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Pair potential in liquid lead

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An effective pair interionic potential for liquid lead has been found using the molecular-dynamics (MD) simulation method. The assumed form of the potential includes long-range soft repulsion as well as steep repulsive and oscillating "Friedel" components. An extensive simulation using 16 384 particles has been carried out in order to fit the assumed parametrized form of the pair potential to the static structure factor of liquid lead measured by neutron scattering close to the melting point. The fit covers the first three peaks in $S(Q)$, as well as the small-Q region, including the long-wavelength limit. The use of a relatively large number of particles avoids the systematic errors typical of smaller-scale simulations and allows us to obtain a quantitatively reliable relationship between the pair potential and $S(Q)$. The calculated diffusion coefficient is in good agreement with the experimental value. Simulation of liquid lead at 1170 K and at the corresponding density using the same pair potential also gave good agreement with the experimental data on $S(Q)$ and the self-diffusion at that temperature. This fact indicates that the interionic interaction in lead may be independent of temperature and density within the liquid domain. The potential for liquid lead derived earlier from the fourth moment of $S(Q,\omega)$ was also tested in an MD simulation and proved to be inadequate. A revised version of this potential obtained after removing constraints has a shape similar to that reported in this paper. The self-diffusion coefficient was found to be highly sensitive to the potential's shape.

I. INTRODUCTION

During the last two decades the molecular dynamics (MD) method of simulation of simple classical liquids has been proven to provide a unique way for microscopic interpretation of the experimental data obtained from neutron scattering in terms of interparticle potentials. The method has been especially widely and successfully applied to the studies of liquid metals. MD simulation is very time consuming and requires a large memory storage. In order to simplify the algorithm and to make the calculations practically manageable the potential function of the simulated system is usually reduced to a sum of isotropic pair potentials. This assumption implies that N-body contributions to the potential energy with $N>2$ are either negligibly small or may be incorporated in the *effective* pair potential as an averaged contribution. The pair potential concept has been proved to be very successful for the description of the rare gases, simple metals, and ionic systems. The validity and limitations of this approximation have been discussed recently by Taylor,[1] who came to the conclusion that it is well justified for transition metals.

Liquid metals have been the subject of extensive studies by neutron scattering, and there is still a vast amount of experimental data to be analyzed. Another factor that stimulated numerous attempts of MD simulation on liquid metals was the progress of the fundamental theory in calculations of the interionic potentials. The pseudopotential approach to the description of the electron-ion interactions generated rather reliable effective pair potentials for several simple metals, which were successfully tested in MD simulations against neutron scattering data. Since different measured properties of the studied liquid might depend on different details of the pair potential, and their sensitivity to the latter may also greatly differ, only a complete MD simulation of all the experimentally available information is a stringent test of the assumed potential. However, there are only a few examples of complete MD simulations of liquid metals which have provided a detailed comparison with the neutron data both on structure and on dynamics.[2,3] Failure of the fundamental theory to generate adequate ion-ion potentials for nonsimple metals makes it highly desirable to try to derive them from the experimental data available. Many researchers have resorted to fitting to the experimental data a functional form of pair potential chosen according to certain physical assumptions. It is clear that successful convergence of such a method to the correct result greatly depends on the physical justification of the assumptions since they impose constraints on the optimization procedure.

Liquid lead has been extensively studied in neutron scattering experiments. Very detailed data both on its static and on its dynamic structure factors at 623 K as well as at 1173 K have been reported.[4-6] Accurate information on $S(Q)$ in the small-Q region at $T=623$ K, reported by Olsson and Dahlborg,[7] is particularly important for comprehensive analysis of the structure of liquid lead. To perform an MD simulation of liquid lead, a pair potential was required. However, because of the limitations of the pseudopotential theory, there is no way to calculate a reliable pair potential for lead from first principles,[1] and those derived by different methods from experimental data[8–10] look strikingly different. An attempt to extract information on the pair potential in liquid lead from the fourth frequency moment of $S(Q,\omega)$, measured near the melting point, has been recently reported by Larsson and Gudowski (LG).[11] The parametrized form of the pair potential they used for fitting has been constructed according to some *a priori* assumptions, based on the results of pseudopotential theory.[12] The optimization procedure was based on the method proposed by Jacobs and Andersen.[13] In this paper we first report about the tests of the LG potential, which has been performed using MD simulation. Since the potential happened to be inadequate according to these tests, the possible reasons are analyzed. Some conclusions will be made about the influence of different details of the potential on structure and other properties of the liquid. The new pair potential for liquid lead derived by fitting to the experimental $S(Q)$ using MD simulation will also be reported. It will be compared with the new result of the fitting to the fourth moment with some of the constraints removed.

For a long time the structure of simple liquids has been considered as the main source of information about the pair potential. Since the early works in that field,[12] integral equations have been often used to extract the pair potential from the structure data. Recently Dharma-wardana and Aers[14] derived pair potentials for several liquids using the modified hypernetter-chain equation (MHNC). The optimization procedure they used is based on calculation of $S(Q)$ for the probe potential rather then on direct inversion of the structure. The method is reported to have been successfully tested against MD data. However, in order to calculate $S(Q)$ from $g(r)$, which was generated in MD simulation, the $g(r)$ was extrapolated using the MHNC equation. Therefore, a correct test of the method without any arbitrary assumption is still needed.

