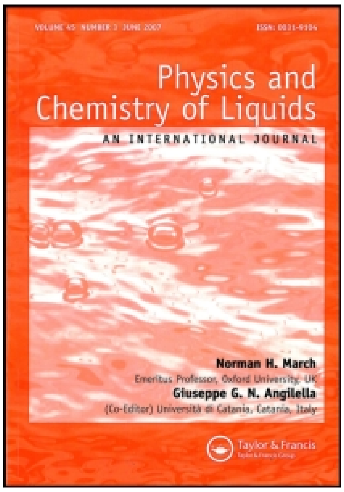

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M. I. Barker[a]; T. Gaskell[a]
[a] Department of Physics, The University Sheffield,

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A Theory of the Diffusion Coefficient in a Liquid Metal : II

M. I. BARKER and T. GASKELL

Department of Physics
The University
Sheffield

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Calculations are reported of the diffusion coefficient and frequency spectrum of the velocity autocorrelation function for a model of liquid sodium using long-range oscillatory interionic potentials. They are based on a theory of the associated memory function which employs a previously known expression for the timedependent pair distribution function. The latter is introduced to try to solve the difficult problem of describing the relative motion of two atoms, but the results are not consistent with the information obtained from molecular dynamics calculations.

On the basis of a physical argument, a modified theory of the pair distribution is then employed and shown to produce results which are in much better agreement with those obtained from computer experiments. Some information is thereby obtained about the relative motion of atoms in a liquid.

1. INTRODUCTION

A means of calculating the velocity autocorrelation function in a liquid, from a theory of the associated memory function, was given in an earlier paper[1] (to be referred to as I). The autocorrelation function is given by $\langle \mathbf{V}_i(t) . \mathbf{V}_i(o) \rangle$, where $\mathbf{V}_i(t)$ denotes the velocity of any atom in the liquid at time t, the brackets, a canonical ensemble average and the memory function $K(t)$ is defined through the equation

$$\frac{d}{dt}\,\psi(t) + \int_0^t d\tau\, K(t-\tau)\,\psi(\tau) = 0 \qquad (1.1)$$

$\psi(t)$ being the normalised velocity autocorrelation function $\langle \mathbf{V}_i(t) \,.\, \mathbf{V}_i(o) \rangle / \langle \mathbf{V}_i^2(o) \rangle$

In I an expression for $K(t)$ was derived by making use of a previous result for the so-called time-dependent pair distribution function,[2] which essentially describes the relative motion of two atoms in a fluid. By means of the latter the memory function was defined for a continuous though strongly repulsive potential for all values of t and in particular it was argued that it might be usefully employed in a calculation of the diffusion coefficient in a liquid metal. The result is

$$K(t) = -\frac{2\rho}{3m}\int \mathrm{d}x\, gy_2(x)\,\frac{\mathrm{d}\phi}{\mathrm{d}x}\,\frac{\mathrm{d}}{\mathrm{d}x}\int \mathrm{d}y\, G_s^*\,(y,t)\, gy_2\,(1x - y1) \qquad (1.2)$$

where ρ is the atomic density in the liquid, $g(x)$ the radial distribution function, G_s^* a modified self-correlation function given by

$$G_s^*(y,t) = \left\{4\pi\, a(t)\right\}^{-3/2} \exp\left(-y^2 / 4a(t)\right)$$

with $a(t) = \frac{k_B T}{m^*} \int_0^t d\tau (t-\tau)\psi(\tau)$ and $m^* = m/_2$, the reduced mass in the relative motion of the two atoms. The diffusion coefficient, D, is obtained from the well known result $D = \frac{k_B T}{m} \int_0^{\infty} dt\, \psi(t)$, which via Eq. (1.1) may be written

$$D = \frac{k_B T}{m}\left\{\int_0^{\infty} \mathrm{d}t\, K(t)\right\}^{-1}$$

The memory function and diffusion coefficient have been investigated for liquid sodium using the long-range oscillatory potentials due to Paskin and Rahman.[3] They computed $g(x)$, $a(t)$ and the diffusion coefficient with these potentials, one of which produced results in reasonably good agreement with the corresponding experimental results for sodium. Finally we applied Eq. (1.2) to a 6-12 potential under conditions of temperature and density corresponding to argon close to the triple point and compared the result with those from a molecular dynamics calculation and previous theoretical investigations.

