

Static and dynamic properties of liquid lead computed by molecular dynamics

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Using a six-center Lennard-Jones (12-6) pair potential, we modeled lead liquid at two different thermodynamic states by molecular-dynamics (MD) computations. While the static structure factor is found to agree with experiment at both states, the pressure is reproduced only for the lower temperature. Self-diffusion and shear viscosity are in reasonable agreement with experimental results. However, the thermal conductivity is predicted far too low. We emphasize the following points: (i) the chosen multiple center pair potential has only *three free parameters* that were fitted by about ten test MD runs, each of which required only 3 min on a supercomputer; (ii) the production computations for the structure factor and the self-diffusion were carried out with 500 molecules, while the transport coefficients were obtained by runs with 32 molecules. Thus our findings stand in sharp contrast to recent calculations of Dzugutov, Larsson, and Ebbsjö [Phys. Rev. A **38**, 3609 (1988)] who claimed that a seven-parameter pair potential and a very large number of particles are required to model liquid lead by MD computations.

I. INTRODUCTION

Computer modeling of liquid metals by simple effective pair potentials is a difficult task, particularly when static as well as dynamic properties ought to be given in agreement with experimental data.^{1,2} A recent good account of the structure and self-diffusion of liquid lead by molecular-dynamics (MD) methods was achieved at the expense of a very complicated and artificial form of the pair potential.³ We present here a simple three-parameter six-center Lennard-Jones (LJ) potential, which we used to calculate various static and dynamic quantities of liquid lead by molecular dynamics with a rather small number of molecules. The proposed potential gives agreement between MD and experimental results for various transport properties and also yields realistic values for even the pressure at lower temperatures. To our knowledge all the earlier computations produced pressures that were orders of magnitude higher than experimental values.

The success of the six-center pair potential seems to originate in a certain flexibility associated with the different interaction sites and partly in its steepness caused by the "internal structure." In the present study, we have examined the ability of the potential of approximating several experimental properties of liquid lead via MD computations rather than optimizing exhaustively the adjustable potential parameters to represent precisely

one or two chosen quantities. Thus we believe that further refined optimization of the potential leads to a better description of many measured and unmeasured properties of liquid lead.

II. THERMODYNAMIC STATES, POTENTIAL MODEL, AND MD COMPUTATIONS

A. Thermodynamic states of liquid lead

For our comparisons we chose two thermodynamic states of liquid lead previously experimentally investigated by Larsson and co-workers⁴ and Olsson and Dahlborg.⁵ These state points lie near the freezing point, i.e., the boiling point of lead, where a lot of measurements have also been carried out for thermodynamic and transport properties.⁶ For these states a few experimental quantities, which are of interest here, have been gathered in Table I. The origin of these data is Ref. 6, if not indicated otherwise. Structure-factor data have not been considered in the table, as we shall discuss them extensively together with our MD results later in the article.

B. The potential model

A multiple-center Lennard-Jones pair potential was chosen for the MD calculations, which may be expressed in the following form:

TABLE I. Thermodynamic and dynamic properties of liquid lead at two states near the freezing and the boiling point. The last three columns represent self-diffusion, shear viscosity, and thermal conductivity coefficient.

State point	T (K)	ρ (g cm ⁻³)	P (bar)	$10^5 D$ (cm ² s ⁻¹)	$10^4 \eta$ (Pa s)	λ (W m ⁻¹ K ⁻¹)
1	615	10.645	0.0	1.9	25.0	16.0
2	1160	9.943	0.0	6.7	11.5	20.0

TABLE II. Potential parameters of the six-center Lennard-Jones pair potential used for the description of the interaction of particle in liquid lead.

