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Self-diffusion in simple liquids

Karl-Erik Larsson

Royal Institute of Technology, S-100 44 Stockholm, Sweden

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Abstract. Using the combined results of extensive MD simulation and neutron scattering studies of liquid lead at 623 and 1170 K, details of the self-diffusion process within the atomic domain are studied. From analysis of $F_s(q, t)$ it is found that there is an element of structural relaxation in the self-diffusion process which may lead to a jump diffusion component. Also from the derivation of memory functions $\Gamma_s(Q, t)$, particularly for the velocity autocorrelation $\Gamma_s(t)$, it is found that the MD results are not well described by present mode-coupling theories. It is believed that a more sophisticated theory which does not separate the characteristic parts of $\Gamma_s(t)$ and takes many-body effects into account more properly is needed to explain the observations.

1. Introduction

The development of the self-diffusion process in space and time may be divided in two regions: firstly the asymptotic long-time region may be described as a *universal* stochastic Markovian process with no memory effects and secondly the atomic domain in which the process is non-Markovian with pronounced memory effects *specific* to the kind of diffusing atomic system. The extension in space and time of the atomic domain is determined by the van Hove correlation function $G(r, t) = G_s(r, t) + G_d(r, t)$. In simple liquids it is a question of 10–30 Å in r -space and of 10–20 ps in time.

Under the assumption of the small change in velocity of the self-particle compared with the rapid change in force correlation, the Langevin form of the spreading out of the particle is valid:

$$\overline{x^2} = \frac{2mk_B T}{f^2} \left[\frac{f}{m} t - 1 + \exp\left(-\frac{f}{m} t\right) \right]. \quad (1)$$

Here m is the particle mass, f the dynamic friction coefficient and T the temperature. This form has the merit of giving correcting limiting behaviour for $t \rightarrow 0$, namely $\overline{x^2} = (k_B T/m)t^2 = v_0^2 t^2$, and, for $t \rightarrow \infty$, namely $\overline{x^2} = 2D(t - t_0)$, where $D = k_B T/f$ and $t_0 = m/f$.

In the atomic domain the friction coefficient as well as other transport coefficients must be considered to be space and time dependent because the velocity and force correlations decay on similar time scales. The atoms are under a continuous force influence. The empirical study of this region is performed by slow neutron scattering (NS) and molecular dynamics (MD) simulation. Of particular interest is the study of the scattering function $S_s(Q, \omega)$ (NS) or the intermediate scattering function $F_s(Q, t)$ (MD), both resulting from Fourier transforms of $G_s(r, t)$. These functions describe the physics of the self-diffusion process.

Of particular interest for theoretical kinetic descriptions of the self-diffusion process is also the velocity autocorrelation function $\Phi(t) = \langle v_x(0)v_x(t) \rangle$ because the memory function $\Gamma_s(t)$ of $\Phi(t)$ was the basic aim of such theories. In general, two coupled integrodifferential equations describe the interdependence between $F_s(Q, t)$ and the time- and space-dependent diffusion coefficient $D(Q, t)$ and its memory function $\Gamma_s(Q, t)$:

$$\frac{\partial F_s(Q, t)}{\partial t} = -Q^2 \int_0^t D(Q, t') F_s(Q, t - t') dt' \quad (2)$$

$$\frac{\partial D(Q, t)}{\partial t} = - \int_0^t \Gamma_s(Q, t') D(Q, t - t') dt'. \quad (3)$$

For $Q = 0$ the latter of these relations simplifies to

$$\frac{\partial \Phi(t)}{\partial t} = - \int_0^t \Gamma_s(t') \Phi(t - t') dt'. \quad (3')$$

In the present report a detailed analysis of $F_s(Q, t)$ over two decades of decay as well as of $\Gamma_s(t)$ are discussed. The empirical background consist of an accurate and extensive NS-calibrated MD simulation of liquid lead at 623 and 1170 K. The simulation was performed on a system of 16 384 particles [1, 2]. The accuracy of data permits $F_s(Q, t)$ to be used down to a value of 0.01. Memory functions for other liquids, namely argon, rubidium and sodium, are also considered for comparison.

2. Detailed study of $F_s(Q, t)$; structural relaxation

The principle adopted in this work is to compare $F_s(Q, t)$ with the corresponding Langevin expression

$$F_L(Q, t) = \exp(-\overline{x^2} Q^2) \quad (4)$$

with $\overline{x^2}$ from equation (1). The aim is to isolate the collective effects existing in the atomic domain from the stochastic Markovian non-collective effects.