The other recently reported optimization procedure, also based on the MHNC equation,[15] derives the pair potential from $g(r)$ using MD simulations. This method, however, includes Verlet's extrapolation of the MD-generated $g(r)$ for calculation of $S(Q)$,[16] which makes the results model dependent. The analysis indicates that both of the methods as well as the self-consistent method by Schommers[17] are still far from being quantitatively reliable.[18,19]

It is a well-established fact that the liquid structure is rather insensitive to the pair potential. Hence a very high precision in both measurements and simulations is required to ensure that the correspondence between the pair potential and the structure data it has been derived from is unique. All the methods, where the pair potential is tested using the calculated $g(r)$, compare the latter to what is usually called an "experimental" $g(r)$ and which is, in fact, a Fourier transformation of the measured $S(Q)$. Since the region of Q, where reliable data on $S(Q)$ are available, is bounded for both large and small Q, the transformation involves a considerable uncertainty. In order to avoid it we suggest that $S(Q)$ generated by MD simulation using the trial potential should be directly compared to the experimental data available.

It is common to refer to the tests of the pair potentials using an MD simulation as "precise" ones. Usually only statistical errors in calculations due to finite MD run time are taken into account.[15] The simulated structure, however, may also be systematically distorted due to interference effects caused by imposed periodical boundary conditions. It is also clear that the information on long-range spatial correlations in the simulated liquid is limited by the size of the system. Meanwhile, the long-range structure of liquid contains significant information on the pair potential. Any attempt to neglect it or to obtain it by extrapolation considerably invalidates the reliability of such a test. Therefore, the proper choice of the size of an MD system is of crucial importance if the simulation is used for derivation of the pair potential from structure data.

The organization of this paper is as follows. In Sec. II we discuss the computational aspects of the simulation method. The resulting pair potential derived from MD fitting to the experimental $S(Q)$ at 623 K is presented in Sec. III as well as the results of MD calculation of $S(Q)$ at 1170 K using this potential. In the same section we also consider results of a simulation using the LG potential and compare our potential with the results of unconstrained fitting to $\langle \omega^4 \rangle$.

II. COMPUTATIONAL PROCEDURE

In this section we describe the computational aspects of the method we have chosen for fitting the pair potential to structure data as well as some details of the MD simulation on which the method is based.

As it has been pointed out above, the test of a trial potential against experimental data should be carried out by comparison of the $S(Q)$, obtained by MD simulation using the potential, with the measured one. Moreover, the calculation of the $S(Q)$ in the fitting procedure should be precise enough to guarantee that the extracted potential is unique. Therefore, it is worthwhile to consider the practical ways of calculation of $S(Q)$ in MD simulation and to analyze the possible relevant errors involved.

The rigorous method of the calculation is based on the definition

$$S(Q)=\langle \rho(\mathbf{Q})\rho^*(\mathbf{Q})\rangle \ , \tag{1}$$

where $\rho(\mathbf{Q})$ is the Fourier transform of the number density of the system,

$$\rho(\mathbf{Q})=N^{-1/2}\sum_j \exp(i\mathbf{Q}\cdot\mathbf{r}_j) \ , \tag{2}$$

$\mathbf{r}_j$ is the position of particle j, and summation is over all the particles within the MD box. The Cartesian components of the vector $\mathbf{Q}$ are multiples of $2\pi/L$, where L is the length of the MD box. It is well known, that the small-Q region data are particularly important when $S(Q)$ is used for the extraction of the pair potential. However, for the smallest values of Q only a few directions of the vector are compatible with the periodic boundary conditions imposed on the system. Therefore, a very lengthy phase trajectory of the system has to be calculated in order to provide a satisfactory statistical accuracy in the simulated $S(Q)$ in that region of Q, and the computational time required is prohibitively long to use such a method in an optimization procedure.

In the MD simulation $S(Q)$ may also be calculated by direct Fourier transformation of the radial distribution function (RDF)

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

The upper limit of integration in the case of the simulated $g(r)$ can be no larger than half of the length of the MD box, and for the system of less than 1000 particles this direct integration would involve large truncation errors. The conventional way to deal with this problem is the analytical extension of $g(r)$ using certain theoretical assumptions[15,16] which makes the calculated results in the small-Q region model dependent.

The systematic errors related to the size of dependence of the computer-simulated liquid structure must also be taken into account. In an MD simulation the RDF is calculated under the assumption that the structure of the system is spherically symmetrical. There are results, however, indicating that in a simulated system of several hundred particles the interference effects due to periodic boundary conditions may cause a considerable anisotropic distortion of the structure.[20] If such an effect takes place, the results of the calculations of $S(Q)$ for the smallest-Q values by Eqs. (1) and (3) may be different. Structure distortions of this kind as well as "explicit" size dependence effects[21] cannot be neglected if a quantitatively reliable test of a potential is required.