(a) Distance from center of mass of molecule to each of six interaction centers	$d=1.05 \text{ \AA}$
Mass of each center	$\frac{1}{6}(207.19 \text{ a.u.})$
(b) Lennard-Jones interaction center parameters	$\sigma=1.77 \text{ \AA}$ $\epsilon/k=268 \text{ K}$ (k is the Boltzmann constant)
(c) MD computation cutoff	
2.30σ	for transport properties
$\frac{1}{2}$ side of model cube	for pressure and structure factor

$$u_{\text{LJ}}(r_{ij}^{\alpha\beta}) = 4\epsilon \sum_{i=1}^n \sum_{j=1}^n \left[\left(\frac{\sigma}{r_{ij}^{\alpha\beta}} \right)^{12} - \left(\frac{\sigma}{r_{ij}^{\alpha\beta}} \right)^6 \right],$$

where $r_{ij}^{\alpha\beta}$ denotes the separation between two interaction centers of two different molecules. The molecules are here numbered by α, β and the interaction centers by i, j . For our purpose we placed $n=6$ interaction centers on a molecule and considered $N=32$ up to $N=500$ molecules for the MD system. The ϵ and σ parameters are the common Lennard-Jones potential parameters.

In order to model compact globular and rigid molecules, we put the six ‘‘LJ centers’’ in rhombic order at equal distance d from the center of mass. This fixed distance and the final LJ potential parameters are listed in Table II. Note that for the calculations each ‘‘LJ center’’ bears $\frac{1}{6}$ of the mass of lead. This table shows (A) the distance from the center of mass of ‘‘molecule.’’ The six interaction centers were placed in rhombic structure. Each center was assumed to bear the mass $m/6$, where m denotes the total mass of lead (207.19 a.u.); (B) the parameters characterizing the Lennard-Jones interaction centers; (C) the cutoffs for the MD computations.

Though, in general, a multiple-center pair potential represents a highly complicated angle-dependent one, it

acts here nearly as a spherically symmetric potential due to its symmetry properties and the extremely small structure parameter d . The presently employed site-site pair potential may be compared with those used for molecular liquids containing globular molecules, for instance SF_6 . However, the d parameter suitable for a SF_6 - SF_6 interaction potential model is by about 50% larger than in our case.⁷

C. The MD computations

Using site-site pair potentials the most appropriate method to perform MD calculations appears to be the ‘‘constraints method.’’ This technique has been introduced by Ciccotti and collaborators and has been reviewed recently.^{8,9} A few comments on this method are in order. The computation proceeds in two steps. In the first step the common equations of motion are solved for the interaction centers of suitable mass m_i . Afterwards, the structure of molecules is iteratively restored by fulfilling certain constraints associated with the molecule structure, which also accounts properly for the forces exerted between the interacting mass centers. (See Table III.)

The self-diffusion coefficient D as well as the shear viscosity and the thermal conductivity coefficients have

TABLE III. Technical details of the MD computations with constraints.

Runs	
Molecule number (N)	32–500
Number of interaction sites per molecule (n)	6
Integration time step	$0.5 \times 10^{-14} \text{ s}$
Number of time steps	4×10^3 [for $S(k)$, P , and D] 10^5 (for η and λ)
Number of equilibration steps	2×10^4
Computation time per 1000 steps	728 s (500) 3.1 s (32)
Further details	
Ensemble	$NVE\mathbf{p}$ (V is the total volume; E is the total energy, \mathbf{p} is the total momentum)
Integration algorithm	Stoermer-Verlet
Number of averaging events for the correlation functions	10^5 [for $S(k)$ and D] 10^4 (for η and λ)

been determined via the Green-Kubo integral relations. These integrals contain the so-called Green-Kubo integrands, which are here the autocorrelation functions (ACF's) of the single-molecule velocity, the off-diagonal part of the pressure tensor, and the heat current of the molecular system. The formulas for the Green-Kubo integrands of η and λ of the molecular system have been given explicitly in a recent work.⁷ D is easily determinable by the center-of-mass velocity of a molecule.

The computations for the collective transport coefficients require about 10^5 integration time steps. Fortunately, these quantities do not depend largely on the number of molecules used for the MD,⁷ and hence we reduced the system size appreciably for the determination of the shear viscosity η and the thermal conductivity λ .

The statistical error for the transport properties is about 10%. We give, however, the precise uncertainties of the coefficients in the relevant tables.