It is found from these investigations that the computed values of D obtained by Paskin and Rahman cannot be reproduced, and a modification of Eq. (1.2) for the memory function is suggested which brings our results for the diffusion coefficient in much better agreement with the computer calculations.

2. MEMORY FUNCTION AND FREQUENCY SPECTRUM FOR MODEL OF LIQUID SODIUM

A feature of the liquid metal potentials used by Paskin and Rahman is the long range oscillatory (LRO) tail and they can be written in the form $\phi(r) = \phi_R(r) + \phi_{\mathrm{LRO}}(r)$, where

$$\phi_R(r) = 0{\cdot}78 \exp(5{\cdot}0724 - 10{\cdot}7863 r/r_0)\,\mathrm{eV}$$

and

$$\phi_{\mathrm{LRO}}(r) = -A\,(r_0/r)^3 \cos\left\{7{\cdot}812\,(r/r_0 + \beta)\right\}$$

$r_0 = 3.72$ Å and A and β were taken as adjustable parameters, whilst those in the Born-Mayer repulsive part ϕ_R were those appropriate for sodium. Two sets of values for A and β were selected to investigate the effect of the oscillatory part of the potential and were called LRO I ($A = 0.048$ eV, $\beta = 0.5954$) and LRO II ($A = 0.027$ eV, $\beta = 0.5689$). The potentials were truncated at 8.2 Å as in the computer experiments.

Changing the variable in Eq. (1.2) for the memory function enables us to write in it a form which involves $g^{1/2}$ rather than its derivative. This is convenient since we have available only tabulated values of the radial distribution function obtained from a graphical plot.[3] It is also convenient to extract the asymptotic value of $g^{1/2}$ from the expression since it makes no contribution to the integral, which is thus obtained as

$$K(t) = \frac{4\rho}{3m}\left(\frac{\pi}{a(t)}\right)^{1/2} \int_0^\infty \mathrm{d}x\, g^{1/2}(x)\,\frac{\mathrm{d}\phi}{\mathrm{d}x} \int_0^\infty \mathrm{d}r\, r\,(g^{1/2}(r) - 1)$$
$$\cdot\left([\exp\left\{-(x-r)^2/4a(t)\right\} - \exp\left\{-(x+r)^2/4a(t)\right\}] + \right.$$
$$\left.\frac{x}{2a(t)}\,[(x-r)\exp\left\{-(x-r)^2/4a(t)\right\} - (x+r)\exp\left\{-(x+r)^2/4a(t)\right\}]\right) \quad (2.1)$$

This expression has been evaluated for both LRO I and LRO II under conditions of density and temperature close to the melting point of sodium ($\rho = 0.0243$ atoms Å^{-3}, $T = 373$°K) and the results are displayed as the upper curves in Figures 1 and 2 respectively. The general shape of the memory function in the two cases is very similar, the main features being the rapid initial decay of $K(t)$ within a time $t \simeq 4 \times 10^{-13}$ s and the very much more slowly decreasing behaviour at larger values of t, although $K(0)$ for LRO I is greater than $K(0)$ for LRO II by approximately a factor of 2. It soon became clear from the calculations for these two cases (and also on the basis of corresponding results for argon where computer data for $K(t)$ is available[4]) that the memory function is not decaying rapidly enough to be realistic, for values of $t \gtrsim 3 \times 10^{-13}\,s$, with the result that the diffusion coefficient, being inversely proportional to $\int_0^\infty \mathrm{d}t\, K(t)$, is far too small. On examining the relative contributions to the memory function from the core and tail of the potential it emerged that the effect of the potential core (the core diameter being defined as the value of r at which $\phi(r)$ first falls to zero) is dominant and that the method exaggerates its contribution to $K(t)$ for values of $t \gtrsim 3 \times 10^{-13} s$.