The considerations discussed above clearly suggest a reasonable criterion for the choice of the MD system size: the length of the MD box has to exceed the double static correlation radius of the structure. The latter may be defined as the distance beyond which structural correlations become smaller than the statistical errors we accept for the required precision of the calculations. If the model liquid satisfies this condition, $S(Q)$ can be obtained from the RDF directly by Eq. (3), without using any arbitrary assumptions for its extension. The proposed method dramatically reduces the CPU time required to obtain the desired statistical accuracy of the calculated $S(Q)$ in comparison with the method based on Eq. (1). Therefore, the method can be used in an iterative procedure for fitting of the pair potential to the experimental $S(Q)$. Besides that, if the model system obeys the proposed criterion, the distortions of its structure due to imposed boundary conditions as well as other size effects would be negligible, and more detailed information about the structure of the model liquid would be available.

Another argument in favor of using large-scale MD simulations of classical fluids follows from the fact that, in the most efficient MD algorithms developed in recent years (for instance Ref. 22), the CPU time required for a single time step depends linearly on the number of particles. On the other hand, the system of MN particles may be considered as an ensemble of M independent systems, each of them of N particles. Therefore, the number of time steps in the MD run required to obtain the same statistical accuracy of the calculated value should be at least M times smaller for the larger system, and the simulation can be carried out in nearly the same CPU time. This consideration is certainly applicable to the calculations of $S(Q)$ using Eq. (1), although the simulation of the RDF for larger distance is considerably more time consuming.

We have found that for the MD simulation of liquid lead close to the melting point the criterion stated above was well satisfied when the system of 16 384 particles was used, as will be clearly demonstrated later (Fig. 2). It is also clear that for the higher-temperature liquid the correlation radius must be considerably shorter.

The procedure of fitting the pair potential to the experimental $S(Q)$ has been arranged in the following way. Tables of the pair potential and its derivative were calculated using an assumed functional form of the potential with a trial set of parameters. After a temperature equilibration run the RDF of the model liquid was calculated, and $S(Q)$, obtained from it by Eq. (3), was compared with the experimental data. The statistical uncertainty in $S(Q)$ calculated this way for a single instantaneous configuration of the system did not exceed 10–15 % in the small-Q region. This accuracy was sufficient for the purpose of fitting. The discrepancies between the calculated and experimental $S(Q)$ data were analyzed in order to make a proper adjustment of the potential parameters. The adjustment was made "manually" using the empirical information about the relationship between different parts of the potential function and $S(Q)$. We have found that it is not practical to use a formal optimization procedure because its convergence is slower and the result depends on the way one chooses the weighting factor with respect to Q.[14]

The MD program we have used comprised 16 384 particles (or 4×16^3, the number consistent with an initial configuration in the fcc lattice for solid lead). The simulations have been carried out at temperatures of 623 and 1170 K and number densities $\rho=0.030\,94$ and 0.0289 Å^{-3}, respectively, that correspond to the conditions at which the experimental $S(Q)$ data on liquid lead have been measured. Because of requirements of the MD algorithm, the reduced unit of length was chosen so that the side of the MD cube would be 1200 reduced units. The choice of units, therefore, provided the desired density. The pair potential was truncated at a distance of 7 Å. The well-known Verlet algorithm[23] was used to integrate the equations of motion. The algorithm is very convenient for a large-scale simulation because of its relatively small memory requirements. We have found that a time step of 2×10^{-14} s provides excellent stability of the full energy of the system even at higher temperature.

For simulation using so large a system of particles, the efficiency of the MD algorithm is very important. The number of possible pairs for the system of N particles is $N(N-1)/2$, while the number of those within the radius of interaction depends linearly on N. Therefore, the performance of the MD program greatly depends on the efficiency of the procedure of selection and sorting of the interacting pairs. We have developed a new MD algorithm, which, according to our experience, works considerably faster, than the one reported by Eastwood *et al.*[22] The detailed description of the algorithm will be published elsewhere.

The most time-consuming part of the computations reported in this paper was the procedure of fitting. It has been carried out by one of us (M.D.) at the Computing Centre of the Helsinki University of Technology in Espoo, Finland, and required more than 100 h of CPU time using an AS 8040 computer. The other calculations reported here were carried out on the VAX 8200 and the CYBER 180/785 at the Studsvik Neutron Research Laboratory, Sweden.

III. RESULTS

A. The LG potential

Our first test simulation run of liquid lead was carried out using the LG pair potential[11] (Fig. 1). The results on $S(Q)$ immediately showed the inadequacy of the potential: the amplitudes as well as positions of the first two peaks of $S(Q)$ were in large disagreement with the ones in the experimental data,[7] and the results in the small-Q region were bigger than the measured values by a factor of 4. Despite the obvious failure of the potential, the simulated liquid provided us with some interesting results. The RDF generated with the LG potential at 640 K and number density $\rho = 0.030\,94$ Å^{-3} is shown in Fig. 2. The curve clearly demonstrates some specific features of the model liquid's structure not observable in other simple liquids at normal conditions. The second peak is split in two subpeaks. In terms of the effective diameter of the ion, σ, which we define as the position of the first peak of the RDF, the subpeaks are located at $r = \sqrt{3}\sigma$ and $r = 2\sigma$. Besides that, an additional peak appears at a distance 3σ. All these features have been observed earlier in an MD simulated structure of supercooled liquid Al.[24] The assumption of a quasiamorphous character of the model system agrees well with the fact that its diffusion coefficient, calculated from the mean-square displacement of the particles, is anomalously small: $D = 0.3 \times 10^{-9}$ m^2/s, which is about six times smaller than the experimental result $D = 1.93 \times 10^{-9}$ m^2/s.[25]