III. ADJUSTMENT OF THE SIX-CENTER LENNARD-JONES PAIR POTENTIAL

Adjustment of the three potential parameters d , ϵ , and σ appeared to be a simple task with the help of experimental values for the pair correlation function (PCF) and the self-diffusion coefficient of liquid lead. We chose for the optimization the state near the melting point indicated as state point 1 in Table I. The height and the position of the first peak of $g(r)$ were obtained by Fourier transforming the experimental data of Larsson *et al.*⁴

A few short runs with 32 and 108 molecules were satis-

factory to find d , ϵ , and σ approximately. Further test runs with 256 molecules gave the final potential parameters listed in Table II. For all the results discussed in the following sections we used these parameters and made no further changes.

IV. RESULTS

A. Structure factor and self-diffusion

The calculations for the static structure factor $S(k)$ and the self-diffusion coefficient D have been done with 500 molecules throughout. Accordingly, the pressure of the system has been determined with this larger number of molecules to avoid significant uncertainties due to cutoff errors involved in computations with LJ-type potentials.

We compare $S(k)$ measured by Larsson *et al.* and computed by MD for state points 1 and 2 in Figs. 1 and 2. Agreement between both data sets is good, although there are some slight discrepancies. While for state 1 the first peak of the computed function appears to be somewhat too low, it exceeds the experimental one at the higher temperature. At the state near the melting point there exists also a small shift of the higher-order peaks of the theoretical function.

For both states, $S(k)$ computed by MD shows several oscillations of minor amplitude in the region of small k values below the first peak. These oscillations stem from the numerical Fourier transformation in space of $g(r)$ originally determined by MD.^{10,11} The effect is particu-

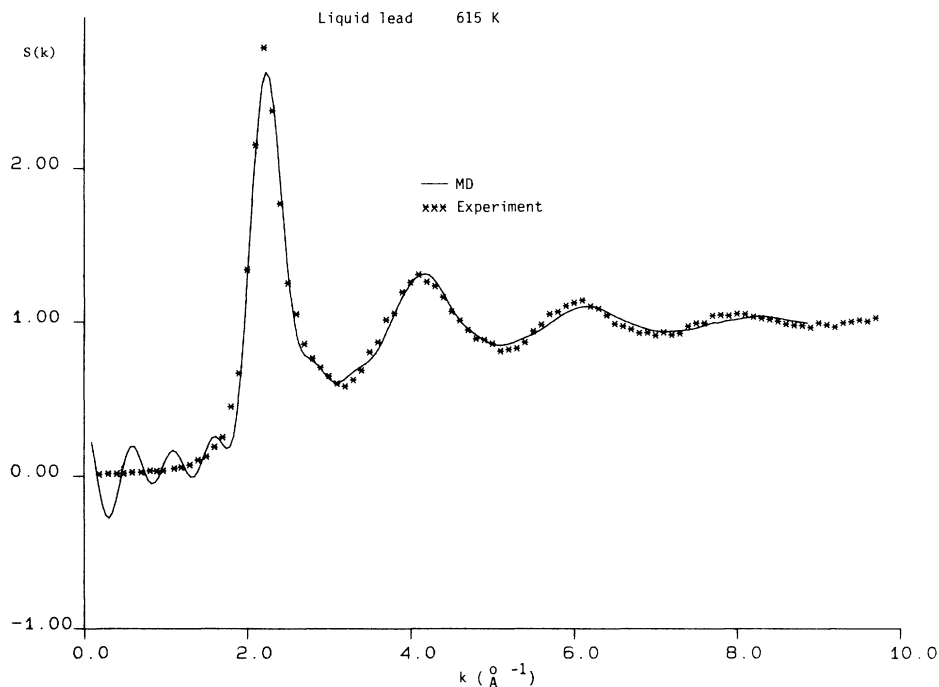


FIG. 1. Static structure factor calculated by MD (—) and measured. $T=615$ K; $\rho=10.645$ g cm⁻³ (near the freezing point).

