Evidence for structural effects in self-diffusion

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Atomic self-motion in liquid lead was studied on the molecular dynamics model of 16 384 particles using the effective pair potential which was derived earlier from the measured structure factor. The simulation was carried out at two temperatures, 623 and 1170 K, the former being close to the melting point. At 623 K, the deviation of the incoherent intermediate-scattering function $F_s(Q,t)$ from its Langevin approximation, for long enough times, was found to display a characteristic pattern of Q dependence which resembles that of the static structure factor $S(Q)$. Some elements of this picture of Q dependence were also found in the high-temperature region. These results indicate that sizable effects of coupling between the diffusion process and the structural relaxation, known to be characteristic of supercooled-liquid dynamics, are well defined in the normal-liquid domain and they may be found even in the temperature region well above the melting point.

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For nearly 35 years atomic motions in liquids have been studied by the neutron-scattering techniques (NS). The molecular-dynamics (MD) simulation techniques have proven to be a unique way of interpreting, on the microscopic level, the experimental information on the liquid-state dynamics provided by the NS. MD delivers the fundamental van Hove correlation functions $G(r,t)$ and $G_s(r,t)$ and their spatial Fourier transforms $F(Q,t)$ and $F_s(Q,t)$. The energy spectra of the scattering functions $S(Q,\omega)$ or $S_s(Q,\omega)$, respectively, may be compared to those measured by the NS. If the two sets of data are congruent, within the limits of experimental accuracy, the MD model may be regarded as being calibrated by the NS measurements.

The MD approach is usually based on the simplifying assumption that the potential energy of the simulated system may be presented as a sum of pair potentials. In the case of liquid metals, the conventional MD simulates only the ionic part of the two-component system comprised of ions and electrons. The full system can be treated, in a rigorous way, by using a self-consistent approach [1]. However, because of its excessive computational cost, this method cannot be applied to calculate the dynamical quantities indicated above. On the other hand, the pair-potential approach has proved to be successful in simulations performed on a wide range of metallic systems [2], which demonstrated that many-body effects in those systems are either negligible or may be incorporated in an effective pair potential.

In this study, liquid lead was simulated at two temperatures, 623 and 1170 K, using the pair potential derived from the NS-measured $S(Q)$ [3]. This MD model was found to reproduce, within the limits of experimental accuracy, the NS data on both the $S(Q)$ and the $S(Q,\omega)$ measured on the real liquid lead at those temperatures [4]. The simulated diffusion coefficient D [3], which is known to be very sensitive to the pair potential, was also found to be in good agreement with the corresponding measured value. The successful reproduction of the mea-

sured viscosity data was another important test, indicating that the model adequately reproduces the atomic dynamics in liquid lead [5].

Using the MD model, which has been comprehensively calibrated against the measured properties of liquid lead as described above, we investigate here the incoherent intermediate-scattering function $F_s(Q,t)$. The information on the properties of the self-diffusion process in the system studied, contained in that correlation function, is analyzed using the approach which will be described below. The main result of this analysis is that, in the long-time domain, the calculated $F_s(Q,t)$ demonstrates considerable and systematic deviation from the behavior predicted by the simple Langevin diffusion model. Analysis of the time behavior of this deviation and the pattern of Q variation of its magnitude lead to the conclusion that we deal with sizable effects of coupling between the atomic self-motion and the structural relaxations. The main finding of this study is that these dynamical features known to be characteristic of the supercooled liquid-dynamics domain also exist in the normal liquid; we have found evidence that these effects, although in a much smaller scale, may be observed even in the high-temperature liquid domain.

The MD simulation study of the liquid-lead dynamics being reported here was carried out using a system comprised of 16 384 particles contained in a cubic box with periodic boundary conditions. The system size was motivated by the following considerations. The periodic order induced by the boundary conditions imposes constraints on the structure and the dynamical properties of the simulated system of particles. The resulting distortions are strongly dependent on the size of the system employed. There are indications that in a system of several hundred particles simulating a liquid close to its triple point, the interference effects due to the periodicity imposed may result in considerable anisotropic structural distortions [6]. By implication, this suggests that in such a system the trajectories of constituent particles might

also be distorted by the artifacts of the same origin, which would introduce systematic errors in the Q-dependent dynamics results. On the other hand, the structure of liquid lead simulated by the MD model used in this study was demonstrated to be free of the distortions described [3]. This conclusion has been supported by the recent results indicating that a MD system of 15 000 particles adequately simulates both normal and supercooled liquid [7].