In order to investigate what particular details of the potential may be responsible for this behavior of the model, we performed several test runs, "switching off" different parts of the potential. When the interaction was truncated beyond the first minimum of the potential, it greatly changed the structure factor and improved its agreement with the experiment, while all the described anomalies of the RDF disappeared and the value of the diffusion coefficient dramatically increased. This observation directly contradicts the suggestion made by Jacobs and Andersen[13] that the behavior of $S(Q)$ at its first peak and for larger Q is mostly determined by the form of the main repulsive part of the pair potential at distances

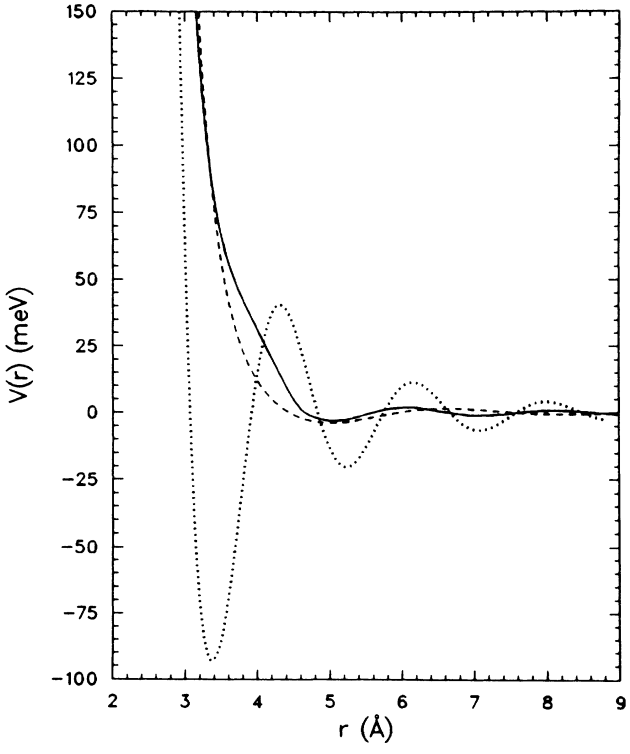

FIG. 1. Pair potentials in liquid lead: dotted line, by Larsson and Gudowski (LG) (Ref. 11); solid line, derived by fitting to $S(Q)$ data using MD simulation; dashed line, revised LG potential, obtained by fitting to the fourth moment with relaxed constraints.

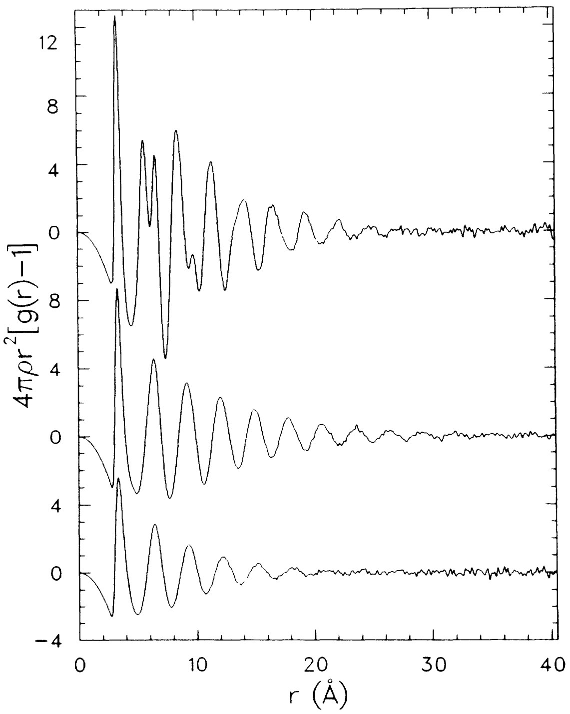

FIG. 2. RDF in liquid lead, simulated using different pair potentials: upper curve, LG potential (Ref. 11), $T = 640$ K; second from the top curve, with the new potential derived from the experimental $S(Q)$, $T = 623$ K; bottom curve, the same potential, $T = 1170$ K.

shorter than the position of the first neighbor. Further simulation runs have shown that it is mainly the first maximum of the potential that causes the described quasiamorphous behavior of the system. Separately "switching off" first the repulsive and then the attractive slope of this maximum, we have found that both of them are equally responsible for the effect. A possible conclusion is that the position of the maximum which is about $\sqrt{2}\sigma$ is important. This distance approximately corresponds to the first minimum of $g(r)$. Hence the potential maximum on that distance, though small, at the melting point can block the creation of some class of local configurations of particles which presumably provide a topological connection between the first- and the second-neighbor shells. A separate peak observed in the RDF of a supercooled liquid at the same distance[24] may also indicate the existence of such configurations. The truncation of the potential beyond its second minimum had almost no influence on the structure.