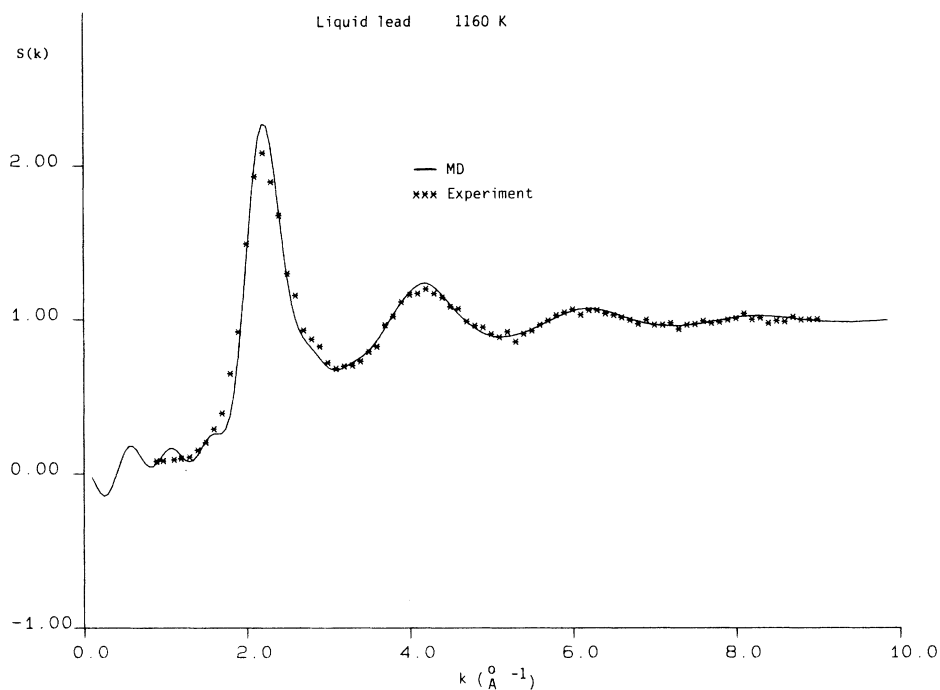


FIG. 2. As in Fig. 1, but for $T=1160$ K, $\rho=9.943$ g cm $^{-3}$ (near the boiling point).

larly pronounced for state 1, where the envelope of $S(k)$ decays more slowly than for state 2.

If high accuracy is required for $S(k)$ at these small k values, the function should be directly computed by MD rather than by inversion of $g(r)$ evaluated with large MD systems.¹¹ MD computations allow a minimum k value of $2\pi/L$, where L denotes the length of the model cubus. In the present examples, we have a minimum k value of 0.25 Å $^{-1}$ for state point 1 and 0.24 Å $^{-1}$ for state point 2. This shows that 500 particles suffice to compare the $S(k)$ results with experimental ones for all the wave vectors experimentally available.

Straightforward computations of $S(k)$ by MD is performed with use of the local-density Fourier components. The Fourier component of the local density may be written as

$$\rho_{\mathbf{k}} = \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i},$$

where \mathbf{k} denotes the wave vector and \mathbf{r}_i the position vector of a particle (molecule center of mass) of the N -particle system. Definition of $S(\mathbf{k})$ involves the ACF of $\rho_{\mathbf{k}}$

$$S(\mathbf{k}) = \frac{1}{N} \langle \rho_{-\mathbf{k}} \rho_{\mathbf{k}} \rangle,$$

where the brackets indicate the thermal average. For the liquid, $S(\mathbf{k})$ depends only on the absolute amount of \mathbf{k} , and thus a chosen $|\mathbf{k}|$ value may allow the determination of several $S(\mathbf{k})$ values compatible with $|\mathbf{k}|$. Hence the recipe of computing $S(\mathbf{k})$ is simple given the constraint $|\mathbf{k}| \geq 2\pi/L$.

We have not exploited this direct way of determining $S(k)$, as a more detailed study is planned for $S(k)$ at small k values, in which we shall make extensive use of that computation method.

Nonetheless, overall agreement of measured and computed $S(k)$ values is good, even for smaller k values, where the experimental curve falls well in line with a smoothed curve which could possibly be drawn through the small oscillations. Related to $g(r)$ is, of course, the pressure of the liquid. However, in MD calculations, we may straightforwardly evaluate the virial sum to yield the pressure value.¹²

For states 1 and 2, the pressure calculated by MD may be compared with the experimental values in Table IV. Evidently, good agreement exists for the neighborhood of the freezing point and disagreement near the boiling point. Apparently, the employed Lennard-Jones potential increases too rapidly with decreasing separation thus causing high repulsion of the molecules at higher temperature and hence giving by far too large pressures. However, the pressure depends very sensitively on form of the pair potential, and for liquid metals, one should not be surprised to find discrepancies of this kind. In any case, the good accordance of the computed and real pressures near the freezing point indicates the general capability of multiple-center potentials of accounting properly for the structure and thermodynamics of liquid metals.

