

## Stress autocorrelation function in liquid rubidium

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A molecular-dynamics simulation of the stress autocorrelation function  $\eta(t)$  is reported for a dense-liquid-rubidium model. The data indicate a rapid decay of the correlation function for  $t \lesssim 0.3$  ps and a somewhat slower time dependence thereafter. Mode-coupling theory, and an alternative dynamical approach involving a conditional probability distribution function, are discussed and then applied in an attempt to explain these data. The former is shown to give a very good account of our results at intermediate and long times, and a simple means of extrapolating the theory to small times is suggested. In our case excellent overall agreement with the computer data is achieved. The dependence of  $\eta(t)$  on the intermediate-scattering function  $F(q, t)$ , as predicted by the mode-coupling result, confirms the importance of collective atomic rearrangements in the dynamics of shear-stress relaxation.

### I. INTRODUCTION

The shear viscosity coefficient  $\eta$  is the simplest transport property of a fluid explicitly associated with its collective dynamics. In this work we report computer-simulation data of the corresponding Green-Kubo integrand, namely, the stress autocorrelation function  $\eta(t)$  in a liquid-rubidium model with a packing fraction close to that at the melting point. Although equivalent studies have been made for hard-sphere<sup>1</sup> and Lennard-Jones fluids,<sup>2</sup> this aspect of liquid-metal-like systems does not appear to have been investigated. The shear viscosity coefficient then follows immediately from the relation  $\eta = \int_0^\infty dt \eta(t)$ .

More generally, the dynamical effects involved in the relaxation of shear stresses are not well understood even in simple liquids, and consequently there is no convincing theory of the time dependence of  $\eta(t)$  which embraces both the short- and long-time regimes. Another purpose of our work, therefore, is to try to clarify the physical processes which underly the decay of the stress autocorrelation function. With this in mind we have investigated its initial decay more carefully than hitherto. In contrast to the rapid relaxation of shear stresses at small  $t$ , the computer data show a much slower decay at intermediate and long times. An explanation of the observed behavior in these regimes is demonstrated in terms of mode-coupling theory. The expression we use for  $\eta(t)$ , in which the dynamics is controlled by the intermediate-scattering function, is not new,<sup>3-5</sup> and an explicit derivation is not attempted although we emphasize the physical concepts and approximations behind the theory. The latter imply the introduction of a wave-vector cutoff, which we exploit in an extrapolation of the theoretical result to small times. It is also pointed out that a strikingly similar description of  $\eta(t)$  can be obtained from different physical arguments involving a time-dependent probability distribution function.

The paper is organized as follows. In Sec. II, after a brief summary of the relevant dynamical quantities, the stress autocorrelation function is expressed in terms of two-, three-, and four-particle contributions, and its short-time behavior is explicitly evaluated. The mode-coupling approach to the dynamics of  $\eta(t)$  is then presented, along with the alternative approach referred to above. In Sec. III we discuss the molecular-dynamics (MD) experiment and report the results of the evaluation of the potential, kinetic, and cross contributions to  $\eta(t)$ . The overwhelmingly dominant contribution is due to the interatomic forces, and is compared with the theoretical predictions in Sec. IV.

### II. THEORY

It is convenient to begin this section by recalling some exact results which connect the stress and transverse-current autocorrelation functions. The time dependence of  $\eta(t)$  is then discussed by (i) the investigation of its initial decay through the derivation of a formally exact expression for the leading term in a small- $t$  expansion and (ii) the application of approximate dynamical theories.

The particle-current density fluctuation in a liquid reads

$$j_{\mathbf{k}}^\alpha(t) = \sum_{i=1}^N v_i^\alpha(t) \exp[i\mathbf{k} \cdot \mathbf{r}_i(t)], \quad (2.1)$$

where  $\alpha$  denotes a Cartesian component. In turn, the microscopic stress tensor  $\sigma_{\mathbf{k}}^{\alpha\beta}$  is defined through the momentum conservation equation ( $m$  is the particle mass)

$$m j_{\mathbf{k}}^\alpha(t) = \sum_{\beta} i k^\beta \sigma_{\mathbf{k}}^{\alpha\beta}(t). \quad (2.2)$$

It is quickly demonstrated that the time integral of the autocorrelation function of its off-diagonal elements, in the limit  $k \rightarrow 0$ , determines the shear viscosity coefficient.