In figures 1(a) and (b), $F_s(Q, t)$ from MD for lead at 623 K and 1170 K, respectively, is compared with the Langevin diffusion case $F_L(Q, t)$. The important observation is that $F_s(Q, t)$ oscillates around $F_L(Q, t)$ in a characteristic way for short and intermediate times. These oscillations are not visible below about 1.5 \AA^{-1} in the figure because of the long time scales, but they are there for shorter times in the same sense as visible about 1.5 \AA^{-1} . For the smaller Q -values with its long time scales it is seen that $F_s(Q, t)$ coalesces with $F_L(Q, t)$ in a way typical for the stochastic Markovian process. For the very small times, $F_s(Q, t)$ coincides with $F_L(Q, t)$ which then is described by the ideal-gas form. This is best illustrated for the largest Q -values of about 7.5 \AA^{-1} . However, only for times $t < 0.5 \times 10^{-13}$ s are the MD data described by the ideal-gas type of free motion:

$$F_s(Q, t \rightarrow 0) = F_L(Q, t) = \exp(-\frac{1}{2} v_0^2 Q^2 t^2). \quad (5)$$

It is to be expected that the oscillations of $F_s(Q, t)$ around $F_L(Q, t)$ contain all the information about the specific atomic dynamics in liquid lead for short and intermediate times. We shall therefore focus our interest on this region.

Because the decay rate of $F_s(Q, t)$ is strongly dependent on Q , it is suitable to introduce a scaling of the time variable. We introduce $\tau = DQ^2t$. The time τ is now measured in the dimensionless variable t/τ_0 , where $\tau_0 = 1/DQ^2$. In NS, $1/DQ^2$ is equivalent to the neutron observation time. DQ^2 is also the hydrodynamic limit for the width function of $S_s(Q, \omega)$. The result is that all the $F_s(Q, \tau)$ -curves now range out to about $\tau \simeq 5-6$ for the present range of t and Q .

In order to emphasize the details of $F_s(Q, \tau)$ compared with the Langevin curve of $F_L(Q, \tau)$, the difference $\Delta F_s(Q, \tau)$ is found:

$$\Delta F_s(Q, \tau) = F_s(Q, \tau) - F_L(Q, \tau). \quad (6)$$

The absolute value of this difference still varies over a wide range because $F_s(Q, t)$ decays from 1 to 0.01 in the region investigated. A second scaling, performed by dividing $\Delta F_s(Q, \tau)$ by $F_L(Q, \tau)$, removes this difficulty. A new function $C_s(Q, \tau)$ is thus obtained [3]:

$$C_s(Q, \tau) = \frac{F_s(Q, \tau) - F_L(Q, \tau)}{F_L(Q, \tau)} \quad (7)$$

which will oscillate around zero. This is so because, at small and long times, $C_s(Q, \tau) \rightarrow 0$ since then $F_s(Q, \tau) \rightarrow F_L(Q, \tau)$.

All the derived MD values for 80 different Q -values are given in a three-dimensional plot in figures 2(a) and 2(b) for 623 K and for 1170 K, respectively. The dominant feature is a resonance in $C_s(Q, \tau)$ in the neighbourhood of $Q = Q_0 = 2.25 \text{ \AA}^{-1}$ for lead. Q_0 is the value of Q at the main peak of the static structure factor $S(Q)$. We also see regions in Q, τ -space where $C_s(Q, \tau)$ is negative.

In order to understand the physical meaning of these features we consider two constant- τ cuts through the family of curves in figure 2. We select $\tau = 0.5$ and $\tau = 2.5$. These curves are given in figure 3 as a function of Q . Using the relation $t = \tau/DQ^2$ the unscaled time t is also given in connection to each curve. It is found that the minima of the curves occur at 0.25 ps for 623 K and 0.20 ps for 1170 K. These are close to the times at which the first minimum of $\Phi(t)$ occurs. Also, at these times the steeply falling part of $\Gamma_s(t)$ reaches its minimum value and goes over into the long-time tail (compare figures 5 and later 7); the memory of basic 'solid-like' behaviour—probably of strongly damped collective nature—within the cage of nearest neighbours is to a large degree lost in this short time. $F_s(Q, t)$ decays more rapidly than $F_L(Q, t)$ because of the rapid loss of memory and therefore $C_s(Q, \tau)$ becomes negative. Between 0.25 and about 1.5 ps at 623 K and between 0.20 and about 0.5 ps at 1170 K, $F_s(Q, t)$ decays more slowly than $F_L(Q, t)$. At 1–2 ps for 623 K and at 0.3–0.6 ps for 1170 K, $F_s(Q, t)$ intersects $F_L(Q, t)$. A comparison with the shape of $\Gamma_s(t)$ shows that within these respective time intervals we find the long-time tails of these memory functions. This is the time region where recollision effects make themselves felt which theoretically were treated as mode-coupling phenomena. If these are described as coupling of the self-motion to various microscopic currents and density fluctuations—as is done in present MC theories—we may call this region the 'collective fluid' region on the atomic scale. The reason that $F_s(Q, t)$ decays more slowly than $F_L(Q, t)$ is that these

(a)