B. Fitting the pair potential to the $S(Q)$ at 623 K

Before we could start the procedure of inversion of the experimental $S(Q)$, a decision had to be made about the parametrized functional form of the potential. There is admittedly no physical justification for the assumption that the pair potential in liquid lead should have a minimum at the first-neighbor shell distance.[1] Theoretical estimations,[1,26] supported by some inversion results,[9,27] indicate that it must include, besides the terms representing strong core repulsion and the usually predicted Friedel oscillation,[28] a "soft" repulsive component. The last component is supposed to represent the screened Coulomb repulsion between the ions. This term is considerably more long ranged than the strong core repulsion and makes the potential well positive beyond the first-neighbor distance, which presumably plays an important role in all the liquids with a very small value of $S(0)$. Therefore, we adopted the following form of the potential:

$$
\begin{aligned}
&V(r)=V_1(r)+V_2(r)+V_3(r)\ ,\\
&V_1(r)=a_1(b_1/r)^{12}\exp[(r-c_1)^{-1}],\quad r<c_1\\
&V_1(r)=0,\quad r\geq c_1\\
&V_2(r)=a_2(b_2/r-c_2)\exp[(r-b_2)^{-1}],\quad r<b_2\\
&V_2(r)=0,\quad r\geq b_2\\
&V_3(r)=a_3r^{-3}\cos(2K_Fr)\ .
\end{aligned}
\tag{4}
$$

The value of the Fermi vector that defines the period of Friedel oscillations in the third term at the melting point density is $K_F=1.5417$ Å^{-1}. The remaining seven parameters were varied during the fitting procedure. Each time the $S(Q)$ for a new version of the potential was generated by MD simulation, its deviation from the experimental data was estimated at the following points in $S(Q)$: the estimated value of $S(0)$, the position and amplitude of the first maximum, and the same characteristics of the second one. We have found that with proper variation of the potential any of these values can be changed while keeping the others fixed. On the other hand, with all of them fixed, the curve of $S(Q)$ is uniquely defined. This makes it possible to suggest that when a good agreement between the simulated $S(Q)$ and the experimental one is achieved in the restricted region of Q, the former may serve as a reliable extrapolation of the latter to the Q values where the experimental data are not available.

The observed constraints on the $S(Q)$ curve also imply that the set of values of the parameters we obtained from the fitting is conceivably nonunique, i.e., another set of values might be found that would approximate the potential curve with required precision.

The final results of $S(Q)$ fitting are shown in Fig. 3 and the corresponding RDF in Fig. 2. The parameters of the derived potential are given in Table I and its final version is shown in Fig. 1. The only region of Q, where noticeable discrepancies between the simulated $S(Q)$ and the experimental data have been found, is around $Q=1$ Å^{-1}. This disagreement is not yet fully understood and, in our opinion, careful analysis of both the experimental data and simulations is needed. The extrapolated value of the calculated $S(Q)$ at $Q=0$ comes out as 0.0105 compared to the corresponding value 0.0091, obtained from the neutron measurement. The latter agrees well with the thermodynamic limit.[7,29]

If both the pair potential $V(r)$ and the $g(r)$ of the studied liquid are available, one can calculate its Einstein frequency by the formula

$$
\omega_E^2=\Omega_0^2=(4\pi\rho/3m)\int_0^\infty r^2dr\,g(r)[V''(r)+2V'(r)/r]\ .
\tag{5}
$$

We obtained the value $\omega_E=6.98$ meV, while the result derived from the experimental $S(Q,\omega)$ is 7.60 meV.[11] Taking into account the lack of precision in the method used to calculate the latter value, the agreement may be considered as quite satisfactory.

The value of the diffusion coefficient for the derived potential, obtained from the asymptotic behavior of the mean square displacement curve is $D=1.82\times10^{-9}$ m^2/s, which agrees well with that obtained experimentally.[25] We monitored the value of D during the fitting runs and found that near the melting point it is very sensitive to minor changes in the potential, while the structure does not react to such changes so much. The same has been observed in MD simulations of liquid potassium.[30] It is our opinion that the diffusion coefficient can be used as a good test of the pair potential for a liquid at these thermodynamic conditions.

For an independent test of the derived potential one of us (I.E.) used it in an MD simulation with a system of 500 particles at the same temperature and density. The computation has been done using a different MD algorithm and on a different computer (CYBER 180/785). The results of the first two oscillations of the RDF agree well within the limits of statistical uncertainty, which is large for the smaller system. The value of the diffusion coefficient for the smaller system, calculated from the velocity correlation function, was $D=2.0\times10^{-9}$ m^2/s.

