

## Theory of Atomic Motions in Simple Classical Liquids

K. S. SINGWI

*Institute of Theoretical Physics, Sven Hultins gata, Göteborg, Sweden*  
and

*Solid State Science Division, Argonne National Laboratory, Argonne, Illinois*

AND

A. SJÖLANDER

*Institute of Theoretical Physics, Sven Hultins gata, Göteborg, Sweden*

(Received 5 September 1967)

This paper is an attempt towards developing a theory of the self-motion of atoms in monatomic classical fluids, based on a simplified Liouville equation and on a knowledge of the interaction potential  $V(r)$  and the static pair correlation function  $g(r)$ . A nonlinear integral equation for the velocity autocorrelation function  $\Phi(t)$  is derived which under certain approximations can be written as

$$\frac{d\Phi(t)}{dt} + \int_0^t K(t-t')\Phi(t')dt' = 0,$$

where the kernel  $K(t)$  is an implicit function of  $\Phi(t)$ . An expression for  $K(t)$  in terms of  $V(r)$  and  $g(r)$  has been given. Explicit numerical calculations for the "memory" function  $K(t)$  have been made for liquid argon at  $T = 85.9^\circ\text{K}$ , and the results have been compared with those obtained by Rahman from his machine computations.

### 1. INTRODUCTION

RECENT slow-neutron scattering experiments<sup>1</sup> and machine computations<sup>2</sup> have revealed some very detailed features of the self-motion of atoms in simple classical liquids. The quantity of main interest here is the velocity autocorrelation function which has been shown to have a rather complicated time dependence; in particular, it is negative in a certain time range. This, as well as other evidence, indicates that the motion of an atom has both a vibratory and a diffusive component. In the past, several models<sup>3</sup> have been proposed to account for this kind of motion. By their very nature, these models involve parameters which are introduced in a rather *ad hoc* manner and cannot, therefore, be easily related to microscopic quantities. The principal aim of this paper is to discuss, essentially from first principles, the dynamics of single atoms in simple classical liquids. Our treatment is based on a knowledge of the interatomic potential and the static pair correlation function.

It has been shown by Berne *et al.*<sup>4</sup> and by others<sup>5,6</sup> that it is possible to write an integrodifferential equation

<sup>1</sup> See, e.g., P. A. Egelstaff, Rept. Progr. Phys. **29**, 333 (1966); K. Sköld and K. E. Larsson, Phys. Rev. **161**, 102 (1967); K. E. Larsson, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), p. 347.

<sup>2</sup> A. Rahman, Phys. Rev. **136**, A405 (1964).

<sup>3</sup> See, e.g., A. Sjölander, in *Thermal Neutron Scattering*, edited by P. A. Egelstaff (Academic Press Inc., New York, 1965), p. 291; V. F. Sears, Proc. Phys. Soc. (London), **86**, 953 (1965); A. G. Gibbs, in *Symposium on Inelastic Scattering of Neutrons by Condensed Systems* (Brookhaven National Laboratory, Associated Universities, Inc., 1965), p. 155; V. Ardent, G. F. Nardelli, and L. Reatto, Phys. Rev. **148**, 124 (1966); P. S. Damle, A. Sjölander, and K. S. Singwi, *ibid.* **165**, 277 (1968).

<sup>4</sup> B. J. Berne, J. P. Boon, and S. A. Rice, J. Chem. Phys. **45**, 1086 (1966).

<sup>5</sup> K. S. Singwi and M. P. Tosi, Phys. Rev. **157**, 153 (1967).

<sup>6</sup> R. Kubo, in *Many-Body Theory, 1965 Tokyo Summer Lectures*

for the velocity autocorrelation function  $\Phi(t)$  of the form

$$\frac{d\Phi(t)}{dt} + \int_0^t K(t-t')\Phi(t')dt' = 0, \quad (1)$$

where the kernel  $K(t)$ , using the notation of Berne *et al.*, has the physical meaning of a "memory" function. The derivation was based on a general formalism given by Zwanzig<sup>7</sup> and also used by Mori<sup>8</sup> in similar contexts. It seems convenient to discuss the velocity autocorrelation function through the memory function for the simple reason that in this way one can easily incorporate both vibratory and diffusive kinds of motions. The former corresponds to choosing a constant for  $K(t)$ . Choosing  $K(t)$  to be a  $\delta$  function, one recovers Langevin's equation, which gives an exponential decay for the velocity autocorrelation function. Machine computations of Rahman<sup>9</sup> for liquid argon have indicated that  $K(t)$  has two important characteristic features: (a) that it drops very sharply from its value at time  $t=0$  to a value which is smaller by an order of magnitude in a time range of  $3 \times 10^{-13}$  sec, and (b) that it has a long tail having a much slower time dependence. It is shown in the present paper that these two characteristic features of the memory function computed by Rahman can be understood in terms of the static pair correlation function and the interatomic potential, and that the values of the calculated  $K(t)$  are in satisfactory agreement with those of Rahman.

in *Theoretical Physics*, edited by R. Kubo (W. A. Benjamin, Inc., New York, 1966), Part I, p. 1.

<sup>7</sup> R. Zwanzig, in *Lectures in Theoretical Physics*, edited by W. E. Brittin (Interscience Publishers, Inc., New York, 1961), p. 106.

<sup>8</sup> H. Mori, Progr. Theoret. Phys. (Kyoto) **33**, 423 (1965).

<sup>9</sup> A. Rahman (unpublished).

The basic physical ideas underlying our treatment can be briefly summarized as follows. We focus our attention on the atom marked "blue", having a velocity  $\mathbf{v}_0(t)$ , and ask how the surroundings will respond to the motion of this marked atom. The change in the density of the surroundings arising from the motion of the blue atom is calculated from a simplified Liouville equation. Knowing the change in the density enables us to calculate the force on the blue atom from the surroundings and, hence, to write its equation of motion. From this equation of motion, we finally obtain an equation for the velocity autocorrelation function.