For this purpose we introduce the transverse-current autocorrelation function

$$C_T(k, t) \equiv \langle j_{-k}^x(0) j_k^x(t) \rangle, \quad (2.3)$$

where  $\mathbf{k}$  is taken along the  $z$  axis and the angular brackets denote a canonical ensemble average. By means of the generalized Langevin equation,<sup>6</sup> its Laplace transform  $\hat{C}_T(k, z)$  can be written as

$$\hat{C}_T(k, z) = C_T(k, t=0) / [z + (k^2/nm)\hat{\eta}(k, z)], \quad (2.4)$$

in which  $n$  is the number density and where  $\hat{\eta}(k, z)$  is interpreted as a generalized viscosity. The hydrodynamic transport coefficient, the shear viscosity  $\eta$ , is given by<sup>7</sup>

$$\begin{aligned} \eta &= \lim_{z \rightarrow 0} \lim_{k \rightarrow 0} \hat{\eta}(k, z) \\ &= (n\beta/N) \int_0^\infty dt \langle \sigma_0^{xz}(0) \sigma_0^{xz}(t) \rangle \end{aligned} \quad (2.5)$$

with the stress tensor component

$$\sigma_0^{xz}(t) = \sum_{i=1}^N [mv_i^x(t)v_i^z(t) + x_i(t)F_i^z(t)]. \quad (2.6)$$

Here,  $\mathbf{F}_i = -\sum_{j(\neq i)} \nabla_i \Phi(r_{ij})$  is the total force on atom  $i$ ,  $\Phi(r)$  being the effective pair potential in the liquid metal.

The shear stresses arise through the transfer of momentum in the liquid and we may give the following physical interpretation of the individual terms in this expression. The first arises from the transfer of an atom's momentum component in (say) the  $z$  direction through the displacement of that atom in the  $x$  direction. The second is due to the transfer of transverse momentum via the interatomic forces. At the packing fraction prevailing in a dense liquid the latter is considerably the more important of the two mechanisms.

Since there are three distinct contributions to the correlation function we write

$$\begin{aligned} (n\beta/N) \langle \sigma_0^{xz}(0) \sigma_0^{xz}(t) \rangle &= \eta(t) \\ &= \eta_{kk}(t) + \eta_{kp}(t) + \eta_{pp}(t). \end{aligned} \quad (2.7)$$

A quantitative assessment of the purely kinetic term  $\eta_{kk}(t)$  and the kinetic-potential cross term  $\eta_{kp}(t)$  will be made in Sec. II using computer-simulation data. For the reason given above we concentrate here on

$$\eta_{pp}(t) = (n\beta/N) \sum_{i,j} \langle x_i(0) F_i^z(0) x_j(t) F_j^z(t) \rangle. \quad (2.8)$$

Using the identity  $\sum_i x_i F_i^z = \frac{1}{2} \sum_i \sum_{j(\neq i)} x_{ij} f_{ij}^z$ , with  $\mathbf{f}_{ij}$  the force on the  $i$ th atom due to the  $j$ th atom, an equivalent result is

$$\eta_{pp}(t) = (1/N) \sum_{\substack{i,j \\ (j \neq i)}} \sum_{\substack{l,m \\ (l \neq m)}} \langle A(\mathbf{r}_{ij}(0)) A(\mathbf{r}_{lm}(t)) \rangle, \quad (2.9)$$

where

$$A(\mathbf{r}_{ij}) = (n\beta)^{1/2} (x_{ij} z_{ij} / 2r_{ij}) \Phi'(r_{ij}).$$

$$\dot{\eta}_{pp}^{(2)}(0) = -(16\pi n / 15m\beta) \int_0^\infty dr r^2 g(r) \{ [a'(r)]^2 + 6[a(r)/r]^2 \}. \quad (2.13)$$

The triplets' contribution to  $\dot{\eta}_{pp}(0)$  can be evaluated in a similar fashion so that

### A. Small- $t$ expansion

We begin by examining the behavior of the correlation function at small  $t$ . The coefficients of odd powers of  $t$  vanish in a Taylor expansion so that

$$\eta_{pp}(t \rightarrow 0) = \eta_{pp}(0) + \dot{\eta}_{pp}(0)t^2/2 + \dots$$

Although after Eq. (2.9) direct evaluation of the coefficients in this expansion appears to involve two-, three-, and four-particle distribution functions, some simplification is possible. As far as  $\eta_{pp}(0)$  is concerned one may exploit the first two equations of the exact Yvon-Born-Green hierarchy to reduce the multiple-particle averages and obtain

$$\eta_{pp}(0) = (2\pi n^2 / 15) \int_0^\infty dr r^4 g(r) (\Phi''(r) + 4\Phi'(r)/r), \quad (2.10)$$

where  $g(r)$  is the pair distribution function. Alternatively, by starting from Eq. (2.8), this result can be derived by using the properties of the canonical distribution function.<sup>8</sup>

To evaluate  $\dot{\eta}_{pp}(0)$  we make use of the expression in Eq. (2.9) and separate the possible choices for the atomic labels. Hence,

$$\begin{aligned} \eta_{pp}(t) &= (2/N) \sum_{\substack{i,j \\ (j \neq i)}} \langle A(\mathbf{r}_{ij}(0)) A(\mathbf{r}_{ij}(t)) \rangle \\ &\quad + (4/N) \sum_{\substack{i,j,l \\ (l \neq j \neq i)}} \langle A(\mathbf{r}_{ij}(0)) A(\mathbf{r}_{il}(t)) \rangle \\ &\quad + (1/N) \sum_{\substack{i,j,l,m \\ (m \neq l \neq j \neq i)}} \langle A(\mathbf{r}_{ij}(0)) A(\mathbf{r}_{lm}(t)) \rangle \\ &\equiv \eta_{pp}^{(2)}(t) + \eta_{pp}^{(3)}(t) + \eta_{pp}^{(4)}(t). \end{aligned} \quad (2.11)$$