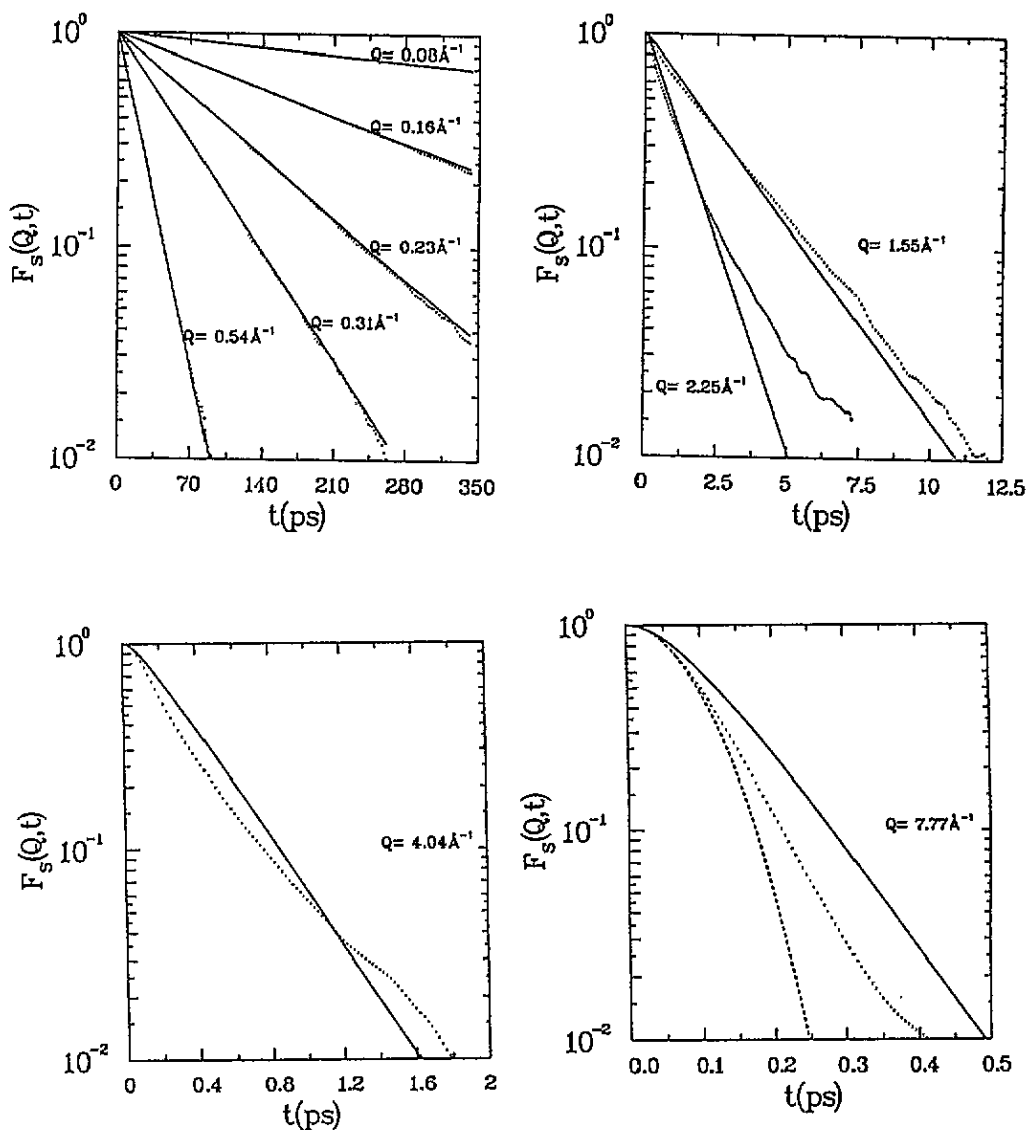


Figure 1. Examples of forms of $F_s(Q, t)$ for 'liquid lead' at (a) 623 K and (b) 1170 K in the small- Q region $Q \leq 0.5 \text{ \AA}^{-1}$ and for large Q -values $Q \geq 1.5 \text{ \AA}^{-1}$. \cdots , MD data; --- , Langevin diffusion; - - - , gas model.

collective phenomena with a mean lifetime of some picoseconds hindered the decay of the self-correlation.

One would perhaps expect that, from this point on, $C_s(Q, \tau)$ should remain at zero, but the new and remarkable feature is that instead of remaining at zero—meaning that $F_s(Q, t)$ should be described as a random stochastic process—a peak appears in $C_s(Q, \tau)$ at Q near Q_0 . For longer times, $C_s(Q, \tau)$ decays towards zero as expected. The peak

(b)