## 2. MATHEMATICAL FORMULATION

In this section we derive an equation of motion for the blue atom, whose position and velocity we denote by  $\mathbf{x}_0(t)$  and  $\mathbf{v}_0(t)$ , respectively. The one-particle distribution function  $f_1(\mathbf{x}, \mathbf{p}, t)$  of the surrounding medium is governed by the equation<sup>10</sup>

$$\frac{\partial f_1(1)}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{x}} f_1(1) - \nabla V[\mathbf{x} - \mathbf{x}_0(t)] \cdot \nabla_{\mathbf{p}} f_1(1) - \int \nabla V(\mathbf{x} - \mathbf{x}') \cdot \nabla_{\mathbf{p}} f_2(1, 1') d(1') = 0, \quad (2)$$

where 1 is here an abbreviated notation for  $(\mathbf{x}, \mathbf{p}, t)$ , and  $\nabla_{\mathbf{x}}$ ,  $\nabla_{\mathbf{p}}$  stand for the gradients with respect to  $\mathbf{x}$ , and  $\mathbf{p}$ , respectively.  $V(\mathbf{x})$  is the interaction potential between two atoms. The third term in the equation is due to the influence from the blue atom. The last term takes into account all interactions between the surrounding atoms and contains the two-particle distribution function  $f_2(1, 1')$ . Let us write

$$f_1(1) = f_1^0(1) + \bar{f}_1(1) \quad (3)$$

and

$$f_2(1, 1') = f_2^0(1, 1') + \bar{f}_2(1, 1'),$$

where  $f_1^0(1)$  and  $f_2^0(1, 1')$  are the equilibrium distributions around the blue particle at  $\mathbf{x}_0(t)$ , and  $\bar{f}_1(1)$ ,  $\bar{f}_2(1, 1')$  refer to deviations from equilibrium.  $f_1^0(1)$  is further given by

$$f_1^0(1) = f^0(\mathbf{p}) g[\mathbf{x} - \mathbf{x}_0(t)], \quad (4)$$

where  $f^0(\mathbf{p}) = (\beta/2\pi m)^{3/2} \exp(-\beta p^2/2m)$  is the Maxwellian distribution of momenta, with  $\beta = 1/k_B T$ ,  $k_B$  being the Boltzmann constant.  $g[\mathbf{x} - \mathbf{x}_0(t)]$  is the static equilibrium pair correlation function centered around the marked atom at  $\mathbf{x}_0(t)$ .

<sup>10</sup> M. Born and H. S. Green, Proc. Roy. Soc. (London) **A188**, 10 (1946); J. Yvon, in *La Theorie Statistique des Fluides et l'Equation d'Etat* (Hermann & Cie., Paris, 1935); N. N. Bogoliubov, J. Phys. USSR **10**, 265 (1946); J. G. Kirkwood, J. Chem. Phys. **14**, 180 (1946); E. G. D. Cohen, in *Fundamental Problems in Statistical Mechanics* (North-Holland Publishing Co., Amsterdam, 1962).

Substituting Eq. (3) in Eq. (2), we have

$$\begin{aligned} \partial \bar{f}_1(1)/\partial t + \mathbf{v} \cdot \nabla_{\mathbf{x}} \bar{f}_1(1) - \nabla V[\mathbf{x} - \mathbf{x}_0(t)] \cdot \nabla_{\mathbf{p}} \bar{f}_1(1) \\ - \int \nabla_{\mathbf{x}} V(\mathbf{x} - \mathbf{x}') \cdot \nabla_{\mathbf{p}} \bar{f}_2(1, 1') d(1') \\ = -\partial f_1^0(1)/\partial t, \end{aligned} \quad (5a)$$

where

$$\partial f_1^0(1)/\partial t = -f^0(\mathbf{p}) \nabla g[\mathbf{x} - \mathbf{x}_0(t)] \cdot \mathbf{v}_0(t). \quad (5b)$$

Here the major complication arises from the last term on the left-hand side of Eq. (5a). It is responsible for the following physical effects:

(i) As is usual in many-body systems, the interaction between the particles is renormalized and some effective interactions enter instead.

(ii) The free-particle flow term, represented by the second term in Eq. (5a), will be modified so as to take into account the erratic Brownian-type motion of a single atom.

(iii) The surrounding atoms will have a tendency to reach thermal equilibrium around the blue atom.

Formally, Eq. (5a) can be written as

$$L_{op} \bar{f}_1(\mathbf{x}, \mathbf{p}, t) = f^0(\mathbf{p}) \nabla g[\mathbf{x} - \mathbf{x}_0(t)] \cdot \mathbf{v}_0(t), \quad (6)$$

where  $L_{op}$  is some complicated operator. In order to illustrate the point of view we are going to adopt in our discussion, we will consider the following special case of Eq. (5a):

$$(\partial/\partial t + \mathbf{v} \cdot \nabla_{\mathbf{x}} + 1/\tau) \bar{f}_1(1) = f^0(\mathbf{p}) \nabla g[\mathbf{x} - \mathbf{x}_0(t)] \cdot \mathbf{v}_0(t), \quad (7)$$

where  $\tau$  is some appropriate relaxation time for the medium. In this way we have incorporated the effects mentioned under (iii) above, but have disregarded the other effects.

The above linear equation can most easily be solved by going over to the Fourier transforms. The solution is

$$\begin{aligned} \bar{f}_1(\mathbf{x}, \mathbf{p}, t) = \int_0^t dt' \int d\mathbf{x}' \left\{ \int \frac{d\mathbf{q}}{(2\pi)^3} \exp[i(\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')) \right. \\ \left. - \mathbf{v} \cdot \mathbf{q}(t - t')] \right\} \exp[-(t - t')/\tau] f^0(\mathbf{p}) \\ \times \nabla g[\mathbf{x}' - \mathbf{x}_0(t')] \cdot \mathbf{v}_0(t'). \end{aligned} \quad (8)$$

The change in the density is obtained by integrating over all momenta and we get from Eq. (8)

$$\begin{aligned} \bar{\rho}_1(\mathbf{x}, t) = \int_0^t dt' \int d\mathbf{x}' \exp\left(-\frac{t-t'}{\tau}\right) G_s^0(\mathbf{x} - \mathbf{x}', t - t') \\ \times \nabla g[\mathbf{x}' - \mathbf{x}_0(t')] \cdot \mathbf{v}_0(t'), \end{aligned} \quad (9)$$

where

$$G_s^0(\mathbf{x}, t) = [\pi a(t)]^{-3/2} \exp[-x^2/a(t)], \quad (10)$$

and  $a(t) = (2k_B T/m)^{1/2}$ ,  $m$  being the atomic mass.  $G_s^0(\mathbf{x}, t)$  is the classical form of the Van Hove<sup>11</sup> self-correlation function for a particle moving freely, and it has the physical meaning of giving the probability for a free particle to move to a position  $\mathbf{x}$  at time  $t$ , if it started from the origin at  $t=0$ .

In a real physical situation the particle does not move as a free particle but performs a complicated Brownian type of motion. One should, therefore, in Eq. (9) replace the free-particle "propagator"  $G_s^0$  by the appropriate propagator, denoted by  $G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t''))$ . This function gives the probability of finding an atom at  $\mathbf{x}$  at time  $t$ , if it was located at  $\mathbf{x}'$  at time  $t'$ , with due consideration of the presence of the blue atom. In this last respect it differs from the proper Van Hove self-correlation function.

