

Pair potential in liquid lead as a test case for the modified hypernetted-chain approximation

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The interionic pair potential derived from the measured structure factor $S(Q)$ of liquid Pb at 613 K using the modified hypernetted-chain approximation was tested in the molecular-dynamics simulation and found to be inadequate. It is shown that the same simple model of the potential with three parameters, having been optimized in an iterative procedure involving the large-scale molecular-dynamics simulation, provides a very good fit to the original structure.

Recently, pair interionic potentials in a number of liquid metals were derived from the measured structure factors $S(Q)$ using the inversion method proposed by Dharma-wardana and co-workers.¹⁻³ In this method, a parametrized pair potential is optimized in an iterative procedure which fits the $S(Q)$, calculated within the modified hypernetted-chain approximation (MHNCA),⁴ to the measured structure factor. The MHNCA is admittedly the most precise semianalytical integral equation approximation, relating space correlation functions and the pair potential in a dense classical fluid, of all those available at the moment. However, the claimed precision of the Dharma-wardana and Aers (DA) inversion was critically discussed,⁵ and a stringent test of its results using a comprehensive simulation is still needed.

Based on the well-documented proposal of Rosenfeld and Ashcroft,⁴ the MHNCA approximates the bridge term $B(r)$ in the formally exact equation obtained from the diagrammatic analysis, relating pair potential $V(r)$ and the structure,

$$g(r) - 1 - c(r) = \ln[g(r)] - V(r)/k_B T + B(r), \quad (1)$$

by that of a hard-sphere fluid $B_{HS}(r, \eta)$ with packing fraction η . Direct correlation function $c(r)$ is connected to $g(r)$ via the Ornstein-Zernike equation, in vector space,

$$c(Q) = [S(Q) - 1]/S(Q), \quad (2)$$

where

$$S(Q) = 1 + 4\pi\rho \int_0^\infty dr r [g(r) - 1] \sin(Qr)/Q. \quad (3)$$

In order to avoid the numerically unreliable procedure of the Fourier transformation (FT) of the measured $S(Q)$, the DA optimization procedure employs the MHNCA to solve (1)–(3) for the trial potential, thus fitting the latter to the experimental structure. The procedure treats η as a free parameter, which can introduce a certain degree of ambiguity in the relationship between the original structure and the derived potential. However, it was claimed that the procedure derives all the parameters uniquely.¹

The molecular-dynamics (MD) simulation being reported here tries the pair interionic potential in liquid Pb derived recently by the DA method³ from the $S(Q)$ measured by neutrons at 613 K.^{6,7} The potential, denoted here as $V_{DA}(r)$, was constructed on the basis of the local

pseudopotential theory. The pseudopotential parametrized by the well depth A_0 and the cutoff radius R_0 as well as the simple local density approximation (LDA) were employed. The third adjustable parameter was effective electron mass m^* . V_{DA} appears to be close to another potential (V_{MD}), derived by an independent method involving MD (Ref. 8) from the same structure data (Fig. 1). Nevertheless, the difference between the

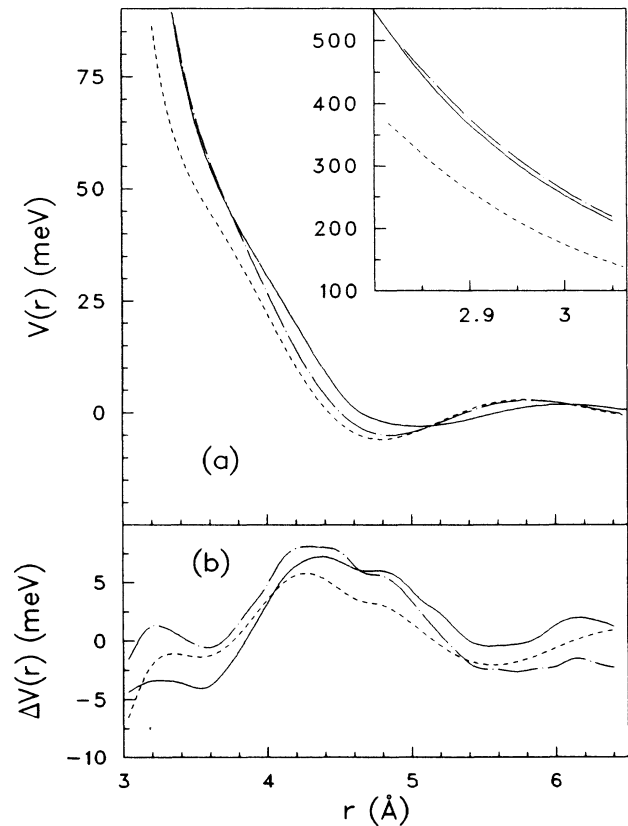


FIG. 1. (a) Pair interionic potentials in liquid Pb at 613 K: solid line, V_{MD} (Ref. 8); dashed line, V_{DA} (Ref. 3); dot-dashed line, the result of new fit of the measured structure data using the RLW procedure (Ref. 9). (b) Dashed line, $V_{MD} - V_4$; dot-dashed line, $U_4 - V_4$; solid line, ΔV_5 .

two results is still considerable enough to leave some room for speculations regarding the DA accuracy. A preliminary MD test of V_{DA} (Ref. 3) has shown certain disagreement between the simulated $g(r)$ and the one obtained by FT of the measured $S(Q)$. Since the Q range where the latter is available is limited, its FT is inherently uncertain. Therefore a direct simulation of $S(Q)$ is desirable to assess the accuracy of the DA inversion. We also examine here to what extent the latter is hindered by the constraint imposed on it by the simple potential model used, and whether a more sophisticated one or even inclusion of many-body terms suggested³ are really needed.