The constant-density simulation has been carried out at two temperatures, 623 and 1170 K, the former being close to the melting point of lead. The number densities were 0.030 94 and 0.0289 Å^{-3}, respectively, which corresponds to the experimental densities of liquid lead at those temperatures. The equations of motion were solved using the well-known leapfrog algorithm. Its superiority in comparison with more sophisticated predictor-corrector methods has been demonstrated recently [8].
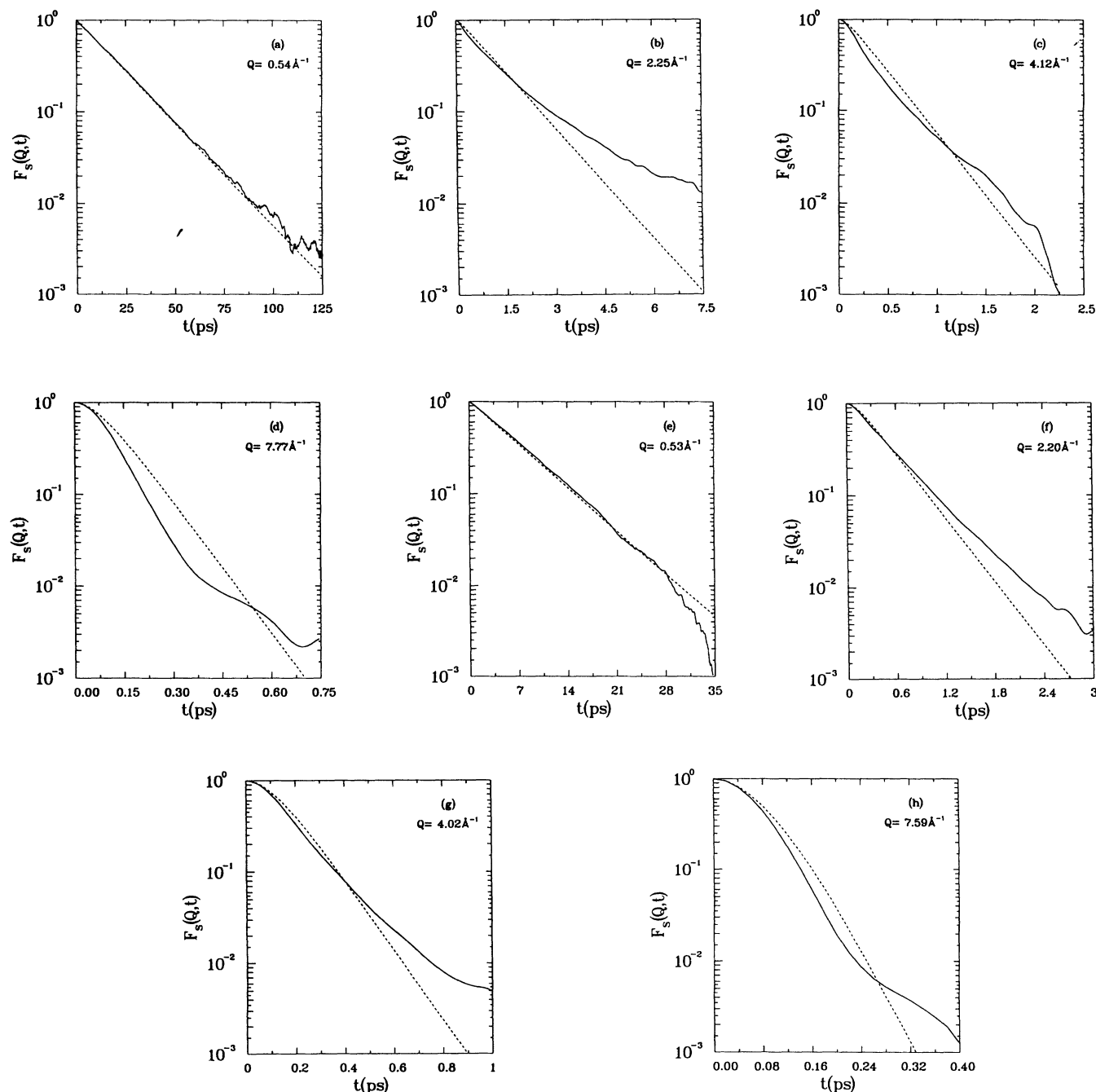