Therefore, instead of Eq. (9), we write

$$\bar{\rho}_1(\mathbf{x}, t) = \int_0^t dt' \int d\mathbf{x}' \exp\left(-\frac{t-t'}{\tau}\right) G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t'')) \times \nabla g[\mathbf{x}' - \mathbf{x}_0(t')] \cdot \mathbf{v}_0(t'). \quad (11)$$

As  $G_s(\dots)$  was introduced above, it does not take into account effects stated under (iii) above, which would be brought about by some complicated Boltzmann-type collision term in  $L_{op}$ . In order to proceed, we have made a standard single relaxation-time approximation.  $\exp[-(t-t')/\tau] G_s(\dots)$  represents, before integration over momenta is performed, the Green's function of the operator  $L_{op}$  in Eq. (6). In this way all the effects mentioned under (i)–(iii) have been taken care of in an approximate way. The time  $\tau$  represents the average time it takes for the surrounding medium to establish complete thermal equilibrium.

The equation of motion for the blue atom is then

$$m \frac{d\mathbf{v}_0(t)}{dt} = - \int d\mathbf{x} \nabla V[\mathbf{x}_0(t) - \mathbf{x}] \bar{\rho}_1(\mathbf{x}, t), \quad (12)$$

which on using Eq. (11) becomes

$$m \frac{d\mathbf{v}_0(t)}{dt} = - \int_0^t dt' \exp\left(-\frac{t-t'}{\tau}\right) \int d\mathbf{x} d\mathbf{x}' \nabla V[\mathbf{x}_0(t) - \mathbf{x}] \times G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t'')) \nabla g[\mathbf{x}' - \mathbf{x}_0(t')] \cdot \mathbf{v}_0(t'). \quad (13)$$

It should be noted here that  $V[\mathbf{x}_0(t) - \mathbf{x}]$  above is the bare potential and not any renormalized interaction potential.

In writing the above equations we have disregarded the presence of a fluctuating part of the force, arising from fluctuations in the density of the surrounding medium. We shall assume these fluctuations not to depend significantly on the velocity of the blue atom. In that case, the fluctuating force will be statistically

independent of the velocity and will disappear in the equation for the velocity autocorrelation function.

Multiplying Eq. (13) with  $\mathbf{v}_0(0)$  and taking a statistical average, we get

$$\begin{aligned} & m \frac{d}{dt} \langle \mathbf{v}_0(t) \cdot \mathbf{v}_0(0) \rangle \\ &= - \sum_{\alpha\beta} \int_0^t dt' \exp\left(-\frac{t-t'}{\tau}\right) \int d\mathbf{x} d\mathbf{x}' \\ & \quad \times \langle \nabla_\alpha V[\mathbf{x}_0(t) - \mathbf{x}] G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t'')) \\ & \quad \times \nabla_\beta g[\mathbf{x}' - \mathbf{x}_0(t')] v_{0\beta}(t') v_{0\alpha}(0) \rangle, \quad (14) \end{aligned}$$

where  $\langle \dots \rangle$  denotes a thermal average and  $\alpha, \beta$  indicate the three Cartesian components.

$G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t''))$  depends on the history of  $\mathbf{x}_0(t)$ . However, the most obvious effect, arising from the presence of the blue particle, is that a surrounding atom is excluded from a small region around the position  $\mathbf{x}_0(t)$  at time  $t$ . We shall average  $G_s(\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t''))$  over all various paths of the blue atom which terminate at  $\mathbf{x}_0(t)$  at time  $t$ , and we substitute the obtained propagator for the one introduced earlier. This averaged propagator will be denoted by  $\bar{G}_s[\mathbf{x}t, \mathbf{x}'t' | \mathbf{x}_0(t)]$ . We further define an effective potential  $\bar{V}(\mathbf{x}, t)$  through the relation

$$\begin{aligned} & \int \nabla V[\mathbf{x}_0(t) - \mathbf{x}] \bar{G}_s[\mathbf{x}t; \mathbf{x}'t' | \mathbf{x}_0(t)] d\mathbf{x} \\ &= \nabla \bar{V}[\mathbf{x}_0(t) - \mathbf{x}', t-t']. \quad (15) \end{aligned}$$

In order to make it evident that the potential so defined really depends only on the differences  $[\mathbf{x}_0(t) - \mathbf{x}']$  and  $t-t'$ , we write

$$\begin{aligned} & \int \nabla V[\mathbf{x}_0(t) - \mathbf{x}] \bar{G}_s[\mathbf{x}t; \mathbf{x}'t' | \mathbf{x}_0(t)] d\mathbf{x} \\ &= \int \nabla V[\mathbf{x}_0(t) - \mathbf{x}' - \mathbf{y}] \bar{G}_s[\mathbf{x}' + \mathbf{y}, t; \mathbf{x}', t' | \mathbf{x}_0(t)] d\mathbf{y} \\ &= \int \nabla V[\mathbf{x}_0(\tau) - \mathbf{x}' - \mathbf{y}] \bar{G}_s[\mathbf{y}, \tau; 00 | \mathbf{x}_0(\tau) - \mathbf{x}'] d\mathbf{y}, \end{aligned}$$

( $\tau = t-t'$ ), since by definition

$$\bar{G}_s[\mathbf{x}' + \mathbf{y}, t; \mathbf{x}'t' | \mathbf{x}_0(t)] = \bar{G}_s[\mathbf{y}, \tau; 00 | \mathbf{x}_0(\tau) - \mathbf{x}'].$$

We thus have

$$\begin{aligned} & \int \nabla V[\mathbf{x}_0(t) - \mathbf{x}] \bar{G}_s[\mathbf{x}t; \mathbf{x}'t' | \mathbf{x}_0(t)] d\mathbf{x} \\ &= \int \nabla_{\mathbf{x}_0} V[\mathbf{x}_0(\tau) - \mathbf{x}' - \mathbf{y}] \\ & \quad \times \bar{G}_s[\mathbf{y}, \tau; 00 | \mathbf{x}_0(\tau) - \mathbf{x}'] d\mathbf{y}. \quad (16) \end{aligned}$$

<sup>11</sup> L. Van Hove, Phys. Rev. **95**, 249 (1954).

Here, it is made obvious that our statement above for  $\bar{V}$  is correct.

Using Eq. (15) in Eq. (14), we have

$$\begin{aligned} & m \frac{d}{dt} \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle \\ &= - \sum_{\alpha\beta} \int_0^t dt' \exp\left(-\frac{t-t'}{\tau}\right) \\ & \quad \times \left\langle \int d\mathbf{x}' \nabla_{\alpha} \bar{V}[\mathbf{x}_0(t) - \mathbf{x}', t-t'] \right. \\ & \quad \left. \times \nabla_{\beta} g[\mathbf{x}' - \mathbf{x}_0(t')] v_{\beta}(t') v_{\alpha}(0) \right\rangle, \quad (17) \end{aligned}$$

where from now on we shall drop the suffix 0 on  $\mathbf{v}$ .