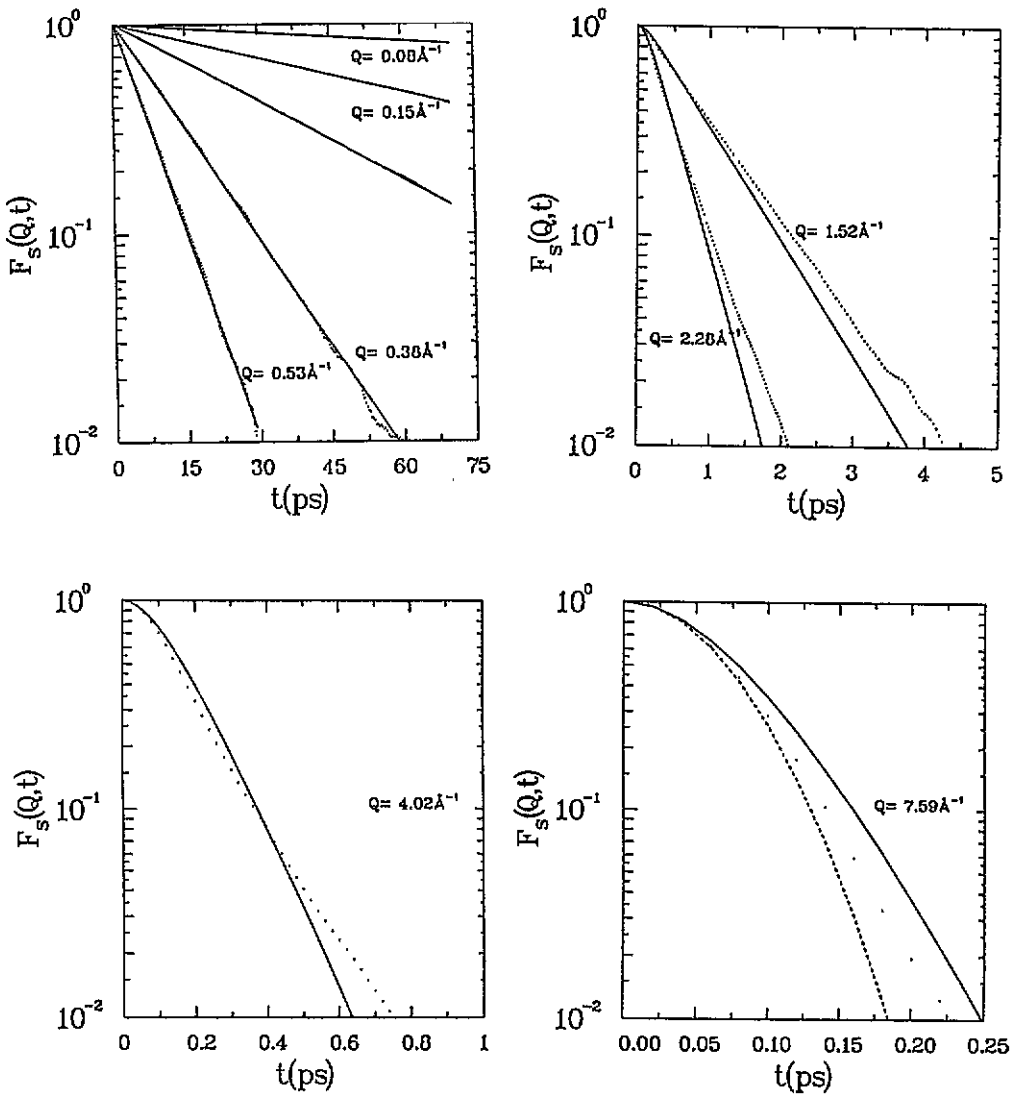


Figure 1. (Continued)

in $C_s(Q, \tau)$ indicates coupling of the self-diffusion process to the structure of the liquid and is an effect of a collective nature. It is remarkable that this feature also exists at the higher temperature. The peaks occur at times t_m of about 4.8 ps for 623 K and 1.6 ps at 1170 K. The self-diffusion coefficients at the two temperatures are $1.8 \times 10^{-5} \text{ cm}^2 \text{ ps}^{-1}$ and $5.4 \times 10^{-5} \text{ cm}^2 \text{ ps}^{-1}$, respectively. The product Dt_m of t_m and D is approximately constant between the two widely different temperatures. If t_m is interpreted as an average lifetime of the cage or, better, the lifetime of the set of spherical shells round any self-atom, the observed constancy of Dt_m is qualitatively understood; the shorter the lifetime of the caging system, the higher is the value of the self-diffusion coefficient. t_m may be considered