FIG. 1. Density self-correlation function $F_s(Q,t)$ in liquid lead compared with its Langevin approximation for the indicated momentum-transfer values. (a)–(d) $T = 623$ K; (e)–(h) $T = 1170$ K. Solid line, molecular-dynamics simulation result; dashed line, the Langevin diffusion model [Eq. (1)].

The size of the system employed provided excellent statistical accuracy of the simulated $F_s(Q,t)$. The level of statistical noise estimated at the long-time domain was well within 1% limit, which was crucial for observation of the fine dynamical effects reported here.

Several characteristic examples of the $F_s(Q,t)$ for liquid lead at 623 and 1170 K simulated in this study are given in Fig. 1. Due to the high statistical accuracy achieved in this simulation, the calculated $F_s(Q,t)$ may be clearly distinguished against the background of statistical noise until it decays below 1% of its initial value (the uncertainty is somewhat larger for $Q = Q_0$, the position of the main peak of $S(Q)$, which is 2.2 Å^{-1} for liquid Pb). This accuracy is a necessary prerequisite for detailed analysis of fine dynamical effects dominating atomic self-motions in the long-time domain.

We used the well-known Langevin diffusion model as a reference to carry out a detailed analysis of the behavior of the simulated $F_s(Q,t)$ in both the Q and the time domains (Fig. 1). In that model, $F_s(Q,t)$ is expressed as [9]

$$F_s(Q,t)_L = e^{-Q^2 \rho(t)} , \qquad (1)$$

where

$$\rho(t) = D \left[\frac{e^{-\gamma t} - 1 + \gamma t}{\gamma} \right] , \quad \gamma = \frac{k_B T}{MD} ,$$

and M is particle mass. The values of the diffusion coefficient used here were $D = 1.82 \times 10^{-9}$ m^2/s for $T = 623$ K and $D = 5.7 \times 10^{-9}$ m^2/s for $T = 1170$ K; these values were directly obtained from the MD simulation carried out on the same model in an earlier study [3]. It is seen from Fig. 1 that over the small Q range where $S(Q) \ll 1$, say up to $Q \sim 1$ Å^{-1}, the deviation of the simulated $F_s(Q,t)$ data from the Langevin approximation described by Eq. (1) is small. For the Q values where $S(Q)$ is of order of 1, say, around $Q = 1.5$ Å^{-1}, that deviation becomes substantial, and its magnitude reaches maximum at Q_0. The time behavior of the non-Langevin component of the simulated $F_s(Q,t)$ changes its character beyond that Q value, which one can clearly see in the results for $Q > 4$ Å^{-1} presented in Fig. 1.

As clearly seen in Fig. 1, the estimated decay time of the simulated correlation function $F_s(Q,t)$ demonstrates wide range of variation within the domain of wave vectors explored in this study, and also exhibits strong temperature dependence. Therefore, in order to present the non-Langevin component of $F_s(Q,t)$ in a form convenient for its analysis in the whole range of Q and time covered by this study, we introduced a reduced time scale. In this presentation, the reduced time is expressed as $\tau = tDQ^2$, which is supposed to compensate the Q variation of the decay time according to the approximation (1). It is also convenient to consider the non-Langevin term in the normalized form:

$$C_s(Q,\tau) = \frac{F_s(Q,\tau) - F_s(Q,\tau)_L}{F_s(Q,\tau)_L} = \frac{F_s(Q,\tau)}{F_s(Q,\tau)_L} - 1 . \qquad (2)$$

The general view of this function, shown in Figs. 2(a) and

2(b) for the two temperatures studied, demonstrates a specific pattern of its variation in the Q and the time domains. The most remarkable fact revealed in that presentation of $C_s(Q,\tau)$ is that, at large enough times, the Q variation of this function follows that of the structure factor $S(Q)$ [3]. This pattern is seen at both the temperatures studied, although at 1170 K the correlation between the Q variation of the non-Langevin component and the structure factor looks less pronounced.