It remains to evaluate the expression within the brackets in Eq. (17). To achieve this we go over to the Fourier transform and write

$$\begin{aligned} & \left\langle \int d\mathbf{x}' \nabla_{\alpha} \bar{V}[\mathbf{x}_0(t) - \mathbf{x}', t-t'] \nabla_{\beta} g[\mathbf{x}' - \mathbf{x}_0(t')] v_{\beta}(t') v_{\alpha}(0) \right\rangle \\ &= - \int \frac{d\mathbf{q}}{(2\pi)^3} q_{\alpha} q_{\beta} \bar{V}(\mathbf{q}, t-t') g(\mathbf{q}) \\ & \quad \times \langle \exp\{i\mathbf{q} \cdot [\mathbf{x}_0(t) - \mathbf{x}_0(t')]\} v_{\beta}(t') v_{\alpha}(0) \rangle, \quad (18) \end{aligned}$$

where  $\bar{V}(\mathbf{q}, t)$  and  $g(\mathbf{q})$  are, respectively, defined by

$$\bar{V}(\mathbf{x}, t) = \int \bar{V}(\mathbf{q}, t) \exp(i\mathbf{q} \cdot \mathbf{x}) \frac{d\mathbf{q}}{(2\pi)^3}, \quad (19)$$

and

$$g(\mathbf{x}) = \int g(\mathbf{q}) \exp(i\mathbf{q} \cdot \mathbf{x}) \frac{d\mathbf{q}}{(2\pi)^3}.$$

Let us consider the expression

$$\begin{aligned} & \sum_{\alpha\beta} q_{\alpha} q_{\beta} \langle \exp\{i\mathbf{q} \cdot [\mathbf{x}_0(t) - \mathbf{x}_0(t')]\} v_{\beta}(t') v_{\alpha}(0) \rangle \\ &= \left\langle \exp\left[ i \int_{t'}^t \mathbf{q} \cdot \mathbf{v}(t'') dt'' \right] [\mathbf{q} \cdot \mathbf{v}(t')] [\mathbf{q} \cdot \mathbf{v}(0)] \right\rangle. \quad (20) \end{aligned}$$

The component of  $\mathbf{v}$  along  $\mathbf{q}$  will be denoted by  $v_q$  and we notice that

$$\begin{aligned} & -iq \left\langle \exp\left[ iq \int_{t'}^t v_q(t'') dt'' \right] v_q(t') v_q(0) \right\rangle \\ &= \frac{d}{dt'} \left\langle \exp\left[ iq \int_{t'}^t v_q(t'') dt'' \right] v_q(0) \right\rangle. \quad (21) \end{aligned}$$

In order to simplify this expression, we shall utilize the same method as was used by Rahman *et al.* to obtain the Gaussian approximation.<sup>12</sup> This approximation<sup>3,12</sup> has been widely used in connection with discussions of self-motion of atoms in liquids and has been found to hold well.<sup>2</sup>

We therefore write as follows:

$$\begin{aligned} \left\langle \exp\left[ iq \int_{t'}^t v_q(t'') dt'' \right] v_q(0) \right\rangle &= \sum_{\nu=0}^{\infty} \frac{(iq)^{\nu}}{\nu!} \int_{t'}^t dt \cdots \int_{t'}^t dt_{\nu} \langle v_q(t_1) \cdots v_q(t_{\nu}) v_q(0) \rangle \\ &= \sum_{\mu=0}^{\infty} \frac{(iq)^{2\mu+1}}{(2\mu+1)!} \frac{(2\mu+2)!}{2^{\mu+1}(\mu+1)!} \left[ \int_{t'}^t dt_1 \int_{t'}^t dt_2 \langle v_q(t_1) v_q(t_2) \rangle \right]^{\mu} \int_{t'}^t d\tau' \langle v_q(\tau') v_q(0) \rangle \\ &= iq \exp\left[ -\frac{1}{2} q^2 \int_{t'}^t dt_1 \int_{t'}^t dt_2 \langle v_q(t_1) v_q(t_2) \rangle \right] \int_{t'}^t d\tau' \langle v_q(\tau') v_q(0) \rangle \\ &= \frac{1}{3} iq \exp\left[ -\frac{1}{3} q^2 \int_0^{t-t'} d\tau (t-t'-\tau) \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle \right] \int_{t'}^t d\tau' \langle \mathbf{v}(\tau') \cdot \mathbf{v}(0) \rangle. \quad (22) \end{aligned}$$

In going from the second to the third step, we have split higher-order velocity correlations into the lowest-order ones as follows:

$$\langle 1234 \rangle = \langle 12 \rangle \langle 34 \rangle + \langle 13 \rangle \langle 24 \rangle + \langle 14 \rangle \langle 23 \rangle \text{ etc.}, \quad (23)$$

disregarding correction terms. For more details we refer to Rahman *et al.*<sup>13</sup>

From Eqs. (22) and (21) we now have

$$\begin{aligned} \left\langle \exp\left[ i \int_{t'}^t \mathbf{q} \cdot \mathbf{v}(t'') dt'' \right] [\mathbf{q} \cdot \mathbf{v}(t')] [\mathbf{q} \cdot \mathbf{v}(0)] \right\rangle &= \frac{1}{3} q^2 \exp\left[ -\frac{1}{3} q^2 \int_0^{t-t'} d\tau (t-t'-\tau) \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle \right] \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle \\ & \quad + \frac{1}{3} q^2 \left\{ \frac{d}{dt} \exp\left[ -\frac{1}{3} q^2 \int_0^{t-t'} d\tau (t-t'-\tau) \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle \right] \right\} \int_{t'}^t d\tau' \langle \mathbf{v}(\tau') \cdot \mathbf{v}(0) \rangle. \quad (24) \end{aligned}$$

<sup>12</sup> G. H. Vineyard, Phys. Rev. **110**, 999 (1958).

<sup>13</sup> A. Rahman, K. S. Singwi, and A. Sjölander, Phys. Rev. **126**, 986 (1962).

The last term takes into account the dynamical correlation between the exponential term and  $v_q(t')v_q(0)$  on the left-hand side of Eq. (20).