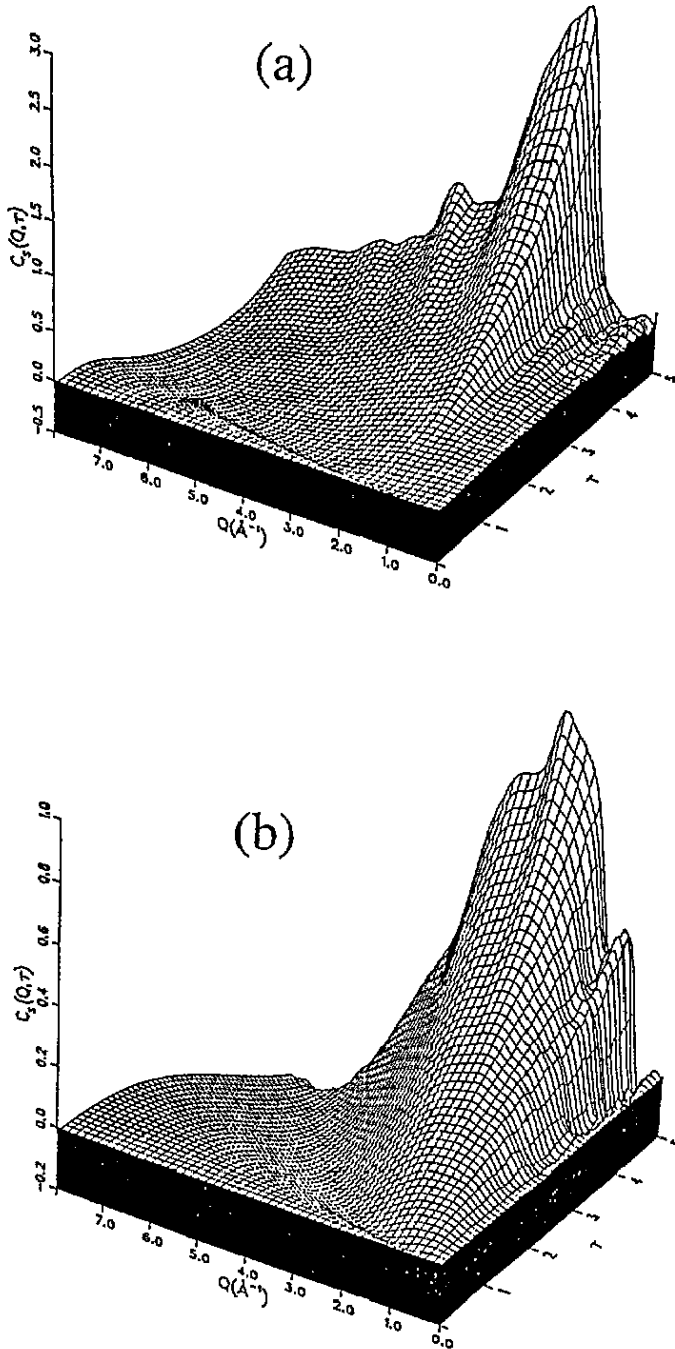


Figure 2. Three-dimensional plot of the function $C_s(Q, \tau)$: (a) 623 K; (b) 1170 K.

as the structural relaxation time. It is natural that this lifetime effect is best observed for Q -values near Q_0 ; $2\pi/Q_0$ is the right wavelength to probe the basic periodic structure in $g(r)$ manifested in the main peak of the static structure factor $S(Q)$.

The physics behind the structural relaxation are illustrated by the time evolution of

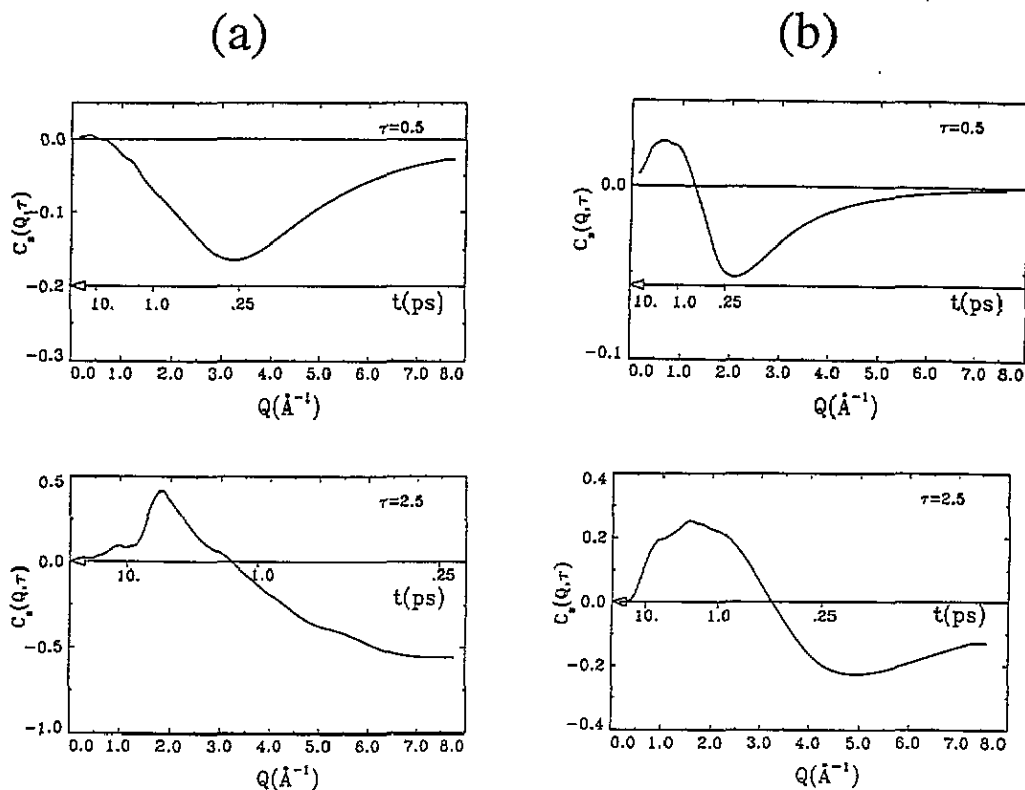


Figure 3. Constant- τ cuts through $C_s(Q, \tau)$ for $\tau = 0.5$ and 2.5 at (a) 623 K and (b) 1170 K. In addition to the Q -scale the real time t is given.