The pairs' contribution to  $\dot{\eta}_{pp}(0)$  is given by

$$\begin{aligned} \dot{\eta}_{pp}^{(2)}(0) &= (2/N) \sum_{\substack{i,j \\ (j \neq i)}} \langle A(\mathbf{r}_{ij}(0)) \ddot{A}(\mathbf{r}_{ij}(0)) \rangle \\ &= -(2/N) \sum_{\substack{i,j \\ (j \neq i)}} \langle \dot{A}(\mathbf{r}_{ij}(0)) \dot{A}(\mathbf{r}_{ij}(0)) \rangle \\ &= -(2/N) \sum_{\substack{i,j \\ (j \neq i)}} \langle [\mathbf{v}_{ij}(0) \cdot \nabla_{ij} A(\mathbf{r}_{ij}(0))]^2 \rangle \\ &= -(4n/m\beta) \int d\mathbf{r} [\nabla A(\mathbf{r})]^2 g(r). \end{aligned} \quad (2.12)$$

Writing  $A(\mathbf{r})$  in terms of polar angles, i.e.,  $A(\mathbf{r}) = a(r) \cos\theta \sin\theta \cos\phi$  with  $a(r) = (n\beta)^{1/2} r \Phi'(r)$ , we finally obtain

$$\begin{aligned}
\ddot{\eta}_{pp}^{(3)}(0) &= -(4/N) \sum_{\substack{i,j,l \\ (l \neq j \neq i)}} \langle \dot{A}(\mathbf{r}_{ij}(0)) \dot{A}(\mathbf{r}_{il}(0)) \rangle \\
&= -(4/N) \sum_{\substack{i,j,l \\ (l \neq j \neq i)}} \langle [\mathbf{v}_{ij} \cdot \nabla_{ij} A(\mathbf{r}_{ij})][\mathbf{v}_{il} \cdot \nabla_{il} A(\mathbf{r}_{il})] \rangle \\
&= -(4n^2/Nm\beta) \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \nabla_{12} A(\mathbf{r}_{12}) \cdot \nabla_{13} A(\mathbf{r}_{13}) g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\
&= -(4n^2/m\beta) \int \int d\mathbf{r} ds \nabla A(\mathbf{r}) \cdot \nabla A(\mathbf{s}) g^{(3)}(\mathbf{r}, \mathbf{s}) .
\end{aligned} \tag{2.14}$$

To perform the angular integrations it is convenient to expand the three-particle distribution function  $g^{(3)}(\mathbf{r}, \mathbf{s})$  in a series of Legendre polynomials:<sup>9</sup>

$$g^{(3)}(\mathbf{r}, \mathbf{s}) = g^{(3)}(r, s, \cos\Theta) = \sum_{l=0}^{\infty} Q_l(r, s) P_l(\cos\Theta) = 4\pi \sum_{l=0}^{\infty} Q_l(r, s) (2l+1)^{-1} \sum_{m=-l}^l Y_{lm}^*(\Omega_r) Y_{lm}(\Omega_s) . \tag{2.15}$$

In the above equations  $\Theta$  is the angle between  $\mathbf{r}$  and  $\mathbf{s}$ , and in the last line we have expressed the Legendre polynomials in terms of spherical harmonics of the polar angles [ $\Omega \equiv (\theta, \phi)$ ] of  $\mathbf{r}$  and  $\mathbf{s}$ . To exploit the orthogonality property of the spherical harmonics we write  $\nabla A(\mathbf{r})$  and  $\nabla A(\mathbf{s})$  also in terms of spherical harmonics by means of the so-called "gradient formula."<sup>10</sup> After some straightforward algebra, Eq. (2.14) becomes

$$\begin{aligned}
\ddot{\eta}_{pp}^{(3)}(0) &= -(8\pi n^2/15m\beta) \int_0^\infty dr r^2 \int_0^\infty ds s^2 \{ (24\pi/35) Q_3(r, s) [a'(r) - 2a(r)/r] [a'(s) - 2a(s)/s] \\
&\quad + (16\pi/15) Q_1(r, s) [a'(r) + 3a(r)/r] [a'(s) + 3a(s)/s] \} .
\end{aligned} \tag{2.16}$$

Equation (2.16) is still exact, but to proceed further we are forced to make use of an approximate theory of the three-particle distribution function. In the superposition approximation the expansion coefficients in Eq. (2.15) are found to be<sup>11</sup>

$$Q_l(r, s) = g(r)g(s)(2l+1) \left[ \delta_{l0} + (1/2\pi^2 n) \int_0^\infty dq q^2 h(q) j_l(qr) j_l(qs) \right] . \tag{2.17}$$