We exploit here the same MD model, comprised of 16384 particles, that was used to derive V_{MD} .⁸ That study has demonstrated that in a simulation of such a spatial scale one can obtain a very precise and reliable $S(Q)$ in the required Q domain by direct FT of the calculated $g(r)$. The necessity to have the two functions strictly numerically consistent for comprehensive analysis of the accuracy of the inversion is apparent from Eqs. (1)–(3). The trial simulation using V_{DA} shows (Fig. 2) that the structure is strongly affected by the difference between V_{DA} and V_{MD} . The calculated structure factor considerably deviates from both the experimental $S(Q)$ and the one predicted by MHNCA.³ Its first peak is much too low and there is a sizable phase shift in the subsequent oscillations. The self-diffusion coefficient and $g(r)$ we obtained agree within the limits of statistical accuracy with those results from the smaller scale MD simulations.³

With the DA inversion of the liquid Pb structure having been found inadequate, we now try to optimize V_{DA} within the framework of the same temptingly simple parametrization model. The optimization technique employed here is based on the idea by Reatto, Levesque, and Weiss (RLW),⁹ who proposed to use the structure simulated by MD iteratively to improve the bridge-function approximation. If $c(r)$ and $g(r)$ represent the real structure that we are trying to reproduce by the fitting, the RLW correction to the potential $\Delta V_i(r) \equiv V_i(r) - V_{i-1}(r)$ at iteration i would be

$$\Delta V_i(r)/k_B T = g(r) - g_{i-1}(r) - c(r) + c_{i-1}(r) - \ln[g(r)/g_{i-1}(r)], \quad (4)$$

where $g_{i-1}(r)$ and $c_{i-1}(r)$ are the results of the simulation using $V_{i-1}(r)$. Since the simulation using V_{MD} reproduces the measured $S(Q)$ within limits of experimental accuracy⁸ (Fig. 2), we considered the corresponding $g(r)$ and $S(Q)$ as representing the real structure. In order to obtain $c_i(r)$ RLW used an analytical extrapolation of the calculated $g(r)$ which introduce a certain degree of arbitrariness in their scheme. This was unnecessary here due to the size of the system we used. As was previously shown,⁸ in this case the truncation errors involved in the direct calculation of $S(Q)$ from the simulated $g(r)$ by (3) are negligible.

Thus the iterative optimization procedure was organized in the following way: (i) A MD simulation is per-