A decoupling scheme similar to the one used in I to derive the memory function has been successfully employed in a calculation of the diffusion coefficient of liquid argon,[5] and the results in this case led us to re-examine the expression which we had used for the time-dependent pair distribution func-

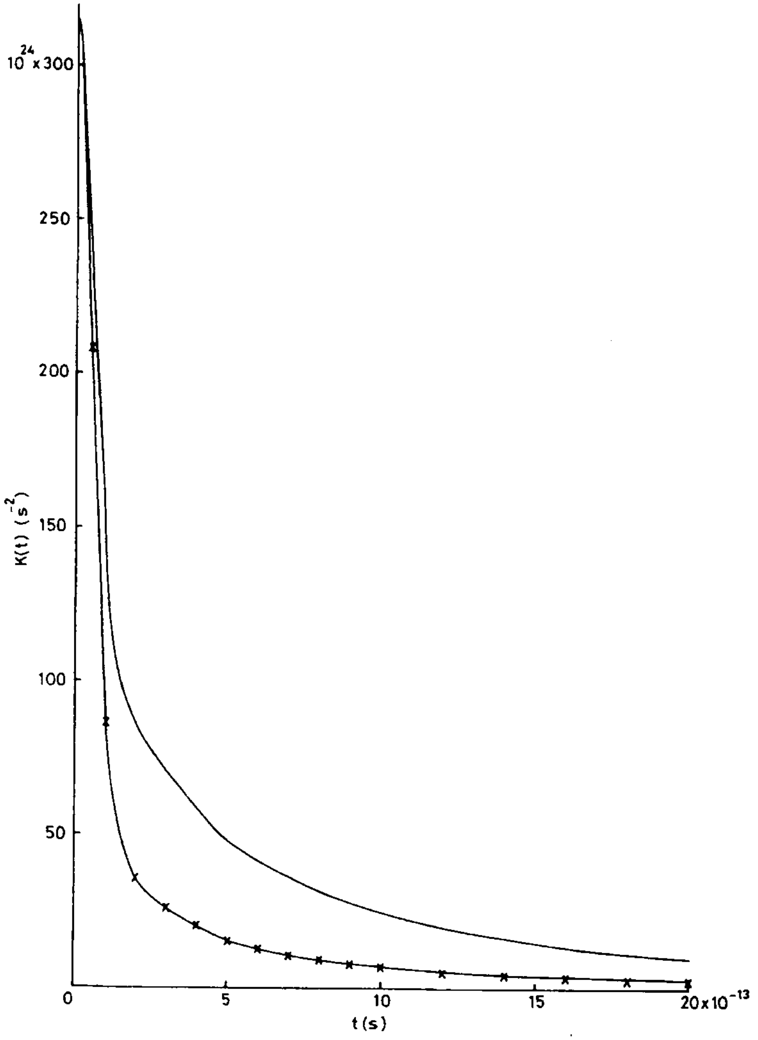

FIGURE 1 Memory function for LRO I. Lower curve obtained with modified time-dependent pair distribution function.

tion,[2] within the context of Eq. (1.2). In the notation of I this correlation function, being essentially the probability that $t = O$ two atoms will be a distance r apart while at $t = \tau$ the separation of the same two atoms will be x, is defined through the ensemble average

$$\frac{1}{N} \sum_{i,j(i \neq j)} < \delta\,(\mathrm{r} - \mathrm{x}_{ij}(\mathrm{o}))\, \delta\,(\mathrm{x} - \mathrm{x}_{ij}(\tau)) > = G(\mathbf{r}, \mathrm{x}, \tau) \qquad (2.2)$$