Using the above result we can write Eq. (18) as follows:

$$\sum_{\alpha\beta} \left\langle \int d\mathbf{x}' \nabla_{\alpha} \bar{V}[\mathbf{x}_0(t) - \mathbf{x}', t - t'] \nabla_{\beta} g[\mathbf{x}' - \mathbf{x}_0(t')] v_{\beta}(t') v_{\alpha}(0) \right\rangle = -\frac{1}{3} \int \frac{d\mathbf{q}}{(2\pi)^3} q^2 \bar{V}(\mathbf{q}, t - t') g(\mathbf{q}) \times \left( \exp[-\frac{1}{4}q^2 a(t - t')] \langle \mathbf{v}(t') \cdot \mathbf{v}(0) \rangle + \left\{ \frac{d}{dt} \exp[-\frac{1}{4}q^2 a(t - t')] \right\} \int_{t'}^t \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle d\tau \right), \quad (25)$$

where

$$a(t) = \frac{4}{3} \int_0^t d\tau (t - \tau) \langle \mathbf{v}(\tau) \cdot \mathbf{v}(0) \rangle. \quad (26)$$

In the Gaussian approximation the proper Van Hove self-correlation function, denoted by  $G_s(\mathbf{x}, t)$ , is given in terms of  $a(t)$  as follows:

$$G_s(\mathbf{x}, t) = [\pi a(t)]^{-3/2} \exp[-x^2/a(t)]. \quad (27)$$

With the help of Eq. (25), Eq. (17) can be written as

$$\frac{d}{dt} \Phi(t) + \int_0^t \Gamma_0(t - t') \Phi(t') dt' + \int_0^t \Gamma_1(t - t') dt' \int_{t'}^t \Phi(\tau) d\tau = 0, \quad (28)$$

where we have defined

$$\Phi(t) = \langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle / \langle v^2 \rangle, \quad (29)$$

and where the "memory" functions  $\Gamma_0(t)$  and  $\Gamma_1(t)$  are, respectively, given by

$$\Gamma_0(t) = -\frac{1}{3m} \int \frac{d\mathbf{q}}{(2\pi)^3} q^2 \bar{V}(\mathbf{q}, t) g(\mathbf{q}) \times \exp\left(\frac{-t}{\tau}\right) \exp[-\frac{1}{4}q^2 a(t)] \quad (30)$$

and

$$\Gamma_1(t) = -\frac{1}{3m} \int \frac{d\mathbf{q}}{(2\pi)^3} q^2 \bar{V}(\mathbf{q}, t) g(\mathbf{q}) \times \exp\left(\frac{-t}{\tau}\right) \left\{ \frac{d}{dt} \exp[-\frac{1}{4}q^2 a(t)] \right\}. \quad (31)$$

One objection to our derivation of Eq. (28) might be that for interaction potentials, mostly used, the Fourier transforms do not exist. However, we could have arrived at the same result without going over to the Fourier space. The memory functions we would have obtained would be the same as those in Eqs. (30) and (31), but are now written as an integral in ordinary space as follows:

$$\Gamma_0(t) = \left[ -\frac{1}{3m} \int \nabla g(\mathbf{x}) \cdot \nabla \bar{V}(\mathbf{x} - \mathbf{x}', t) \times G_s(\mathbf{x}', t) d\mathbf{x} d\mathbf{x}' \right] \exp\left(\frac{-t}{\tau}\right) \quad (32)$$

and

$$\Gamma_1(t) = \left[ -\frac{1}{3m} \int \nabla g(\mathbf{x}) \cdot \nabla \bar{V}(\mathbf{x} - \mathbf{x}', t) \times \frac{\partial G_s(\mathbf{x}', t)}{\partial t} d\mathbf{x} d\mathbf{x}' \right] \exp\left(\frac{-t}{\tau}\right). \quad (33)$$

$G_s(\mathbf{x}, t)$  is the Van Hove self-correlation function, given in Eq. (27). When evaluating the contribution to the memory functions from the hard-core part of the interaction potential, Eqs. (32) and (33) have to be used instead of Eqs. (30) and (31).

It is convenient for the following calculations to introduce  $V_{\text{eff}}(\mathbf{x}, t)$  and  $\tilde{V}_{\text{eff}}(\mathbf{x}, t)$ , defined as follows:

$$\nabla V_{\text{eff}}(\mathbf{x}, t) = \int \nabla \bar{V}(\mathbf{x} - \mathbf{x}', t) G_s(\mathbf{x}', t) d\mathbf{x}' \quad (34)$$

and

$$\nabla \tilde{V}_{\text{eff}}(\mathbf{x}, t) = \int \nabla \bar{V}(\mathbf{x} - \mathbf{x}', t) \frac{\partial G_s(\mathbf{x}', t)}{\partial t} d\mathbf{x}'. \quad (35)$$

In terms of these quantities, our memory functions have a very simple form;

$$\Gamma_0(t) = \left[ -\frac{1}{3m} \int \nabla g(\mathbf{x}) \cdot \nabla V_{\text{eff}}(\mathbf{x}, t) d\mathbf{x} \right] \exp\left(\frac{-t}{\tau}\right) \quad (36)$$

and

$$\Gamma_1(t) = \left[ -\frac{1}{3m} \int \nabla g(\mathbf{x}) \cdot \nabla \tilde{V}_{\text{eff}}(\mathbf{x}, t) d\mathbf{x} \right] \exp\left(\frac{-t}{\tau}\right). \quad (37)$$

Equation (28) constitutes our basic equation. It is to be compared with the following equation in Refs. 4-6:

$$\frac{d}{dt} \Phi(t) + \int_0^t K(t - t') \Phi(t') dt' = 0,$$

where  $K(t)$  has been referred to in the Introduction as the memory function. In general, Eq. (28) cannot be brought in the above form, unless the term containing  $\Gamma_1(t)$  is negligible. Indeed, we do not expect this term to be very significant but certainly not completely negligible. This does not imply any contradiction, since in the derivations of Eq. (1) one has forced the equation to have the particular form given above. In fact, from Eq. (28) we could determine  $\Phi(t)$  and then always define a function  $K(t)$  through Eq. (1). Our memory

functions  $\Gamma_0(t)$  and  $\Gamma_1(t)$  are, therefore, in principle quite different from the one in Eq. (1) and we stress this by using different notations.

It is evident from Eqs. (26)–(28) and from the definitions of the  $\Gamma$ 's, that our equation for  $\Phi(t)$  is nonlinear and can only be solved numerically. In our subsequent discussion, we shall make use of earlier knowledge of how  $a(t)$  varies in time, noting that the detailed form of  $\Phi(t)$  will have a quite small influence on the integrated value in  $a(t)$ .