The self-diffusion coefficient calculated and measured can be compared for both states in Table IV. Reasonable agreement appears, although the theoretical value lies somewhat below the experimental one for the low-temperature state. The computed D values are mean values determined from the mean-square displacement of

TABLE IV. Pressure, self-diffusion, shear viscosity, and thermal conductivity coefficient of liquid lead calculated by MD and measured. Experimental values appear in parentheses.

State point	P (bar)	$10^5 D$ ($\text{cm}^2 \text{s}^{-1}$)	$10^4 \eta$ (Pa s)	λ ($\text{W m}^{-1} \text{K}^{-1}$)
1	0 ± 10^3 (0.0)	1.3 ± 0.1 (1.9)	30.0 ± 6.0 (25)	0.26 ± 0.03 (16)
2	$17.5 \times 10^3 \pm 10^3$ (0.0)	2.8 ± 0.2 (6.7)	22.0 ± 4.0 (12)	0.27 ± 0.03 (20)

a molecule and the velocity ACF. Usually the results inferred from the mean-square displacement differed by only 3% from those obtained by the velocity ACF.

B. Shear viscosity and thermal conduction

Collective transport processes depend explicitly on the behavior of all molecules.¹⁰ Thus comparison of collective transport coefficients like η and λ determined by experiment and computer calculation indicates unambiguously the usefulness of the pair potential inserted. Table IV contains experimental and theoretical values for the shear viscosity and thermal conductivity constants at state points 1 and 2. Evidently the computed values for η agree roughly with the experimental ones, while the MD λ values fall below the experimental data by about the same amounts two orders of magnitude.

Though the shear viscosity is not reproduced within the mutual error bars, the theoretical numbers fall reasonably well in the range expected from experiment. Furthermore, the state dependence of the measured data is quite well reflected by the computations. A finer optimization of the six-center potential might certainly improve the computer calculation results. Apparently, the steep repulsive part of the present form of the potential leads to this overestimate of the shear forces.

The heat transport process in a liquid metal is certainly much more difficult to understand on the basis of a pseudopotential. This is indicated by the considerable disagreement of the theoretical and experimental λ values. Apparently, the characteristically high thermal conductivity in metals cannot be accounted for by the present pseudo-pair potential. At present, we have no simple proposal for a modification of the six-center potential in order to avoid this defect.

V. DISCUSSION

Our MD results for the static structure factor, the pressure, and various transport coefficients of liquid lead

indicate clearly the effectiveness of the proposed six-center Lennard-Jones potential. The potential is a simple three-parameter potential, which acts nearly spherically symmetrically and permits MD calculations with small particle numbers. Our finds are in remarkable contrast to recent MD calculations of Dzugutov *et al.*³ who propose a complicated seven-parameter potential to determine the self-diffusion coefficient and the structure factor in good agreement with experiment. These authors are, of course, forced to utilize a large amount of computation time to optimize the potential parameters, and they furthermore claim that they must perform the production runs with 16,000 particles to avoid distortions in their $S(k)$ functions.

Moreover, these authors do not report any thermodynamic values or collective transport coefficients obtained from their calculations. As they use this artificial pair potential, we expect that the pressure as well as the shear viscosity coefficient would lie far off the experimental values, had these quantities been reported in that work. Preliminary results of those authors for the pressure indicated indeed far too high values.¹³

With regard to all these aspects, we should like to recommend the use of the potential presented here for model calculations on liquid metals. A more sophisticated version of the applied multiple center potential could be constructed for closer agreement of MD and experimental results. A physically more reasonable approach to reliable pseudopotentials has been proposed by another group.¹⁴ This way of calculating the pair potentials is, however, very expensive.

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