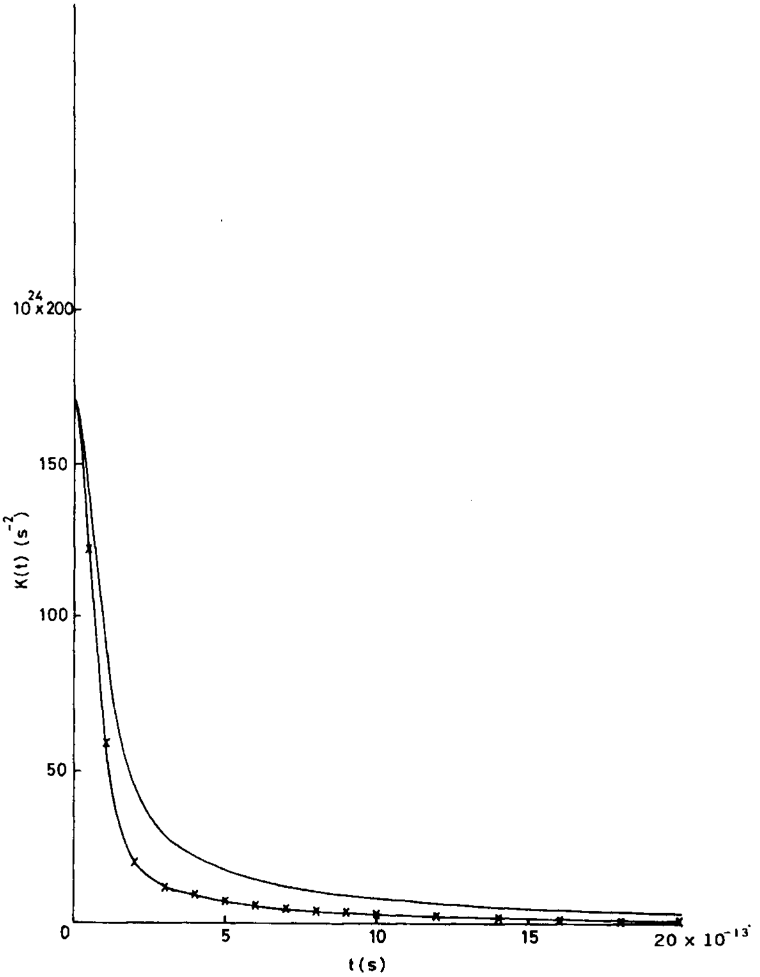

FIGURE 2 Memory function for LRO II. Lower curve obtained with modified time-dependent pair distribution function.

and the result of Oppenheim and Bloom is given by

$$G(\mathbf{r},\mathbf{x},\tau)=\rho\, g^{1/2}(r)\, g^{1/2}(x)\quad G_s^*(|\mathbf{r}-\mathbf{x}|,\tau) \tag{2.3}$$

On the basis of what might be termed a time-dependent superposition approximation one attempts to evaluate (2.2) in the following way. Average over the initial configurations of the atoms giving $\rho g(r)$, the probability density that the two atoms will be found a distance r apart. Then allow them to migrate to their final positions which means multiplying by $G_s^*(|\mathbf{r}-\mathbf{x}|,\tau)$, the probability that the atomic separation has increased by $|\mathbf{r}-\mathbf{x}|$ in time τ. Thus far we have neglected the correlation in their final positions due to their mutual interaction and we attempt to correct this by further multiplying by $g(x)$. Hence one obtains

$$G(\mathbf{r},\mathbf{x},\tau)\simeq\rho\, g(r)\, g(x)\, G_s^*(|\mathbf{r}-\mathbf{x}|,\tau) \tag{2.4}$$

The Oppenheim and Bloom result might therefore be interpreted as a time-dependent superposition in the above sense but modified so that the boundary condition

$$G(\mathbf{r},\mathbf{x},\mathrm{o})=\rho\, g(r)\,\delta(\mathbf{r}-\mathbf{x}) \tag{2.5}$$

is correctly given.

Now $g(x)\equiv\exp(-U(x)/_{k_BT})$, where $U(x)$ is the effective potential between the two atoms in the presence of the surrounding medium of the other atoms. Therefore $g^{y\frac{1}{2}}(x)=\exp(-U(x)/_{2k_BT})$ and the modification of (2.4) which leads to the result of Oppenheim and Bloom is to effectively double the temperature of these two atoms as far as the structural part of the correlation function is concerned. Apart from the incorrect boundary condition at $\tau=0$ arising from the approximation (2.4) it seems physically unreasonable to expect the instantaneous atomic distribution about any one of our two atoms to be the equilibrium distribution $g(x)$ and Eq. (2.3) represents a less well ordered distribution corresponding to a higher effective temperature $T^*=2T$. In its effect on $g(x)$ this is tantamount to softening the atomic core and thus increasing the probability that the two atoms may be found a distance x apart. The potential derivative which occurs in Eq. (1.2) arises from the mutual force which two atoms exert on each other in the liquid, and softening the core in this way exaggerates the average force since the radial distribution function with the effective temperature decays less rapidly for values of $x\lesssim$ the repulsive core of the potential. We therefore propose that to be consistent within this scheme we should modify the effective temperature of these two atoms in the dynamic part of the correlation function $G_s^*(|\mathbf{r}-\mathbf{x}|,\tau)$. The temperature dependence of this modified self correlation func tion arises through $a(t) = \frac{2k_BT}{m}\int_0^t d\tau(t-\tau)\psi(\tau)$ and the factor $\frac{2k_BT}{m}$ appears from the mean square speeds of the two atoms under consideration. The effective temperature of these atoms is doubled by redefining $a(t) = \frac{2k_BT^*}{m}\int_0^t d\tau\,(t-\tau)\psi(\tau)$ where $T^* = 2T$. The boundary condition given in Eq. (2.5) is of course unaffected by this modification.