$G(r, t)$ for liquid lead at 623 K (figure 4). $G(r, t) = G_s(r, t) + G_d(r, t)$, where $G_s(r, t)$ is the self-part and $G_d(r, t)$ is the distinct or pair correlation part. It is seen that the structure of $G_d(r, t)$ is smeared out almost completely at longer times and that $G_s(r, t)$ —the central peak—and $G_d(r, t)$ will overlap in an increasing range of r -values as time goes on [4]. Perhaps it is then possible for the self-atom to jump over the 'barrier' of ever-decreasing height. If $6Dt_m$ is interpreted as the mean square \bar{l}^2 of a jump length, the observed numbers give $\bar{l}^2 \simeq 5.2 \text{ \AA}^2$. This corresponds to the reasonable jump length of about 2.3 \AA . At still longer times the neighbouring atoms are almost randomly distributed and therefore the self-atom becomes increasingly freer to diffuse away; the Langevin diffusion is approached.

3. Comparison with mode-coupling predictions

By use of equations (2) and (3), $D(Q, t)$ and $\Gamma_s(Q, t)$ were calculated from $F_s(Q, t)$ [5]. The results are given in a three-dimensional plot in [5]. Of particular interest are the results for $Q = 0$ in which case $\Gamma_s(t)$ is directly determined by use of the velocity autocorrelation function $\Phi(t)$ (equation (3')). The result for this case is given in figure 5(a). In this figure

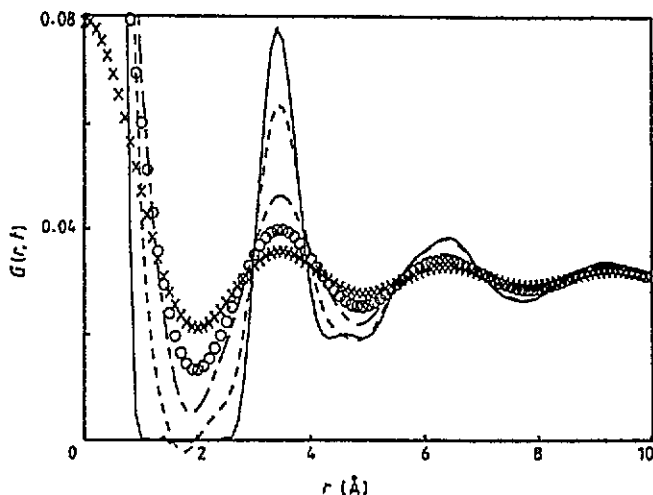


Figure 4. Time evolution of the van Hove correlation function for liquid lead at 623 K for different constant times: —, $t = 0.2$ ps; ---, $t = 0.4$ ps; - · -, $t = 1.0$ ps; O, $t = 1.5$ ps; ×, $t = 2.0$ ps.

is also given the best possible fit to the derived $\Gamma_s(t)$ for lead at 623 K of a formula derived by Levesque and Verlet (LV) [6] from MD simulations on a Lennard-Jones system:

$$\Gamma_s(t) = A \exp(-a^2 t^2) + B t^4 \exp(-b t^2). \quad (8)$$

This formula cannot describe the memory function of $\Phi(t)$ for lead. To produce a better but still not satisfactory fit the addition of a third term is necessary:

$$\Gamma_s(t) = A \exp(-a^2 t^2) + B t^4 \exp(-b t^2) - C t^\gamma \exp(-c^2 t^2). \quad (9)$$

Such a prescription with $\gamma = 14$ provides a good description of the dip at 0.25 ps as is also seen in figure 5(a).

The mode-coupling theory for $\Gamma_s(t)$ proposed by Sjögren and Sjölander (SS) [7] is basically founded on the LV formula. If this fails, there is good reason to believe that the SS theory will fail. This is indeed the case, as seen in figure 5(b). The long-time tail including the mode-coupling terms exceeds the MD result by a factor of 2. Also, as expected, the theory does not describe correctly the dip between the steeply falling 'phonon' part and the tail; the theory is indeed tailored not to do so.

On the other hand the SS theory describes rather well the long-time tail of both the argon and the rubidium data according to Sjögren [8]. The reason for the difference between the mode-coupling results could be the totally different effective pair potentials governing the atomic motions (figure 6). In the case of lead, the neighbouring atoms are under a continuous force action whereas in argon and rubidium there is an approximately force-free region at the nearest-neighbour distance. The assumption of the theory that atoms move in a free gas-like fashion between binary collisions may have some approximate reality for argon and rubidium but not for lead. The steeply falling part of the memory function—called the binary collision part in the SS theory—is only very approximately given by an *ansatz*. In