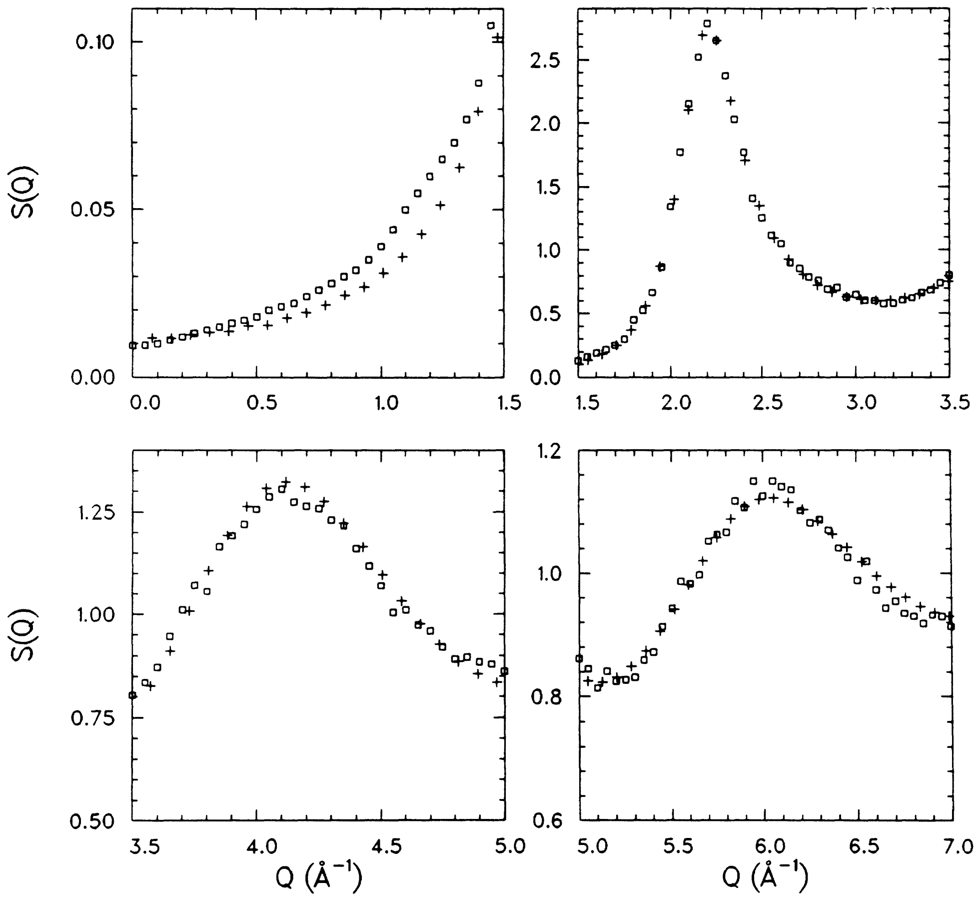

FIG. 3. Result of fitting the pair potential to $S(Q)$ for liquid lead at 623 K: crosses, MD simulation; open squares-experimental data [7].

C. Results on liquid lead at 1170 K

Having established a pair potential from the structure of liquid lead at the melting point, the question arises about the temperature and density ranges over which this result is valid. We performed an MD simulation of the $S(Q)$ in liquid lead at 1170 K and corresponding density, using the derived potential, and compared the result with the experimental data available.[4] The oscillations of $S(Q)$ are considerably smeared out at 1170 K, in contrast to the pronounced structure at the melting point. Since the pair potential in liquid metals is usually considered to be density and temperature dependent, the MD simulation had to demonstrate to what extent the observed structural changes can be related to the change in the pair potential.

It was initially our intention to repeat the above procedure to fit the pair potential to the experimental $S(Q)$ at 1170 K. However, the potential derived at 623 K, which was used as the starting point, appeared to be the best approximation. The comparison of the $S(Q)$, obtained from MD simulations with the experimental data, is shown in Fig. 4. The self-diffusion coefficient value, estimated from the asymptotic behavior of the calculated mean square displacement function is 5.45×10^{-9} m^2/s, while the one obtained from the velocity correlation function is 5.7×10^{-9} m^2/s. These results are in reasonable agreement with the experimental value $D=6.7\times10^{-9}$ m^2/s.[25] The long-wavelength limit of the simulated $S(Q)$ comes out as 0.025. Reliable experimental data on $S(Q)$ in the small-Q area are not available for this temperature. The value of $S(0)$, calculated from the measured compressibility,[29] is 0.0235.

It should be noted that we have found both the structure factor and self-diffusion coefficient at 1170 K to be much less sensitive to the details of pair potential than they were when simulated at the conditions close to the melting point. On the other hand, the experimental $S(Q)$ data at 1170 K are less accurate than at 623 K. These

TABLE I. The parameters for the pair potential given by Eq. (4).

a_1 meV	b_1 Å	c_1 Å	a_2 meV	b_2 Å	c_2	a_3 meV·Å^3
102.5	3.284	5.72	90.0	4.83	0.5	418.3