### 3. CALCULATION OF THE MEMORY FUNCTIONS

It was stated earlier that the function  $\bar{G}_s(\mathbf{x}t; \mathbf{x}'t' | \mathbf{x}_0)$  describes the probability that an atom arrives at the position  $\mathbf{x}$  at time  $t$ , if it was at  $\mathbf{x}'$  at time  $t'$  and the blue atom is at the position  $\mathbf{x}_0$  at time  $t$ . This probability is obviously zero for  $|\mathbf{x} - \mathbf{x}_0| < \sigma$ , where  $\sigma$  is the radius of the hard core of the interatomic potential. It is important to keep this fact in mind. We may write

$$\bar{G}_s(\mathbf{x} + \mathbf{y}, t; \mathbf{x}, 0 | \mathbf{x}_0) = \alpha(\mathbf{x} + \mathbf{y} - \mathbf{x}_0) G_s(\mathbf{y}, t) / \int \alpha(\mathbf{x} + \mathbf{y}' - \mathbf{x}_0) G_s(\mathbf{y}', t) d\mathbf{y}', \quad (38)$$

where  $G_s(\mathbf{y}, t)$  is the Van Hove self-correlation function. The normalization condition

$$\int \bar{G}_s(\mathbf{x} + \mathbf{y}, t; \mathbf{x}, 0 | \mathbf{x}_0) d\mathbf{y} = 1 \quad (39)$$

is automatically fulfilled. The function  $\alpha(\mathbf{x} - \mathbf{x}_0)$  should be such that it drops sharply to zero for  $|\mathbf{x} - \mathbf{x}_0| < \sigma$ , and is of the order unity whenever  $|\mathbf{x} - \mathbf{x}_0| > \sigma$ . Its precise form is not known to us. It plays the role of excluding a certain volume, corresponding to the hard-core radius around  $\mathbf{x}_0$ . Some of our further discussion will not be based on any detailed knowledge of  $\alpha(\mathbf{x} - \mathbf{x}_0)$ , not even on the assumption in Eq. (38) of the form of  $\bar{G}_s$ .

We shall first derive asymptotic expressions for  $\Gamma_0(t)$  and  $\Gamma_1(t)$  and shall later make more explicit calculations, based on a certain form of  $\alpha(\mathbf{x} - \mathbf{x}_0)$ .

For the interatomic potential we shall in the present context use a 6–12 Lennard-Jones potential,

$$V(x) = 4\epsilon [(\sigma/x)^{12} - (\sigma/x)^6]. \quad (40)$$

For mathematical reasons the above potential will be divided into a hard core and a soft part,

$$V(x) = V_c(x) + V_s(x), \quad (41)$$

such that  $V_c(x)$  does not contain any of the smoothly varying attractive part of the potential (see Fig. 1).

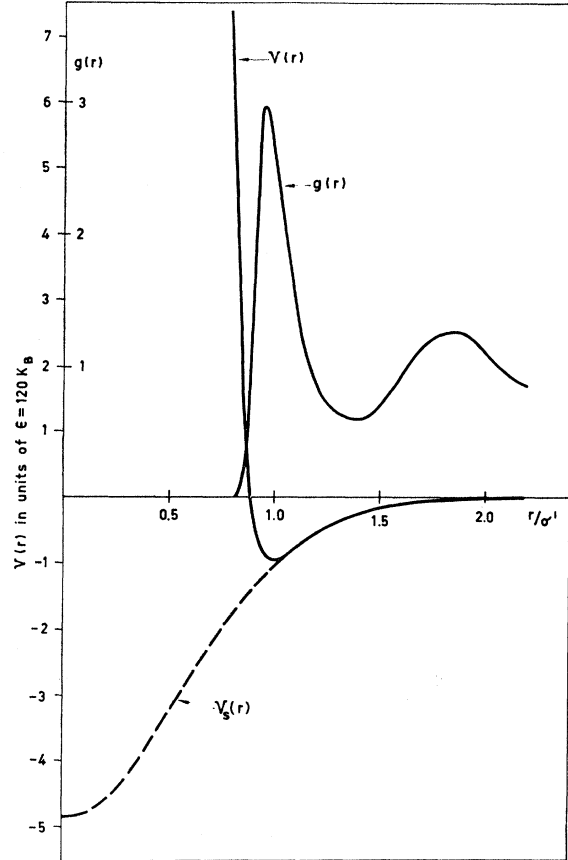


FIG. 1. Lennard-Jones potential (in units of  $\epsilon = 120k_B$ ) and the pair correlation function  $g(r)$  (based on Rahman's computations for liquid argon at  $T = 85.9^\circ\text{K}$ ) versus distance (in units of  $\sigma' = 3.817 \text{ \AA}$ ). The dashed curve represents the assumed Gaussian form for the soft part of the potential.

#### Case 1: Hard-Core Contribution

$$t = 0$$

For this case we have by definition

$$\bar{G}_s(\mathbf{x}, t; \mathbf{x}'0 | \mathbf{x}_0) = \delta(\mathbf{x} - \mathbf{x}') \quad (42)$$

and

$$G_s(\mathbf{x}, t) = \delta(\mathbf{x}), \quad (43)$$

and hence from Eq. (15)

$$\bar{V}_c(\mathbf{x}) = V_c(\mathbf{x}). \quad (44)$$

Substituting the above expression in Eq. (32) we get

$$\Gamma_0^c(0) = -\frac{1}{3m} \int \nabla V_c(\mathbf{x}) \cdot \nabla g(\mathbf{x}) d\mathbf{x}. \quad (45)$$

From the knowledge that  $a(t)$ , appearing in Eqs. (28) and (27), varies as  $t^2$  for small times, we can also conclude that

$$\Gamma_1^c(0) = 0. \quad (46)$$

The expression above for  $\Gamma_0^e(0)$  is known to be an exact result.<sup>4,5</sup>

$$a(t) \gg \Delta$$

The function  $V_c'(y)\alpha(y)$ ,  $V'$  denoting the derivative of  $V$ , has a sharp peak at  $y=\sigma_0=\sigma$  with a width  $\sqrt{\Delta}$ . The area under the peak will be denoted by  $C$  and is defined by

$$\int_0^\infty V_c'(y)\alpha(y)dy = -C. \quad (47)$$

We shall here consider times such that the width  $a(t)$  of  $G_s(\mathbf{x},t)$  is much broader than  $\Delta$ . In that case we have

$$\nabla \bar{V}_c(\mathbf{x}-\mathbf{x}',t) = C \int \frac{\mathbf{x}''-\mathbf{x}}{|\mathbf{x}''-\mathbf{x}|} G_s(\mathbf{x}''-\mathbf{x}',t) dS_{\mathbf{x}''} / \int_{|\mathbf{x}_1-\mathbf{x}| \geq \sigma_0} G_s(\mathbf{x}_1-\mathbf{x}',t) d\mathbf{x}_1, \quad (48)$$

after using Eqs. (47) and (38) in Eq. (15). The integration in the numerator extends over the surface of the sphere  $|\mathbf{x}''-\mathbf{x}|=\sigma_0$ . It is straightforward to show after angular integration that Eq. (48) becomes