Here,  $h(q) = S(q) - 1$ ;  $S(q)$  being the static structure factor of the liquid and  $j_l(x)$  is a spherical Bessel function. Within the superposition approximation, Eq. (2.16) now becomes

$$\begin{aligned}
\ddot{\eta}_{pp}^{(3)}(0) &= -(32n/75m\beta) \int_0^\infty dq q^2 h(q) \left[ 3 \left[ \int_0^\infty dr r^2 g(r) j_3(qr) [a'(r) - 2a(r)/r] \right]^2 \right. \\
&\quad \left. + 2 \left[ \int_0^\infty dr r^2 g(r) j_1(qr) [a'(r) + 3a(r)/r] \right]^2 \right] .
\end{aligned} \tag{2.18}$$

Finally, the quadruplets' contribution to  $\ddot{\eta}_{pp}(0)$  reads

$$\begin{aligned}
\ddot{\eta}_{pp}^{(4)}(0) &= -(1/N) \sum_{\substack{i,j,l,m \\ (m \neq l \neq j \neq i)}} \langle \dot{A}(\mathbf{r}_{ij}) \dot{A}(\mathbf{r}_{lm}) \rangle \\
&= -(1/N) \sum_{\substack{i,j,l,m \\ (m \neq l \neq j \neq i)}} \langle [\mathbf{v}_{ij} \cdot \nabla_{ij} A(\mathbf{r}_{ij})][\mathbf{v}_{lm} \cdot \nabla_{lm} A(\mathbf{r}_{lm})] \rangle = 0 ,
\end{aligned} \tag{2.19}$$

since the ensemble average contains the scalar product of the velocities of four different particles.

Consequently, the decay of  $\eta_{pp}(t)$  at short times is determined by  $\ddot{\eta}_{pp}(0) = \ddot{\eta}_{pp}^{(2)}(0) + \ddot{\eta}_{pp}^{(3)}(0)$ , with  $\ddot{\eta}_{pp}^{(2)}(0)$  given exactly by Eq. (2.13) and  $\ddot{\eta}_{pp}^{(3)}(0)$  by Eq. (2.18), in the superposition approximation.

## B. Dynamical theories

In this section we discuss an approximate treatment of the dynamics of the stress autocorrelation function, initially using mode-coupling arguments. It is well known that mode-coupling theories were originally introduced to describe critical dynamics. Subsequently, they have

proved useful in several other areas,<sup>12</sup> the common feature in every case being the emphasis on aspects of the dynamics outside a certain "microscopic" time region. For a given correlation function  $f(t)$  the conventional time scale which characterizes this region may be obtained as  $[|\dot{f}(0)|/f(0)]^{-1/2}$ . Typically, in a dense fluid, this is  $\sim 10^{-13}$  s, which is of the order of a binary collision time.

The basis of the calculation is the idea that the decay of a fluctuation of a dynamical variable can be predominantly described in terms of bilinear products of a limited set of variables  $\{A_\mu(\mathbf{k})\}$ . Let  $P$  represent the standard projection operator over this set; in the present context it is sufficient to consider the (orthogonal) set to consist of

the three components of the current density fluctuation  $\mathbf{j}_k$ , and the fourth to be the density fluctuation

$$n_{\mathbf{k}} = \sum_i \exp[i\mathbf{k} \cdot \mathbf{r}_i(0)] - (2\pi)^3 n \delta(\mathbf{k}).$$

For small values of  $k$  these variables are quasiconserved and therefore their dynamics becomes rather slow. In addition, for subsequent interpretation it is worthwhile to stress that  $n_{\mathbf{k}}$  also shows a considerable slowing-down effect for wave vectors near the position of the principal peak of  $S(k)$  ("de Gennes narrowing").

An appropriate starting point is the memory function  $(k^2/nm)\eta(k, t)$  associated with the transverse current, so that we may eventually obtain  $\eta(t) = \lim_{k \rightarrow 0} \eta(k, t)$ . The philosophy behind mode-coupling theory is to extract the slowly decaying part of the memory function in an approximate way. This is achieved in two stages. The *first approximation* involves projecting the random force onto the subspace which is spanned by bilinear products of the type  $(1-P)A_{\mu}(\mathbf{q})A_{\lambda}(\mathbf{k}-\mathbf{q})$ , and eventually summing over all "modes"  $\lambda, \mu$ , as well as over the internal wave vector  $\mathbf{q}$ . This procedure is strictly justified only if the leading contribution to the sum comes from the slowly varying terms. The *second approximation* is to factorize the four  $A$ -variable products which now arise in the memory function into products of two-variable correlation functions, and at the same time replace the anomalous propagator  $\exp[it(1-P)\mathcal{L}]$  by the ordinary one,  $\exp[it\mathcal{L}]$ .  $\mathcal{L}$ , of course, refers to the usual Liouville operator. This replacement is strictly only valid if the external wave vector  $k \rightarrow 0$ .<sup>7</sup> For the stress autocorrelation function, therefore, the latter procedure is justified.