The significance of the described observation is that it explicitly demonstrates the existence of a non-Langevin
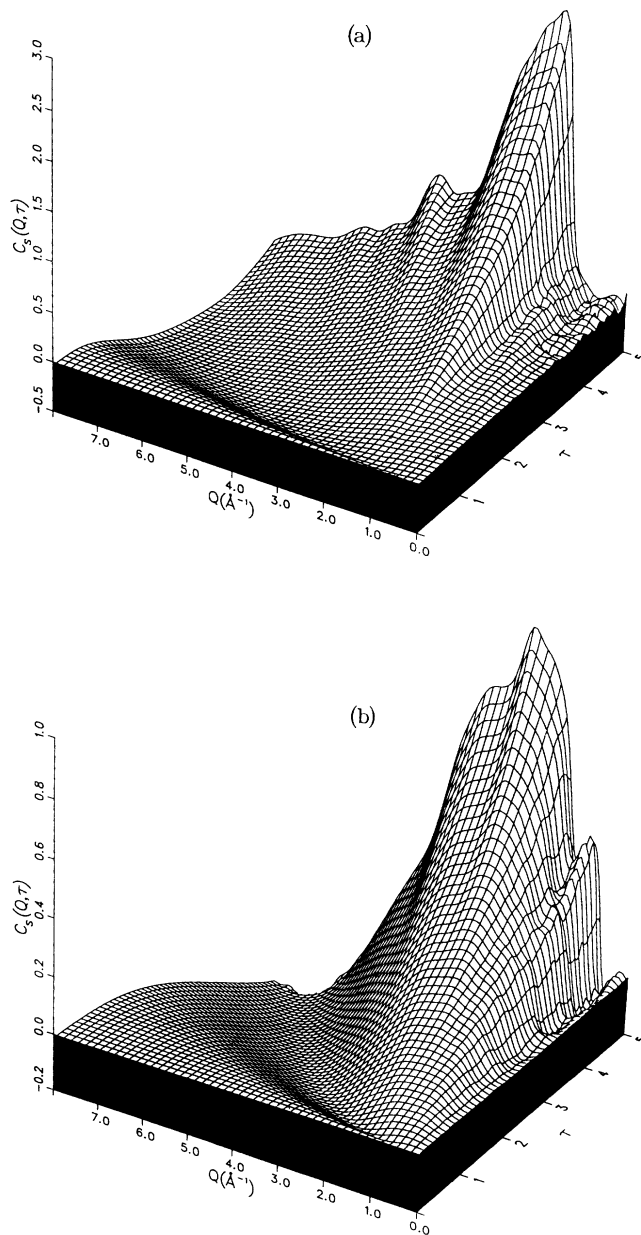

FIG. 2. The correction function $C_s(Q,\tau)$ which represents the normalized deviation of the simulated intermediate-scattering function $F_s(Q,t)$ from its Langevin approximation form [see Eqs. (1) and (2)] for the two temperatures explored in this study: (a) $T = 623$ K, (b) $T = 1170$ K.

component in the atomic self-motion in the simulated liquid, which is strongly coupled with the structural relaxations. It has to be stressed that quantitatively this is a very small-scale effect, the presence of which has been revealed here only due to the high accuracy of the simulation data on $F_s(Q,t)$; however, the reported result is of a great conceptual interest. It may be regarded as a strong indication that the diffusive atomic motion in a liquid system close to its melting point is a highly collective process, which is controlled by the local order. It is a point of particular interest that the described effect also persists into the temperature domain much above the melting point.

Coupling between the structure and the dynamics of a tagged particle in a supercooled-liquid domain is explicitly predicted by the mode-coupling theory developed in the past few years [10,11]. It is not clear, however, whether at its present state that theory can account for the coupling effects reported in this paper, which have been observed in a normal-liquid domain well above the melting point. The second-order memory function of the density self-correlation function, which is used to calculate the coupling terms in the mode-coupling formalism, decays to zero value in about 2.5 ps [12], too early to be immediately identified with the structure-coupling effects described here. The neutron-scattering experiments confirming existence of coupling modes [13] have so far

been limited to the analysis of the half-widths of the self-scattering function $S_s(Q,\omega)$. This quantity, however, is rather insensitive to the effects described in this report.