$$\begin{aligned} \bar{V}_c'(\mathbf{x},t) &= -C\sigma_0 \{ [1-\gamma(x,t)] \bar{G}_s(x-\sigma_0,t) \\ &\quad + [1+\gamma(x,t)] \bar{G}_s(x+\sigma_0,t) \} / \\ &\quad \int_{\sigma_0}^\infty x' [\bar{G}_s(x'-x,t) - \bar{G}_s(x'+x,t)] dx' \quad (49a) \\ &\approx -C\sigma_0 \bar{G}_s(x-\sigma_0,t) / \int_{\sigma_0}^\infty x' \bar{G}_s(x'-x,t) dx', \quad (49b) \end{aligned}$$

where  $\gamma(x,t) \equiv [a(t)/2\sigma_0 x]$  is much smaller than unity, since only  $x \gtrsim \sigma_0$  is of importance for calculating  $\Gamma_0(t)$  and  $\Gamma_1(t)$  and  $a(t) \ll \sigma_0^2$  for times of interest. In Eqs. (49a), (49b) and in what follows, the bar on  $G_s$  denotes the one-dimensional Van Hove correlation function

$$\bar{G}_s(x,t) = [\pi a(t)]^{-1/2} \exp[-x^2/a(t)]. \quad (50)$$

For  $V_{\text{eff}}^e$ , defined by Eq. (34), after replacing  $\bar{V}$  by  $\bar{V}_c$ , we have after angular integration

$$\begin{aligned} V_{\text{eff}}^e(x,t) &= \frac{a(t)}{2x^2} \int_0^\infty dy \bar{V}_c'(y,t) \left\{ \left[ \frac{2xy}{a(t)} - 1 \right] \bar{G}_s(y-x,t) \right. \\ &\quad \left. + \left[ \frac{2xy}{a(t)} + 1 \right] \bar{G}_s(y+x,t) \right\} \quad (51a) \end{aligned}$$

$$\begin{aligned} &\approx \frac{1}{x} \int_0^\infty dy y \bar{V}_c'(y,t) \bar{G}_s(y-x,t), \\ &\quad a(t) \ll \sigma_0^2. \quad (51b) \end{aligned}$$

For  $\bar{V}_{\text{eff}}^e(x,t)$  we have exactly the same expression, except that  $\bar{G}_s(y-x,t)$  is replaced by  $\partial \bar{G}_s(y-x,t)/\partial t$ .

Now, using Eq. (51b) in Eq. (36) with  $\bar{V}_c'$  given by Eq. (49b), we have for the hard-core contribution

$$\begin{aligned} \exp(t/\tau) \Gamma_0^e(t) &= \frac{4\pi C \sigma_0}{3m} \int_0^\infty dy \left\{ \left[ y \bar{G}_s(y-\sigma_0,t) / \right. \right. \\ &\quad \left. \left. \int_{\sigma_0}^\infty y' \bar{G}_s(y'-y,t) dy' \right] \right. \\ &\quad \left. \times \int_0^\infty dx x g'(x) \bar{G}_s(x-y,t) \right\}, \quad (52) \end{aligned}$$

which is valid for  $a(t) \ll \sigma_0^2$ . After the following change of variables,

$$y-\sigma_0 \rightarrow y\sqrt{a}, \quad y'-\sigma_0 \rightarrow y'\sqrt{a}, \quad x-\sigma_0 \rightarrow x\sqrt{a},$$

and replacing  $-\sigma_0/\sqrt{a}$  by  $-\infty$  and further neglecting terms like  $y(\sqrt{a})/\sigma_0$  relative to unity at appropriate places, Eq. (52) becomes

$$\begin{aligned} \exp\left(\frac{t}{\tau}\right) \Gamma_0^e(t) &= \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \int_{-\infty}^\infty dy f(y) \\ &\quad \times \int_{-\infty}^\infty \exp(-x^2) g'(\sigma_0 + y\sqrt{a} + x\sqrt{a}) dx, \quad (53) \end{aligned}$$

where  $f(y) = \{ \exp(y^2) \int_{-\infty}^y \exp(-u^2) du \}^{-1}$ . That  $a$  depends on time is implicit here.

The function  $g'(x)$  has a narrow positive peak at  $x=x_0$  with a half width  $\sqrt{\Delta_0}$  and a somewhat broader and smaller negative peak at  $x=x_1$ , ( $x_1 > x_0$ ), having the half width  $\sqrt{\Delta_1}$  (see Fig. 2).  $x_0$  is very close to  $\sigma_0$ , and we shall for simplicity put  $x_0=\sigma_0$ . On the other hand,  $x_1$  is significantly displaced from  $\sigma_0$ . We shall approximate  $g'(x)$  by the following expression:

$$\begin{aligned} g'(x) &= A_0(\pi\Delta_0)^{-1/2} \exp[-(x-x_0)^2/\Delta_0] \\ &\quad - A_1(\pi\Delta_1)^{-1/2} \exp[-(x-x_1)^2/\Delta_1], \quad (54) \end{aligned}$$

where  $A_0$  and  $A_1$  are the areas under the two peaks. Since the function  $g(x)$  is known, we can determine all the parameters in Eq. (54). In Fig. 2 the function  $g'(x)$  has been plotted for liquid argon at  $T=85.9^\circ\text{K}$ . The values of the parameters chosen are

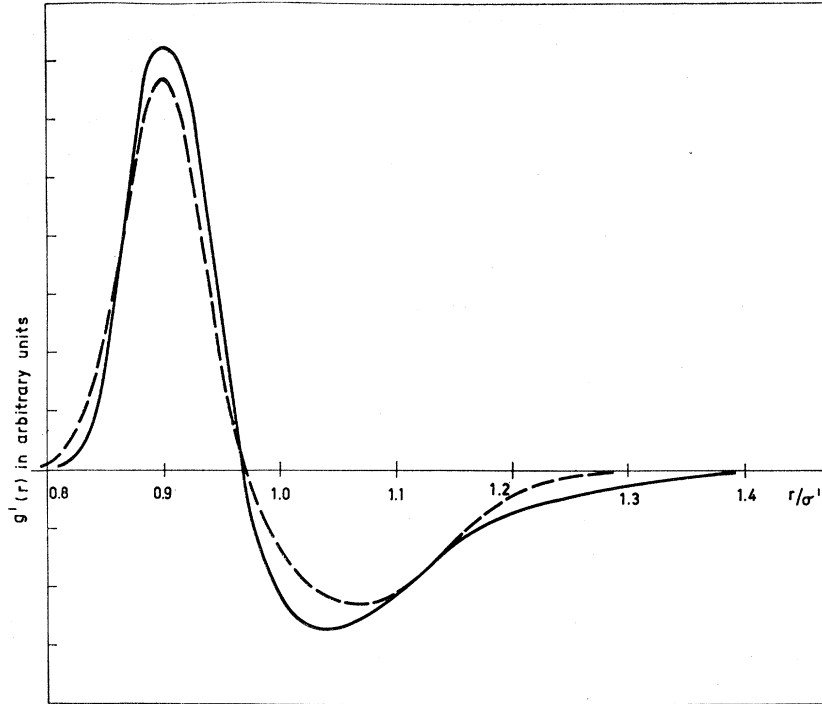
$$\sqrt{\Delta_0} = 0.19 \text{ \AA}, \quad \sqrt{\Delta_1} = 0.38 \text{ \AA}, \quad x_0 = 3.4 \text{ \AA}, \quad x_1 = 4.0 \text{ \AA},$$

and

$$A_0 = 3.0n, \quad A_1 = 2.0n,$$

where  $n$  is the particle-number density. The approximated  $g'(x)$  is shown as the dashed curve in Fig. 2.