The actual nature of the dynamical modes is determined by the static "vertex" functions, which arise in the projection of the random force. Taking advantage of the expectation that at liquid densities the potential contribution  $\eta(t)$  is the dominant one, it is found that only vertex functions involving products of the density fluctuations are nonzero. On the basis of the above arguments the following mode-coupling result may be obtained:<sup>3-5</sup>

$$\eta_{pp}(t) = (n^2 k_B T / 60\pi^2) \int_0^{q_c} dq q^4 [c'(q)]^2 F^2(q, t). \quad (2.20)$$

The intermediate-scattering function  $F(q, t) \equiv \langle n_{-\mathbf{q}}(0)n_{\mathbf{q}}(t) \rangle / N$  and  $c(q) \equiv (1/n)[1 - S^{-1}(q)]$  is the direct correlation function. The finite upper limit to the integral is to emphasize that this expression can be justified only when the integral is dominated by a limited range of wave vectors [up to a value of the order of the first maximum of  $S(q)$ , for the above-mentioned reasons]. We expect this criterion to be satisfied at sufficiently long times when the magnitude of  $q_c$  can increase indefinitely without affecting the result for  $\eta_{pp}(t)$ .

In contrast, the short-time dynamics is expected to be dominated by large wave vectors, of the order of (or higher than) the inverse of the mean free path. In this regime a strict mode-coupling approach breaks down.

Before closing this section it is interesting to note that a result similar to Eq. (2.20) can be obtained without any

appeal to mode-coupling arguments. We start from Eq. (2.9), which can be written in the form

$$\eta_{pp}(t) = \int \int d\mathbf{R}_0 d\mathbf{R} A(\mathbf{R}_0) A(\mathbf{R}) P(\mathbf{R}_0, 0; \mathbf{R}, t), \quad (2.21)$$

where

$$P(\mathbf{R}_0, 0; \mathbf{R}, t) = (1/N) \sum_{\substack{i,j \\ (j \neq i)}} \sum_{\substack{l,m \\ (l \neq m)}} \langle \delta(\mathbf{R}_0 - \mathbf{r}_{ij}(0)) \times \delta(\mathbf{R} - \mathbf{r}_{lm}(t)) \rangle \quad (2.22)$$

represents the joint probability that two particles are separated by  $\mathbf{R}_0$  at  $t=0$  and by  $\mathbf{R}$  at time  $t$ . The particles referred to at the later time may be either or both of the two original particles (i.e., pairs and triplets), or they may be different particles (quadruplets). An approximate expression for this time-dependent distribution function can be obtained on the basis of intuitive physical arguments. The probability of the initial configuration of two atoms is  $ng(R_0)$ . Let  $\mathbf{r}$  be the separation between the initial position of one of these and the location of one of the atoms in the pair referred to at time  $t$ ; then the equivalent separation of the remaining two atoms is  $\mathbf{r} + \mathbf{R} - \mathbf{R}_0$ . Taking into account the correlation of the pair at time  $t$  we express the joint probability function as

$$P(\mathbf{R}_0, 0; \mathbf{R}, t) \simeq ng(R_0)g(R) \times \int d\mathbf{r} G(r, t)G(|\mathbf{r} + \mathbf{R} - \mathbf{R}_0|, t), \quad (2.23)$$

in which  $G(r, t) = G_s(r, t) + G_d(r, t)$  is the van Hove pair distribution function. By writing the latter in terms of its self- and distinct components, it can be seen that the above result takes into account, in an approximate way, all the possible identities of the final pair of atoms.

If we now introduce the intermediate scattering function through the relation

$$G(r, t) = n + (1/V) \sum_{q(\neq 0)} F(q, t) \exp(i\mathbf{q} \cdot \mathbf{r}),$$

it is found from Eqs. (2.21) and (2.23) that after some manipulation we may obtain the approximate result

$$\eta_{pp}(t) = (4n^2 / 15k_B T) \times \int_0^{\infty} dq q^2 F^2(q, t) \times \left[ \int_0^{\infty} dR R^3 g(R) \Phi'(R) j_2(qR) \right]^2. \quad (2.24)$$

The similarity between the latter and the mode-coupling result in Eq. (2.20) can be made even more transparent by noting that Eq. (2.24) has the alternative form

$$\eta_{pp}(t) = (n^2 k_B T / 60\pi^2) \int_0^{\infty} dq q^4 [E'(q)]^2 F^2(q, t), \quad (2.25)$$

with  $E(R) \equiv (1/k_B T) \int_R^\infty dr g(r) \Phi'(r)$  and  $E(q)$  its Fourier transform given by

$$E(q) = \int dR E(R) \exp(iq \cdot r) \\ = 4\pi \int_0^\infty dR R^2 E(R) j_0(qR). \quad (2.26)$$

Apart from the wave-vector cutoff, Eq. (2.25) is identical in form to the mode-coupling result in Eq. (2.20). Although perhaps this is surprising, it is not entirely fortuitous, since the physical arguments behind the result in Eq. (2.23) amount to a repeated factorization of ensemble averages similar to those adopted in mode-coupling theory. Neither approach is expected to be correct as  $t \rightarrow 0$ , and we have found that the mode-coupling result gives a much better description of the MD data at intermediate and long times.