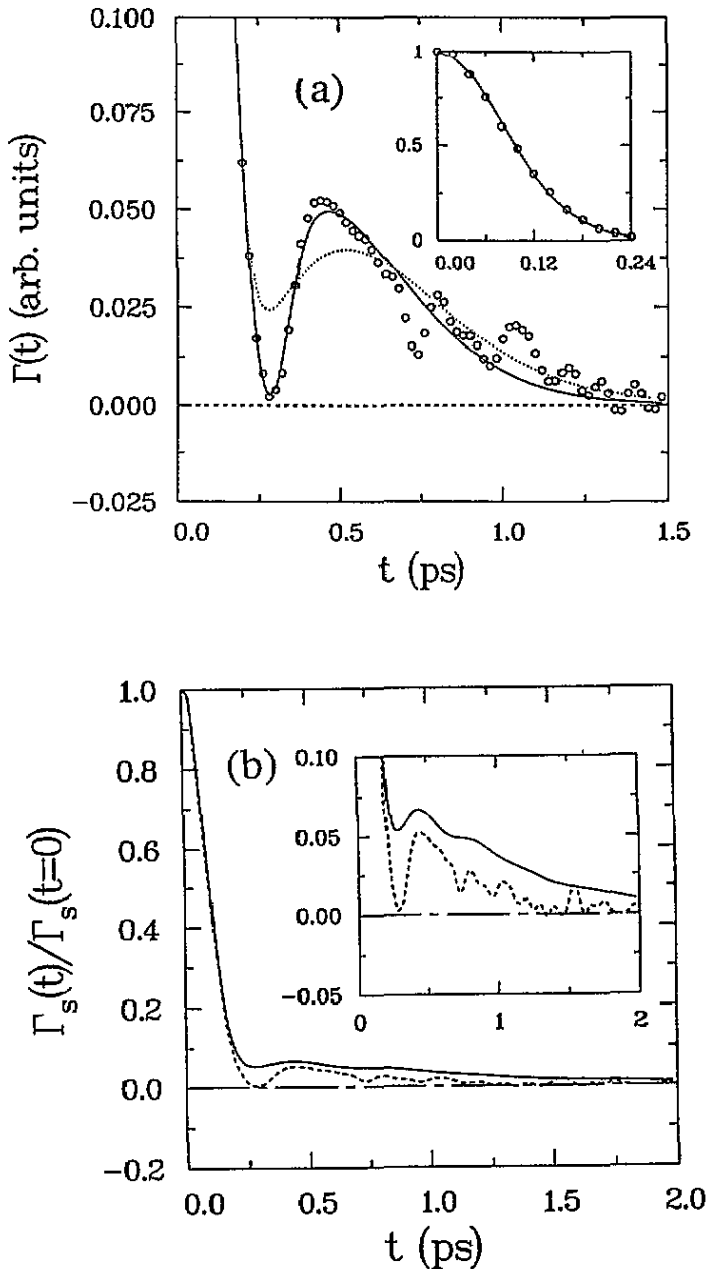


Figure 5. Memory function $\Gamma_s(t)$ of the velocity autocorrelation function $\langle v_x(0)v_x(t) \rangle$ for liquid lead. (a) At 623 K together with a fit to the LV form and the form proposed to fit the data: \circ , MD; —, form proposed for the best fit; \cdots , LV. The inset shows the main peak. (b) Mode-coupling prediction (—) of $\Gamma_s(t)$ for liquid lead compared with MD data (---).

reality the time evolution of this part of $\Gamma_s(t)$ must be determined by the atomic motions of a complicated many-body system consisting of a central atom and its cage of neighbouring

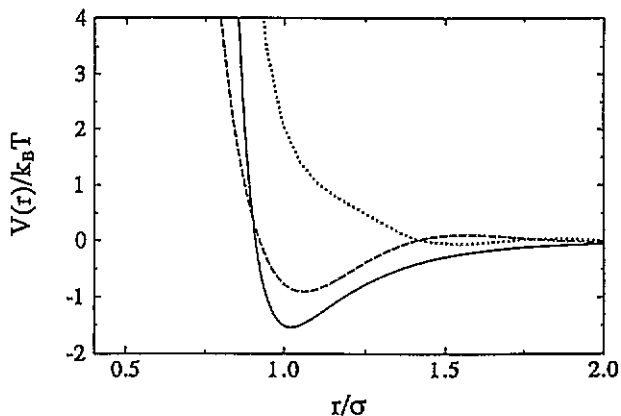


Figure 6. Effective pair potential for liquid lead, liquid sodium and liquid argon (Lennard-Jones potential): —, argon; ---, sodium; ·····, lead. The unit of distance is the position of the first peak of $g(r)$ in the corresponding liquid.

atoms.

Also the mode-coupling terms in the SS theory are based upon a similar assumption; the density fluctuation correlations in $F(Q, t)$, longitudinal current correlations in $C_l(Q, t)$ and the transverse current correlations in $C_t(Q, t)$ are coupled to a term $F_s(Q, t) - F_0(Q, t)$, where $F_0(Q, t)$ describes the free atomic motion. This construction indeed for small times gives a leading mode-coupling term starting as $\frac{1}{24} Q^2 v_0^2 \Omega_0^2 t^4$, where $v_0^2 = k_B T/m$ and Ω_0 is the Einstein frequency. The mode-coupling term thus is forced to start as t^4 to agree with the LV formula.

A critical examination of the shape of the memory functions of argon, rubidium and sodium [9] and lead obtained from MD data for $\Phi(t)$ for these liquids shows that the LV form (equation (8)) only approximately describes the gross features of $\Gamma_s(t)$ (figure 7). There are systematic deviations from the smooth LV form, and in particular, the dip between the two components is not well described by this form for *any case*. In argon this deviation goes in one direction, and in liquid metals in the opposite direction, lead being the extreme case.