The effect of the latter proposal on the memory function is again displayed in Figures 1 and 2. According to the computations of Paskin and Rahman, LRO II provided a significantly better fit to the experimentally determined structure and diffusion coefficient in liquid sodium and consequently it is the results for this potential, shown in Figure 2, which we have examined in more detail. The diffusion coefficient obtained from the molecular dynamics result is $D = 5.8 \times 10^{-5}\ \mathrm{cm}^2\ s^{-1}$ and this we have used in our calculation of the memory function through $a(t)$ which for large t has the limit $a(t) \rightarrow 4Dt + C$ where C is a constant. The value of $D \simeq 5.75 \times 10^{-5}\ \mathrm{cm}^2\ s^{-1}$ obtained from $K(t)$ is satisfyingly consistent with this. The frequency spectrum is defined by

$$f(w) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dt\ \exp(-iwt)\ \psi(t) \tag{2.6}$$

and it is easily shown that this can be written in the form

$$f(w) = \frac{K_c(w)\,/\,\pi}{\left\{w - K_s(w)\right\}^2 + K_c^2(w)}$$

where

$$K_s(w) = \int_0^{\infty} dt\, K(t) \sin wt$$

and

$$K_c(w) = \int_0^{\infty} dt\, K(t) \cos wt$$

This expression has been evaluated and the normalised frequency spectrum is shown in Figure 3. Paskin[6] has discussed the frequency spectrum of the velocity autocorrelation function obtained in molecular dynamics calculations with LRO II. However the diffusion coefficient quoted in this latter reference ($D = 4.9\ \mathrm{cm}^2 s^{-1}$) is not that given in the earlier report of the molecular dynamics calculations and used in our work, so that a strict comparison of the two results is not possible. Nevertheless the general features of the two frequency spectra are clearly very similar. The height of the peak in the two cases agrees closely, although its position as shown in Figure 3 occurs at a smaller value of

$\omega \simeq 1.1 \times 10^{13}\ s^{-1}$ compared to the molecular dynamics result of $\omega \simeq 1.4 \times 10^{13}\ s^{-1}$.

For LRO I a value of $D = 1.9 \times 10^{-5}$ cm^2 s^{-1} was used in the asymptotic form of $a(t)$ employed in $G_s^*(1\mathbf{r}-\mathbf{x}1,\tau)$. The calculated value of the diffusion coefficient from the memory function in this case ($D \simeq 3.1 \times 10^{-5}$ cm^2 s^{-1}) does not show the consistency obtained with potential II. Again it should be added that the value of D later quoted by Paskin is again different (2.3×10^{-5} cm^2 s^{-1}) so that there may be some inconsistency in the structure data we have used and the