### III. THE COMPUTER SIMULATION EXPERIMENT

The autocorrelation function of the stress tensor component in Eq. (2.6) has been evaluated by following the trajectories of  $N=500$  "rubidium" particles, in a cubic box with periodic boundary conditions, through a standard MD program. The thermodynamic state point is chosen to be close to that investigated by Rahman,<sup>13</sup> at a density  $n^* = n\sigma^3 = 0.905$  and  $T = 338$  K. In such conditions the box length is  $L = 36.15$  Å. The density-dependent interatomic potential has been evaluated according to the prescriptions in the theory implemented by Price *et al.*,<sup>14</sup> and it turns out that the characteristic parameters are  $\sigma = 4.405$  Å and  $\epsilon/k_B = 402.8$  K. It has been shown that such a pseudopotential model is able to reproduce, in a satisfactory way, the static and dynamical structure factors of liquid Rb close to this state point.<sup>13,15</sup>

Relatively less attention has been paid to the ability of this model to match the experimental values of the transport coefficients. Only recently have shear viscosity calculations appeared, which make use of two different nonequilibrium molecular dynamics (NEMD) methods.<sup>16,17</sup> The values of  $\eta$  reported in Ref. 17 (obtained by the NEMD method devised by Evans *et al.*<sup>18</sup>) are in better agreement with the experimental data at the three thermodynamic states investigated. To our knowledge, no equilibrium MD calculations of the stress correlation function have been reported for liquid Rb, so that it is interesting to compare our value of the shear viscosity with other available data.

The quantities which appear on the right-hand side of Eq. (2.6) have been evaluated every two time steps of the MD run (in our case  $\Delta t = 1 \times 10^{-14}$  s). The autocorrelations and cross correlations of the kinetic and potential contributions have been calculated separately in order to determine their relative importance. Finally, the three independent off-diagonal components of the stress tensor were checked in order to ascertain any possible anisotropy of the system. On average, of course, they have to be the same and the attainment of this equality gives a criterion to judge whether the number of time steps is sufficient for a proper evaluation of the functions under investigation. In practice, we proceeded as follows. The correlation functions up to  $400\Delta t$  were evaluated in a

block of 6200 time steps, over which the three independent components turn out to be virtually identical; eight such blocks were then repeated and the mean-square deviation calculated. Four other successive blocks were performed, and the correlation functions were found to be close to the previous average within the estimated statistical error.

The results for the three different terms in Eq. (2.7) [normalized to  $\eta_{pp}(0)$ ] are reported in Fig. 1. As expected, the potential part gives the overwhelming contribution to the stress autocorrelation function. Moreover, it is practically negligible beyond 3 ps, thus assuring that the evaluation of the Green-Kubo integral up to 4 ps gives an accurate assessment of the shear viscosity. In this calculation we obtained  $\eta = 5.50$  mP. The experimental value at the same density and temperature is 5.93 mP,<sup>19</sup> and the extrapolated NEMD result of Ref. 17 is 6.14 mP. In view of the statistical uncertainties which affect the evaluation of this quantity by both NEMD and equilibrium MD, the 12% discrepancy is considered to be not unreasonable.

The present result appears to be consistent with some data reported in a previous paper,<sup>20</sup> in which we investigated the transverse-current correlation function for a range of wave vectors. We found that at the smallest accessible wave vector,  $k\sigma = (2\pi/L)\sigma = 0.766$ , the transverse current  $C_T(k, t)$  showed a "quasihydrodynamic" behavior. From these data the corresponding memory function was obtained, and the comparison with  $\eta(t)$  is shown in Fig. 2, where both functions have been normalized to their respective  $t=0$  values. In the time range of the figure the two curves are very close. Significant differences only appear at later times, where the memory function becomes negative.

### IV. DISCUSSION

In this section we compare the theoretical results of Sec. II with our MD simulation data for  $\eta_{pp}(t)$ . As already pointed out, an immediate problem is the expected

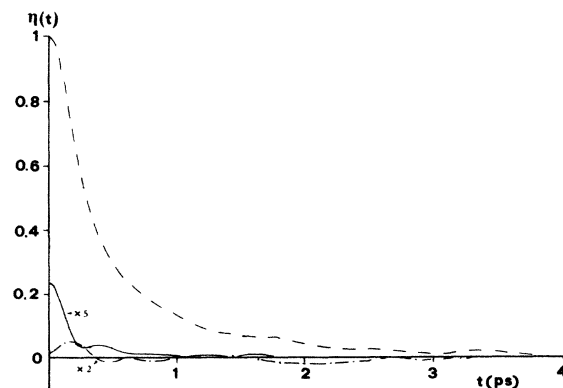


FIG. 1. Contributions to the stress autocorrelation function in liquid rubidium. Dashed line, MD data of the potential part  $\eta_{pp}(t)/\eta_{pp}(0)$ ; solid line, the kinetic part  $\eta_{kk}(t)/\eta_{pp}(0)$ ; dotted-dashed line, the cross part  $\eta_{kp}(t)/\eta_{pp}(0)$ . The kinetic and cross contributions have been multiplied by 5 and 2, respectively.