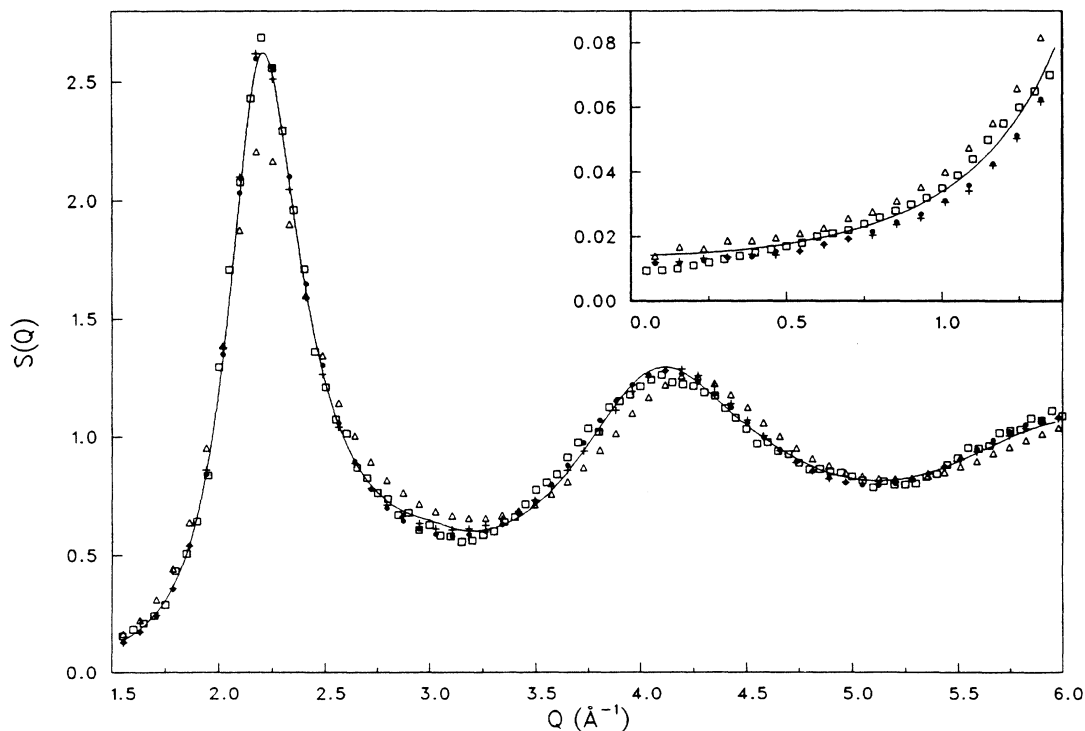


FIG. 2. Structure factors in liquid Pb at 613 K, calculated in a MD simulation using different potentials, discussed in this report: dots, V_{MD} (Ref. 8); open triangles, V_{DA} ; crosses, V_4 . The experimental data (Refs. 6 and 7) are shown by open squares. Solid line: the result for V_{DA} predicted by the MHNCA (Ref. 3).

formed with the estimate potential $V_{i-1}(r)$; (ii) the calculated structure functions are substituted into (4) to obtain $\Delta V_i(r)$; (iii) a new parametrized potential $V_i(r)$ is fitted to $U_i(r) = V_{i-1}(r) + \Delta V_i(r)$. As a starting point we assumed $V_0 = V_{DA}$. The convergence of the scheme happened to be amazingly fast. After four iterations we arrived at the potential V_4 (Fig. 1) which perfectly agrees with the V_{MD} around the nearest-neighbor distance (3.37 Å). In order to analyze the origin of the difference between the two potentials visible at large distances, $V_{MD} - V_4$ is compared with the $V_4 - U_4$ and the next estimated correction ΔV_5 in Fig. 1(b). The fact that the three curves agree well indicates that the remaining discrepancies between V_4 and V_{MD} beyond 4 Å are mostly due to the constraints imposed by the model we used to parametrize the potential. A more sophisticated local-field approximation could presumably help to make the model flexible enough to obtain a better fit. However, Fig. 2 demonstrates that V_{MD} and V_4 produce practically indistinguishable $S(Q)$ when used in the same MD model. The calculated diffusion coefficient comes out as $1.88 \times 10^{-5} \text{ cm}^2/\text{s}$, as to compare with $1.82 \times 10^{-5} \text{ cm}^2/\text{s}$ obtained in the case of $V_{MD}(r)$.⁸ Therefore, in contrast to the conclusion made in Ref. 3, the simple model of the potential we tried was not found to hinder the convergence of the inversion procedure.

Once a potential has been tried in MD, its bridge function can be recovered from the simulated structure using (1). The final bridge function corresponding to V_4 , which may be considered as the real one in this liquid, is compared in Fig. 3 to that for V_{DA} and B_{HS} . In spite of the large difference between the structures produced by V_{DA} and V_4 , there is much more similarity between the corresponding bridge functions than between any of them and B_{HS} . This probably indicates that the hard-sphere bridge function is not an appropriate approximation for the liquid metals with long-range repulsive potentials.

We conclude with the following remarks. In spite of the obvious success of the optimization scheme reported here, there are two basic difficulties one may encounter when trying to implement it to invert the measured structure of other liquid metals. First, a more flexible model would presumably be needed to construct potentials with

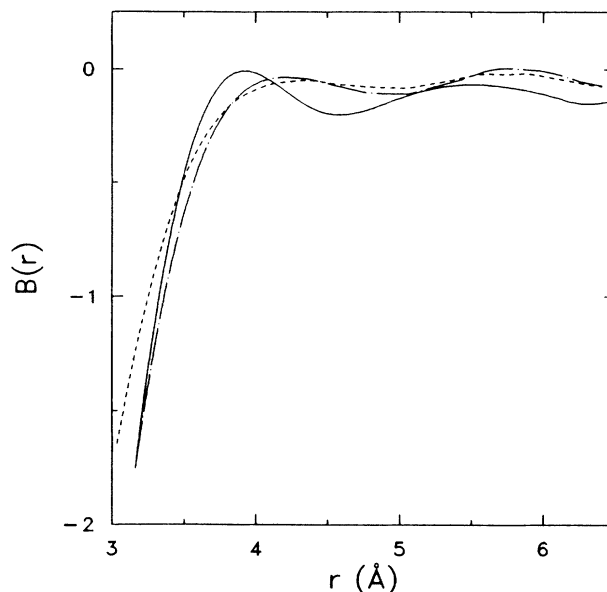


FIG. 3. Bridge functions: dashed line and dot-dashed line, calculated from the results of the MD simulations with the potentials V_{DA} and V_4 , respectively; solid line, B_{HS} obtained in Ref. 3.

more pronounced long-range repulsion. These were assumed in liquid polyvalent metals with specific structural anomalies.¹⁰ Another problem is to find a physically justifiable $g(r)$, the FT of which would reproduce the measured $S(Q)$ with required precision within the Q range where the latter is available. As one can see in Fig. 2, the DA inversion is able to rather successfully solve this problem. Minor discrepancies at the very small wave vectors could probably be corrected with the use of proper weighting factors. Therefore the DA procedure, in spite of its failure demonstrated by this study, may be used as a starting point in the iterative inversion scheme reported here.

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