It is an interesting fact that the oscillatory features in the long-time tail repeat themselves for all four liquids. The effective pair potentials are, however, radically different for these liquids, as illustrated in figure 6. One may speculate that these oscillations are the result of recollisions caused by back reactions from atoms in neighbouring shells. (Compare the overlap of $G_s(r, t)$ with $G_d(r, t)$ as time proceeds (figure 4).) Are such oscillations signalling memory effects from the dying structure? In fact for liquid lead at 623 K the remnants of periodicity in $C_l(Q, t)$ creating the maximum in $C_l(Q, \omega)$ at $\omega \simeq 9$ meV ([2] (figures 6–8) corresponds approximately to the periodicity of about 0.45 ps in the oscillations of $\Gamma_s(t)$ (time distance from $t = 0$ to the first peak at $t = 0.45$ ps. Also the longitudinal phonon dispersion relations in the solid state for all three metals have maxima at frequencies corresponding to the observed periodicity in $\Gamma_s(t)$. In any case the form predicted by present MC ideas does not fit the observations; either one has to manipulate the widths of the binary part to obtain a fit which was the case for liquid argon and rubidium [8] or one finds a distinct discrepancy in the recollision part as for liquid lead in the present study. Stronger coupling to the 'phonon'-like modes of motion are necessary. These may

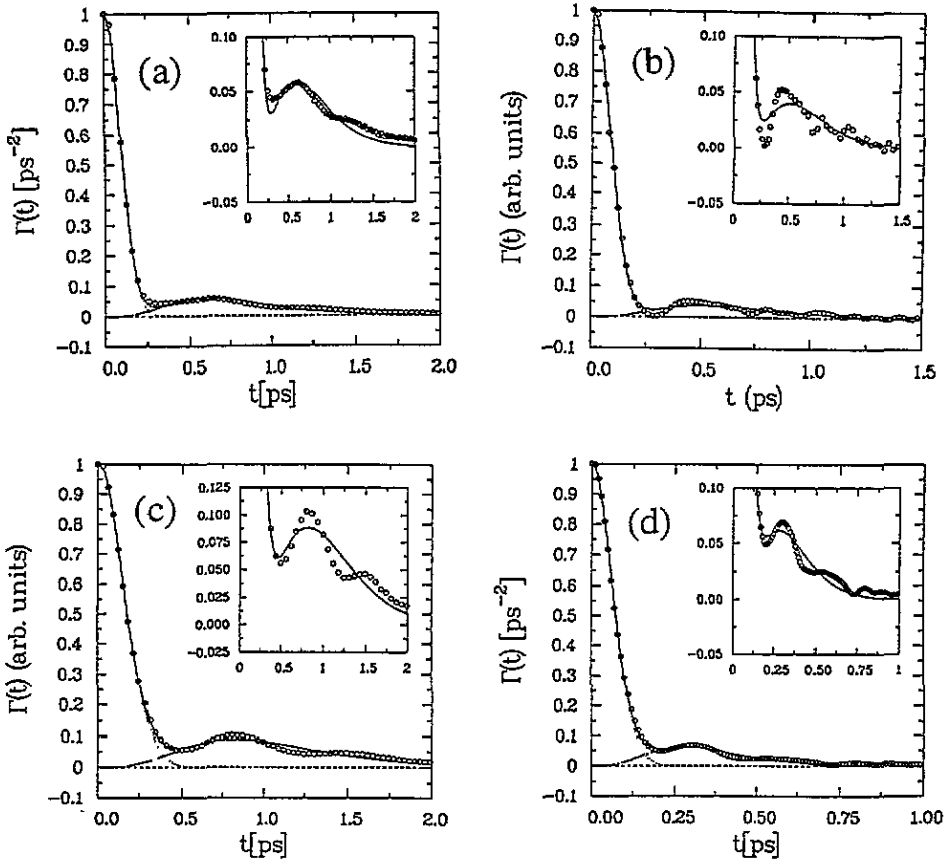


Figure 7. Memory function $\Gamma_s(t)$ of the velocity autocorrelation function $\langle v_x(0)v_x(t) \rangle$ from MD data for the four different liquids, (a) liquid argon at 85 K, (b) liquid lead at 623 K, (c) liquid rubidium at 315 K and (d) liquid sodium at 370 K: O, MD data; —, LV form; ·····, Gaussian part; - - -, tail. The inset in each case gives the tail of $\Gamma_s(t)$ on an enlarged scale. The best fit of the LV form is also given.

result in the occurrence of strongly damped oscillations before the jump to another position is performed by the self-atom when the hindering $G_d(r, t)$ has decayed sufficiently. It is possible that the so-called 'binary collision' part of $\Gamma_s(t)$ should not be separated from the oscillations in the 'recollision' part as is done in the present theoretical approximation. These oscillations should be caused by coupling of $F(Q, t)$ to $F_s(Q, t)$, but in the SS theory the basic first peak ('binary collision') is separated out

4. Conclusions

The two basic results of this report are as follows.

(1) The self-diffusion process is strongly structure related and contains an element of structural relaxations, indicating the possibility of a jump component in the process.

(2) The structure of the memory function of the velocity autocorrelation function may indicate a strong interdependence between the 'binary' and 'recollision' parts of $\Gamma_s(T)$. the oscillatory shape of $\Gamma_s(t)$ may signal the importance of treating the true many-body problem more properly than hitherto has been done.

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