inability of any mode-coupling approach to describe the short-time dynamics, or even the initial value. There are several ways to bypass this difficulty. In a rigorous approach one should recognize that at sufficiently short times the dynamics of the system is dominated by a propagator which describes uncorrelated binary collisions. In a hard-sphere system, for example, this gives rise to the Enskog values for the transport coefficients. Approximate treatments of short-range atomic dynamics have also been proposed for continuous potentials.<sup>21,22</sup> Unfortunately, in dense systems, the problem of including binary collision effects has proved difficult and a rather phenomenological ansatz is usually employed to describe the initial decay of the correlation function.<sup>22</sup> We choose a slightly more heuristic and much simpler procedure. It was noted earlier that in the mode-coupling result for  $\eta_{pp}(t)$  the large wave-vector contributions to the integral will become significant at small times. We exploit this by requiring that in Eq. (2.20) the cutoff value  $q_c$  is chosen so that  $\eta_{pp}(0)$  has the value found in the computer simulation. To determine this single "fitting parameter" we need only the structure factor  $S(q)$  as input data.

The behavior at finite  $t$  is determined by the intermediate scattering function and, in principle, one can use a self-consistent theory which gives  $F(q, t)$  as a solution of a set of coupled equations based on kinetic and mode-coupling arguments.<sup>21,22</sup> However, such self-consistent calculations are numerically involved and often a simpler procedure has been followed by using approximate terminations of the Mori continued fraction for the relevant correlation functions. In our case we exploit the fact that for liquid rubidium a good description of the dynamic structure factor is provided by the viscoelastic model.<sup>23</sup> After the rapid initial decay of the stress correlation function we find that the smaller wave vectors in the integral (2.20) become more and more important. Eventually, a time domain is reached in which the results essentially become independent of the chosen value for  $q_c$ , provided that it is large enough to include the range of wave vectors around the principal peak in  $S(q)$ . This was to be expected from our earlier comments. In fact, these wave

vectors make the dominant contribution to the integral for the time range shown in Fig. 3.

In practice, the MD value  $\eta_{pp}(t=0)=1.08 \times 10^{10} \text{ g cm}^{-1} \text{ s}^{-2}$ , which fixes a cutoff  $q_c=11.1\sigma^{-1}$ . This wave vector is large enough to include the main peak and the first minimum of  $S(q)$ . The theoretical result for  $\eta_{pp}(t)$ , using computer-generated structure data and with  $q_c=11.1\sigma^{-1}$ , is reported in Fig. 3 together with the MD data. It can be seen that the overall agreement is very good. Surprisingly, it appears that the theory is able to reproduce even the initial decay of  $\eta_{pp}(t)$ . This is controlled by the quantity  $\ddot{\eta}_{pp}(0)$ , which according to Eq. (2.20) is given by

$$\ddot{\eta}_{pp}(0) = -(nk_B T)^2 / (30\pi^2 m) \int_0^{q_c} dq q^6 [c'(q)]^2 S(q). \quad (4.1)$$

An evaluation of this expression gives  $\ddot{\eta}_{pp}(0) \simeq -22.47 \times 10^{34} \text{ g cm}^{-1} \text{ s}^{-4}$ , in close accord with the MD value  $-22.7 \times 10^{34} \text{ g cm}^{-1} \text{ s}^{-4}$ , which was estimated by fitting the  $\eta_{pp}(t)$  data at very small  $t$ . This agreement, however, is to be considered somewhat fortuitous, both for the general physical reasons mentioned at the beginning of this section and because rather precise knowledge of the structure factor is required to evaluate the above expression accurately. It is interesting to note, at this stage, that when this second derivative is calculated from Eqs. (2.13) and (2.18) we obtain, instead,  $\ddot{\eta}_{pp}(0) = -14.9 \times 10^{34} \text{ g cm}^{-1} \text{ s}^{-4}$ . The reason for this discrepancy obviously lies in the use of the superposition approximation when evaluating the triplets' contribution. The latter, unfortunately, makes a substantial contribution to the second derivative. We find  $\ddot{\eta}_{pp}^{(2)}(0) = -52.8 \times 10^{34} \text{ g cm}^{-1} \text{ s}^{-4}$ , and  $\ddot{\eta}_{pp}^{(3)}(0) = 37.9 \times 10^{34} \text{ g cm}^{-1} \text{ s}^{-4}$ , so that calculating the latter in an approximate way can lead to a substantial error in  $\ddot{\eta}_{pp}(0)$ , due to the large cancellation between  $\ddot{\eta}_{pp}^{(2)}(0)$  and  $\ddot{\eta}_{pp}^{(3)}(0)$ .