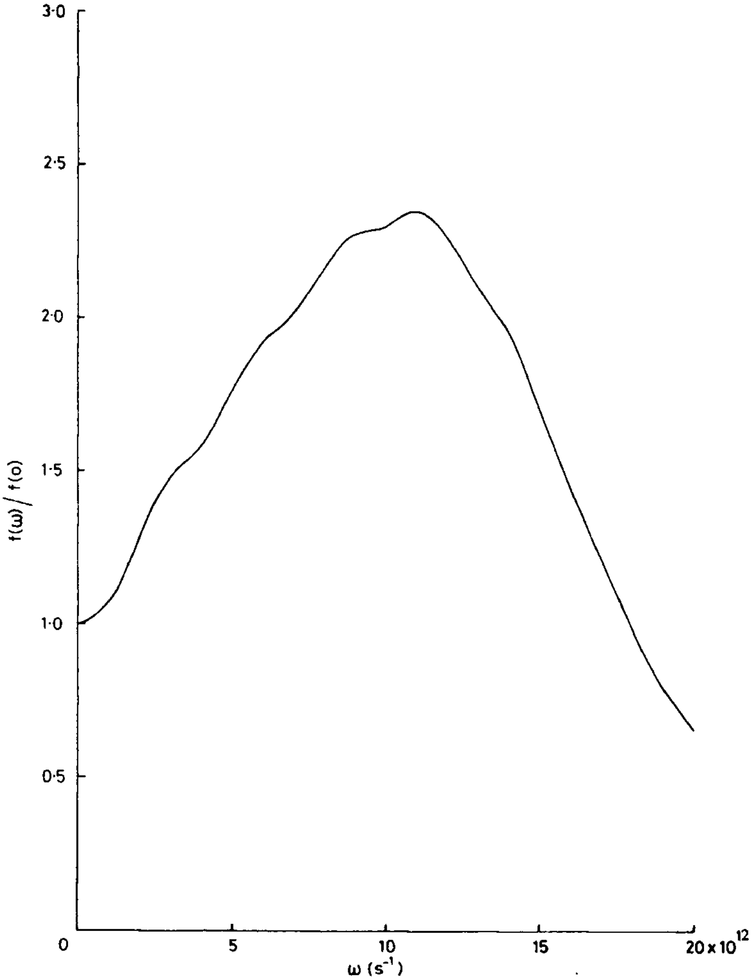

FIGURE 3 Frequency spectrum for LRO II ($D \simeq 5.75 \times 10^{-5}$ cm^2 s^{-1}).

dynamics as contained in G_s^*. This could have more significance in the case of LRO I because the amplitudes of the oscillations in this potential are larger, which might tend to make any inconsistency have more serious consequences.

Finally it must be added that the accuracy of our calculations is difficult to assess, since our data for $a(t)$ and the radial distribution function were read from a graphical plot given by Paskin and Rahman. The evaluation of the contribution to the memory function from the core region of the potential in Eq. (2.1) is particularly sensitive, because it involves the derivative of a rapidly increasing function. We believe however that the general features of the results are correct.

3. MEMORY FUNCTION FOR MODEL OF LIQUID ARGON

In this section we briefly explore the application of our equation for the memory function to a model of liquid argon. The interatomic potential we have used is a 6-12 potential given by

$$\phi(r) = 4\epsilon \left\{ \left(\frac{6}{r}\right)^{12} - \left(\frac{6}{r}\right)^{6} \right\}$$

with $\epsilon/k_B = 119.8^\circ\mathrm{K}$ and $\sigma = 3.405$ Å, under conditions of temperature and density which closely resemble those near the triple point of argon ($\rho = 0.024$ atoms Å^{-3}, $T = 86.5^\circ$K). Our input data for the radial distribution function is that due to Verlet,[7] whilst the data for $a(t)$ has been obtained from some computer results by Nijboer and Rahman.[8] Again, as shown in Figure 4, unless we use the effective temperature $T^* = 2T$ in the modified self correlation function the memory function does not decay quickly enough to be realistic. With the modification to the temperature the behaviour for larger values of t is corrected. The diffusion coefficient consistent with the data for $a(t)$ which we have used in the calculation is 1.88×10^{-5} cm^2 s^{-1} whilst that obtained from the lower curve in Figure 4 is $\simeq 1.41 \times 10^{-5}$ cm^2 s^{-1}.

The results in this case certainly do not improve those of an earlier calculation of the diffusion in argon by Barker and Gaskell.[5] In fact the theory in the latter reference seems to be preferable in this case, because their treatment of the problem of correlating the motion of two interacting atoms has a simple physical interpretation, and the extremely difficult derivation of a time-dependent pair distribution function is avoided. Although the result is not shown we have calculated the frequency spectrum associated with the memory function in Figure 4. Just as with the diffusion coefficient it compares rather less favourably with the molecular dynamics result than that previously derived by Barker and Gaskell.