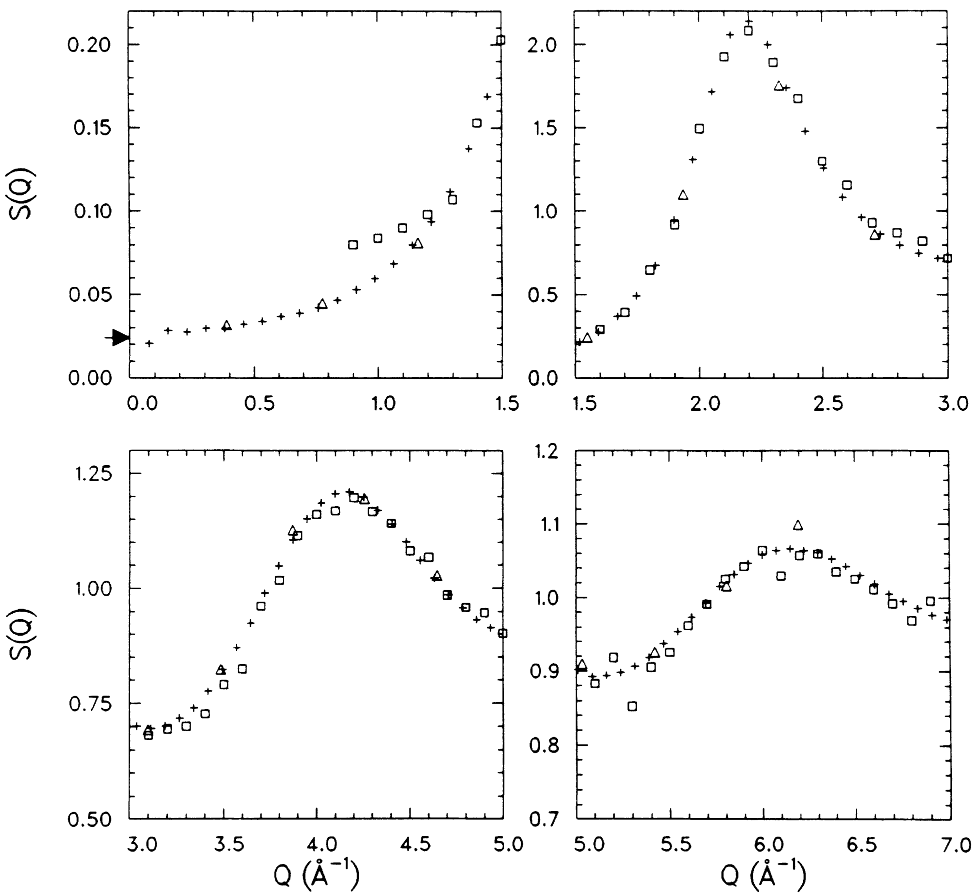

FIG. 4. The result of fitting the pair potential to $S(Q)$ for liquid lead at 1170 K: crosses, MD simulation, open squares experimental data (Ref. 4); open triangles, $S(Q)$, calculated by formula (1). The arrow indicates the value of $S(0)$, obtained from the measured isothermal compressibility (Ref. 29).

two facts prevented us from performing a more detailed adjustment of the potential parameters which otherwise could elucidate its possible fine dependence on temperature and density. Nevertheless, considering the described results, we are led to the conclusion that within the limits of precision of the experimental data the pair potential for liquid lead we derived is valid from the melting point to about 1200 K.

We also performed alternative calculations of $S(Q)$ using Eq. (1) to check the method based on Fourier transformation of the isotropic RDF by Eq. (3). The two sets of results of the simulations, presented in Fig. 4, are in good agreement, taking into account statistical uncertainty. The absence of systematic errors, particularly in the small-Q area, indicates that the RDF in our system is spherically symmetrical and not distorted by periodic boundary conditions.

D. Independent confirmation of the potential form from a fit to the experimental $\langle \omega^4 \rangle$

We have shown earlier that the LG potential[11] failed to describe the observed $S(Q)$. The potential was the result of an attempt to fit a theoretical expression of the fourth moment of $S(Q,\omega)$ to the experimental $\langle \omega^4 \rangle$ data. The latter were constructed from about 50 Q-cuts in the experimentally measured $S(Q,\omega)$ surface from $Q=1.8$ Å^{-1} to $Q=6.8$ Å^{-1}. An important assumption about the form of the pair potential was made: the latter was supposed to have a minimum close to the position of the first peak of RDF that is about 3.4 Å. Therefore, the minimization procedure was performed under a constraint: the position of the first potential minimum could not exceed 4 Å.

When the new pair potential we report in this paper was derived from the experimental $S(Q)$, its form, shown in Fig. 1, suggested removal of the constraint on the position of the potential minimum. We assumed that the latter can occur at any distance. A new unconstrained form of pair potential, minimizing the difference between the theoretically calculated fourth moment and the one obtained from experimental $S(Q,\omega)$ was immediately derived. The revised LG potential, also presented in Fig. 1, is in sharp contrast to the first LG potential. The first minimum of the new potential occurs at 5.0 Å and its depth is only about 3.8 meV. The result clearly demonstrates the fact that the pronounced structure of the LG potential is related to the constraint on the position of its first minimum.

We also used the revised LG potential in an MD run, performed with the system of 500 particles. The simulated RDF shows none of the structure anomalies observed when using the old version of the LG potential. The self-diffusion coefficient was $D=1.2\times10^{-9}$ m^2/s when calculated from the mean square displacement function, and the integration over the velocity correlation function gives $D=1.4\times10^{-9}$ m^2/s. Earlier we attributed the quasiamorphous behavior of the system with the LG potential to the pronounced first maximum of the potential. The absence of this peak at the same distance in the revised LG potential is an argument in favor of this suggestion. The self-diffusion coefficient is still about 30% smaller due to a rather minor difference in shape of the two new potentials (Fig. 1). This result also illustrates the extreme sensitivity of the diffusion coefficient to the shape of the potential as well as the role of its "soft" repulsive component.