The situation improves greatly at intermediate times, where the dependence of the mode-coupling results on  $q_c$  decreases rapidly. This is demonstrated by the observa-

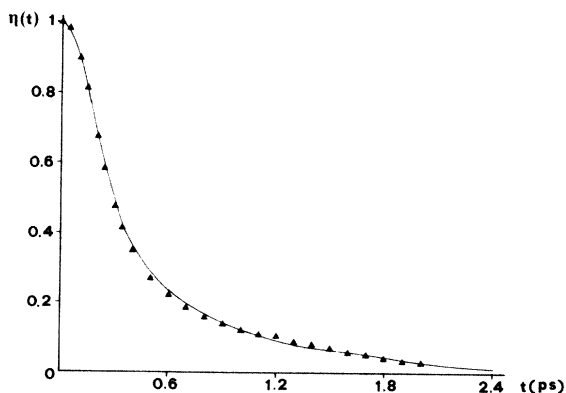


FIG. 2. Solid line showing the stress autocorrelation function. The triangles represent the normalized memory function  $\eta(k, t)/\eta(k, 0)$  of the transverse current for the wave vector  $k\sigma=0.766$ , obtained directly from computer-simulation data.

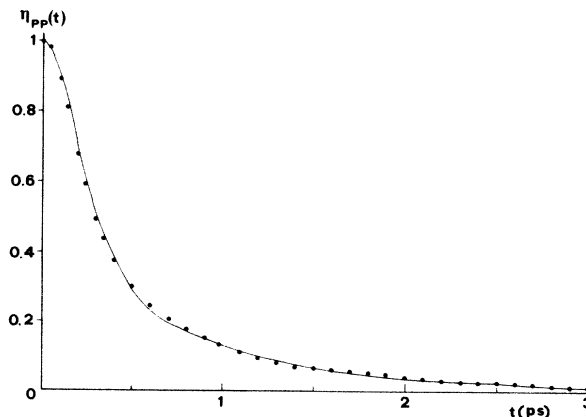


FIG. 3. Solid line showing the result of the mode-coupling calculation of  $\eta_{pp}(t)/\eta_{pp}(0)$ , and the dots indicate the corresponding computer data.

tion that, even for  $t=0.3$  ps, increasing the cutoff to  $48\sigma^{-1}$  [which is the maximum wave vector for which  $S(q)$  data are available] changes the value of  $\eta_{pp}(t)$  by only 6%. Beyond  $t=0.5$  ps, changing  $q_c$  in this way has no significant effect on the results. This feature of the theory and the very good agreement with the MD data give us confidence in the mode-coupling result for  $t \gtrsim 0.5$  ps. We conclude that the decay of the stress autocorrelation function is controlled at intermediate and long times by the behavior of the intermediate scattering function, or, since the latter is essentially the Fourier transform of the van Hove correlation function  $G(r,t)$ , by collective atomic rearrangements in the liquid.

Our alternative theory, based on the approximation in Eq. (2.25) for the joint probability density  $P(\mathbf{R}_0, 0; \mathbf{R}, t)$  also involves the intermediate scattering function. However, the predicted decay of  $\eta_{pp}(t)$  does not agree quantitatively with mode-coupling theory, showing that the weighting factor  $[c'(q)]^2$  is also very significant.

### V. CONCLUDING REMARKS

In this work we have reported MD data for the stress autocorrelation function in a system modeling liquid rubidium. Roughly speaking, the dynamical behavior of this Green-Kubo integrand is characterized by a fast initial decay followed by a rather weaker time dependence thereafter, which is typical of many other correlation functions in dense fluids. We have not attempted a microscopic treatment of the dynamics at short times. Nevertheless we have made some progress towards a theoretical description of the effects by deriving an expression for the leading coefficient in a small- $t$  expansion of the dominant component  $\eta_{pp}(t)$ .

The situation appears much more encouraging at intermediate and long times, where an approach based on mode-coupling concepts has been shown to account remarkably well for the computer-simulation data. We have emphasized too the importance of those density modes whose wave vectors lie near the first maximum of the static structure factor. Furthermore, in our particular case, excellent overall agreement has been attained by introducing a finite limit  $q_c$  in the wave-vector integral of the mode-coupling expression for  $\eta_{pp}(t)$ . There is no serious justification for this step, as we have pointed out, and it should be regarded as a useful extrapolation procedure. This is emphasized by noting that the calculated value of the shear viscosity coefficient is  $\eta=5.46$  mP, to be compared to the MD value of 5.5 mP.

A recent MD study of a soft-sphere fluid has demonstrated a marked slowing down in the decay of the stress autocorrelation function (and consequent enhancement of the shear viscosity) as the system is supercooled.<sup>24</sup> It will be interesting to see if the nonlinear coupling to the intermediate-scattering function can explain the effect. Further work in this direction is in progress, and the need for a fully self-consistent theory for  $F(q,t)$  may become extremely important.

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