effective interionic pair potential, as has been already reported [8, 10].

6. Conclusions

In this study, a parametrized NFE model of pseudopotential in the functional form suggested by Dagens *et al* was demonstrated to be able to reproduce the structure factor of liquid Cu

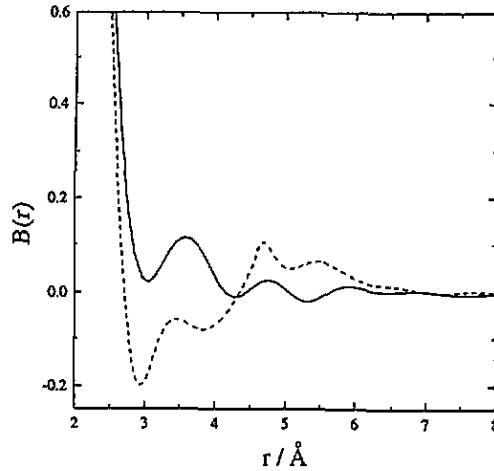


Figure 3. Bridge functions for molten Cu at 1393 K. Solid line: $B(r)$ extracted from the simulated data using equations (3), (4); dashed line: $B_{HS}(r; \sigma)$ optimized using the vw-HC approach as described in section 5.

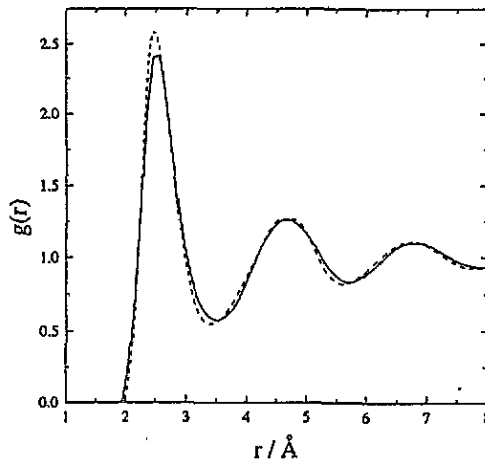


Figure 4. Pair distribution functions: solid line, $g(r)$ obtained from MD simulation; dashed line, $g(r)$ calculated from the MHNC using the optimized hard-sphere bridge function.

measured by neutron diffraction at 1393 K [5]. The successful inversion of the measured structure was facilitated by using an iterative fitting routine based on the MHNC approach, which involved extensive MD simulation.

The potential derived in this study shows the feature of being positive and repulsive around the first-neighbour distance, in agreement with what seems to be a generic pattern for ion-ion potentials in polyvalent metals. Nevertheless, the set of parameters entering the functional form employed appears to be within the range of variation of the corresponding parameters for simple metals. It is rather surprising that the NFE approach, developed to describe interactions in simple metals, happened to be applicable to the description of a

non-simple metal with appreciable interaction between the core and the valence electrons. This result raises a possibility that the model might possess enough flexibility to be extended to the description of other non-simple metals.

Finally, concerning the bridge functions extracted from simulation data, two aspects deserve to be stressed. First, our data confirm previous results that indicated that the hypothesis of universality [12] of the bridge function in simple monoatomic fluids is somewhat restricted in its applicability, since there is a strong correlation between the interaction and the shape of the bridge function itself. Second, despite these limitations, we observe that large differences in the bridge functions lead to subtle discrepancies in the correlation functions. A precise knowledge of the bridge function would then be required whenever highly accurate pair distribution functions are desired.

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