In the terms of r space, the described effect may be presented in the following way. The fact that the non-Langevin long-time tail of $F_s(Q,t)$ is modulated by $S(Q)$ implies that at the corresponding times, the spatial variation of the van Hove correlation function $G_s(r,t)$ is expected to resemble $g(r)$. One can interpret this picture as an indication that the single-particle diffusive motion is a strongly cooperative process which, to a considerable extent, involves the environment of a particle. Since the latter is defined by the local order, this is expected to impose constraints on the long-time distribution of the diffusing particles with respect to the distance from their initial positions. It is interesting to note that similar effects were observed in the behavior of the van Hove function $G_s(r,t)$ simulated in the supercooled-liquid domain [14,15]. That observation was interpreted as a result of the onset of the supercooled dynamical regime predicted by the mode-coupling theory. The remarkable result of this study is that the structure-coupling effects in the atomic self-motion have been found to exist in a normal-liquid state close to the melting point, and it persists well above this temperature. It is difficult to say at the moment whether or not the theory is able to account for the observations reported here.

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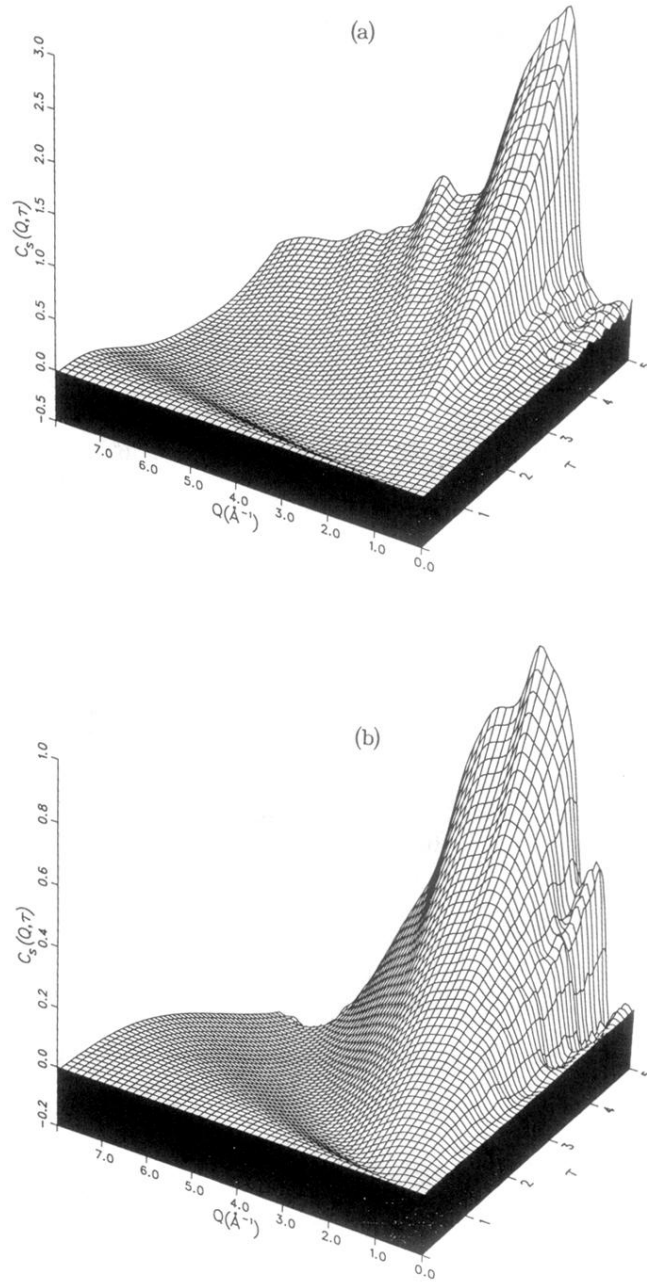FIG. 2. The correction function $C_s(Q,\tau)$ which represents the normalized deviation of the simulated intermediate-scattering function $F_s(Q,t)$ from its Langevin approximation form [see Eqs. (1) and (2)] for the two temperatures explored in this study: (a) $T = 623$ K, (b) $T = 1170$ K.