In spite of the described differences between the results of MD simulations using the potential presented in this paper and the revised LG potential, the potentials look remarkably similar. Since no assumptions regarding the form of the revised LG potential were made during the fitting to the $\langle\omega^4\rangle$, the similarity may be regarded as an indicative of uniqueness of the potential we have found from the structure data.

IV. CONCLUSIONS

This publication describes an effective pair potential in liquid lead obtained by fitting to the experimental structure data using MD simulation. It is worthwhile to list here some conclusions we arrived at during this study.

The structure of a simple liquid close to the melting point appears to be a unique source of information on its interparticle interaction potential. Assuming the latter to be pair additive, it can be successfully derived by fitting to the experimental $S(Q)$ using MD simulation. Both the experiment and the simulation have to be sufficiently precise to provide a quantitatively reliable result. For this reason we consider the use of an MD system of $\sim10^4$ particles to be necessary to avoid systematic errors. We also found that the self-diffusion coefficient at this temperature is very sensitive to rather small variations in the pair potential and, therefore, comparison of the calculated value with the experimental one may be regarded as a valuable test of the adequacy of the potential. The choice of the functional form of the potential is supported by the results of fitting the potential to the experimental $\langle\omega^4\rangle$. However, the latter method is not quantitatively reliable because of imprecision in the $\langle\omega^4\rangle$ data.

The fact that, using the potential derived at the melting point, we obtained adequate results at 1170 K is rather surprising. However, at the higher temperature both the structure and self-diffusion appear to be much less sensitive to the shape of the pair potential, and taking into account experimental errors, we have to assume that some minor changes in the potential due to the temperature and density differences might not be revealed in the present study.

The potential we report here was also used for MD simulation of the dynamics of liquid lead. The results are in good agreement with experimental data and will be published later.

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[1] R. Taylor, J. Phys. (Paris) Colloq. **46**, C4-309 (1985).

[2] A. Rahman, Phys. Rev. Lett. **32**, 52 (1974); Phys. Rev. A **9**, 1667 (1974).

[3] T. Kinell, U. Dahlborg, O. Söderström, and I. Ebbsjö, J. Phys. F **15**, 1033 (1985).

[4] U. Dahlborg, M. Davidovich, and K. E. Larsson, Phys. Chem. Liq. **6**, 149 (1977).

[5] U. Dahlborg and L. G. Olsson, J. Phys. (Paris) Colloq. **41**, C8-214 (1980).

[6] O. Söderström, Phys. Rev. A **23**, 785 (1981).

[7] L. G. Olsson and U. Dahlborg, Phys. Chem. Liq. **11**, 225 (1982).

[8] S. K. Mitra, J. Phys. C **11**, 3551 (1978).

[9] I. L. McLaughlin and W. H. Young, Phys. Chem. Liq. **11**, 263 (1982).

[10] A. Giro, J. M. Gonzalez, J. A. Padro, and V. Torra, J. Chem. Phys. **73**, 2970 (1980).

[11] K. E. Larsson and W. Gudowski, Phys. Rev. A **33**, 1968 (1986).

[12] M. D. Johnson, P. Hutchinson, and N. H. March, Proc. R. Soc. London, Ser. A **282**, 283 (1964).

[13] E. Jacobs and H. C. Andersen, Chem. Phys. **10**, 73 (1975).

[14] M. W. Dharma-wardana and G. C. Aers, Phys. Rev. B **28**, 1701 (1983).

[15] D. Levesque, J. J. Weiss, and L. Reatto, Phys. Rev. Lett. **54**, 451 (1985).

[16] L. Verlet, Phys. Rev. **165**, 201 (1968).

[17] W. Schommers, Phys. Rev. A **28**, 3599 (1983).

[18] M. W. Dharma-wardana and G. C. Aers, Phys. Rev. Lett. **56**, 1211 (1986); D. Levesque, J. J. Weiss, and L. Reatto, *ibid.* **56**, 1212 (1986).

[19] W. Schommers, Phys. Rev. Lett. **58**, 427 (1987).

[20] L. R. Pratt and S. W. Haan, J. Chem. Phys. **74**, 1864 (1981); **74**, 1873 (1981).

[21] M. J. Mandel, J. Stat. Phys. **15**, 299 (1976).

[22] J. W. Eastwood, R. W. Hockney, and D. N. Lawrence, Comput. Phys. Commun. **19**, 215 (1980).

[23] L. Verlet, Phys. Rev. **159**, 98 (1967).

[24] V. A. Polukhin, M. M. Dzugutov, V. F. Ukhov, and N. A. Vatolin, J. Phys. (Paris) Colloq. **41**, C8-284 (1980).

[25] M. Tanigaki, Y. Toyota, M. Harada, and W. Eguchi, J. Chem. Eng. Jpn. **16**, 82 (1983).

[26] A. H. Macdonald and R. Taylor, Can. J. Phys. **62**, 796 (1984).

[27] I. Yokoyama and S. Ono, J. Phys. F **15**, 1215 (1985).

[28] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[29] S. I. Filippov, N. B. Kazakov, and L. A. Prounin, Chem. Abstracts **65**, 1410 (1966).

[30] J. M. Gonzales Miranda, J. Phys. F **16**, 1 (1986).