It is not strictly necessary in any of these calculations to have prior information about the function $a(t)$. In fact it might be argued that instead of using a computer result for $a(t)$ it would be more satisfactory to use a self-consistent value. However since $a(t)$ is obtained from an integration of $\psi(t)$ the detailed

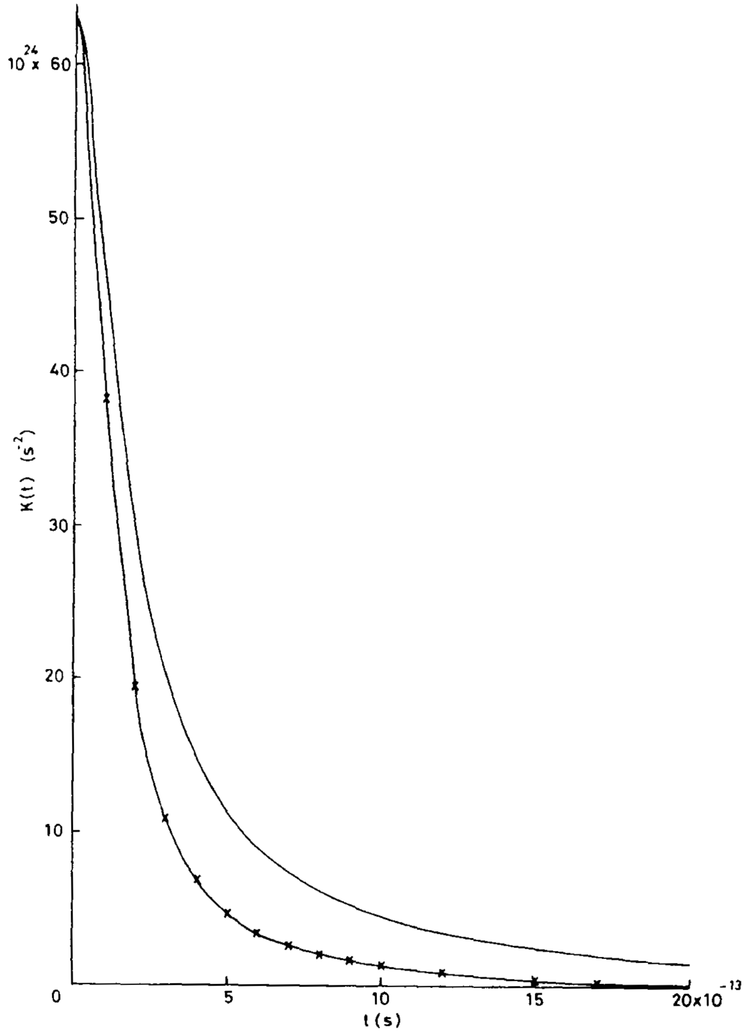

FIGURE 4 Memory function for model of liquid argon. Lower curve obtained with modified time-dependent pair distribution function.

shape of the latter is not very significant and this procedure would probably not alter to any great extend the features of our results for the memory function.

4. DISCUSSION

We have investigated the expression for the memory function given in Eq. (1.2), which incorporates a theory of the time-dependent pair distribution function, and found that the results are not consistent with the information obtained from molecular dynamics computations. The modification to the time-dependent correlation function which we suggest, within the context of our theory of the memory function, is based on what might be roughly called a time-dependent superposition approximation and one would expect it to be most appropriate for large values of t. It is interesting to note that the application of the Oppenheim and Bloom result, given in Eq. (2.3) with their asymptotic form of $a(t) = 2Dt$, was not as successful in a theory of nuclear relaxation times[9] in gases and liquids as one employing the ideal gas form of $a(t) = kTt^2/m$. With the latter form for $a(t)$ the Oppenheim and Bloom result is correct for sufficiently small values of t^9, but $a(t) = kTt^2/m$ is not an accurate representation at the liquid densities used here beyond $t \simeq 1 \times 10^{-13}$ s. In the present problem its use would be closely related to the linear trajectory approximation but seems to have very little theoretical justification. If employed for the two liquid metal potentials it produces results for the diffusion coefficient which are within 20% of those given earlier, although the detailed shape of the memory functions is different. Our suggested modification for $a(t) = \frac{2k_BT^*}{m}\int_0^t d\tau(t-\tau)\psi(\tau)$ does not reproduce the correct result for $a(t) = kTt^2/m$ at small t and should be regarded as an attempt to obtain a more accurate result for $K(t)$ at large t whilst still maintaining the correct boundary condition for the memory function at $t = 0$. We suggest therefore that the successful introduction of the effective temperature T^*, and the fact that similar results for the diffusion coefficient can be obtained with the ideal gas form of $a(t)$, is a very good indication that a more random description of the dynamics via G_s^* is consistent with the description of the static correlations by the square root of the radial distribution function. This might be further tested through application of the time-dependent pair distribution function in the calculation of nuclear quadrupole relaxation times in liquid metals.[10]

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