FIG. 2. The derivative  $g'(r)$  versus  $r$  (in units of  $\sigma' = 3.817 \text{ \AA}$ ). The solid curve is based on Rahman's numerical computations for liquid argon at  $T = 85.9^\circ\text{K}$ . The dashed curve represents a Gaussian approximation, Eq. (52), with the values of the parameters given by Eqs. (83) and (84).



Substituting Eq. (54) in Eq. (53) and integrating, we have

$$\exp\left(\frac{t}{\tau}\right)\Gamma_0^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \left\{ \frac{A_0}{(a+\Delta_0)^{1/2}} \int_{-\infty}^{\infty} f(y) \exp\left[\frac{-ay^2}{(a+\Delta_0)}\right] dy - \frac{A_1}{(a+\Delta_1)^{1/2}} \int_{-\infty}^{\infty} f(y) \exp\left[\frac{-a(y-\eta)^2}{(a+\Delta_1)}\right] dy \right\}, \quad (55)$$

where  $\eta = (x_1 - x_0)/\sqrt{a}$ . We have then assumed  $\sigma_0 = x_0$ . Equation (55) is valid for  $\Delta \ll a \ll \sigma_0^2$ .

For  $a \gg \Delta$ ,  $\Delta_0$ , and  $\Delta_1$  such that  $\eta$  is small, but still  $a \ll \sigma_0^2$ , the above expression reduces to

$$\exp\left(\frac{t}{\tau}\right)\Gamma_0^e(t) = \left\{ \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \int_{-\infty}^{\infty} f(y) \times \exp(-y^2) dy \right\} \frac{A_0 - A_1}{\sqrt{a}}. \quad (56)$$

Proceeding in the same way as for  $\Gamma_0^e(t)$ , we have for  $\Gamma_1^e(t)$ , analogous to Eq. (52),

$$\exp\left(\frac{t}{\tau}\right)\Gamma_1^e(t) = \frac{4\pi C\sigma_0^2}{3m} \int_0^{\infty} dy \left\{ \left[ \frac{\bar{G}_s(y - \sigma_0, t)}{\int_{\sigma_0}^{\infty} \bar{G}_s(y' - y, t) dy'} \right] \times \int_0^{\infty} dx g'(x) \frac{\partial \bar{G}_s(x - y, t)}{\partial t} \right\}. \quad (57)$$

Using the relation

$$\frac{\partial \bar{G}_s(x, t)}{\partial t} = \bar{G}_s(x, t) \left( \frac{x^2}{a} - \frac{1}{2} \right) \frac{\dot{a}}{a}, \quad (58)$$

where  $\dot{a}$  is the time derivative of  $a(t)$ , and making a change of variables as before, we get

$$\exp\left(\frac{t}{\tau}\right)\Gamma_1^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \left[ \int_{-\infty}^{\infty} dy f(y) \int_{-\infty}^{\infty} (2x^2 - 1) \times \exp(-x^2) g'(\sigma_0 + y\sqrt{a} + x\sqrt{a}) dx \right] \frac{\dot{a}}{2a}, \quad (59)$$

valid for  $a \ll \sigma_0^2$ . Analogous to Eq. (56), we have

$$\exp\left(\frac{t}{\tau}\right)\Gamma_1^e(t) = \left\{ \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \int_{-\infty}^{\infty} (2y^2 - 1) f(y) \times \exp(-y^2) dy \right\} \frac{A_0 - A_1}{\sqrt{a}} \frac{\dot{a}}{2a}, \quad (60)$$

for  $a \gg \Delta$ ,  $\Delta_0$ , and  $\Delta_1$ , but  $a \ll \sigma_0^2$ .

### Case 2: Soft-Part Contribution

The calculation of the contribution to  $\Gamma_0(t)$  and  $\Gamma_1(t)$  from what we have referred to as the soft part of the interaction potential proceeds in an analogous way as for the hard-core part. The main difference, however, lies in the evaluation of  $\bar{V}_s(\mathbf{x}, t)$ . The width  $\Delta_s$  of  $V_s(\mathbf{x})$ , whose form we have taken to be Gaussian for mathematical simplicity, is much larger than the width  $a(t)$  of



the Van Hove correlation function for all times of interest. Therefore, we can write for  $\bar{V}_s(\mathbf{x}, t)$ , which is defined by Eq. (15) after replacing  $V(\mathbf{x})$  by  $V_s(\mathbf{x})$ ,

$$\begin{aligned}\nabla\bar{V}_s(\mathbf{x}, t) &= \int \nabla V_s(\mathbf{x}-\mathbf{y})\alpha(\mathbf{x}-\mathbf{y}) \\ &\quad \times G_s(\mathbf{y}, t) d\mathbf{y} / \int \alpha(\mathbf{x}-\mathbf{y}')G_s(\mathbf{y}', t) d\mathbf{y}' \\ &= \nabla V_s(\mathbf{x}).\end{aligned}\quad (61)$$

This follows from the fact that  $\nabla V_s(\mathbf{x}-\mathbf{y})$  is a very smooth function of  $\mathbf{y}$  compared to  $G_s(\mathbf{y}, t)$  for  $a \ll \Delta_s$ , and as such it can be taken out of the integration sign.

Substituting Eq. (61) in Eq. (34), we have for the same reason as above

$$\nabla V_{\text{eff}}^s(\mathbf{x}, t) = \nabla V_s(\mathbf{x}), \quad (62)$$

and inserting this in Eq. (36) we have finally

$$\exp\left(\frac{t}{\tau}\right)\Gamma_0^s(t) = -\frac{1}{3m} \int \nabla V_s(\mathbf{x}) \cdot \nabla g(\mathbf{x}) d\mathbf{x}. \quad (63)$$

Thus for all times of interest ( $\lesssim 10^{-11}$  sec),  $\exp(t/\tau)\Gamma_0^s(t)$  remains constant.

In order to determine  $\Gamma_1^s(t)$ , we first calculate  $\bar{V}'_{\text{eff}}^s(\mathbf{x}, t)$  from the expression [see Eq. (51a) for  $V'_{\text{eff}}^s$  and the remarks below]

$$\begin{aligned}\bar{V}'_{\text{eff}}^s(x, t) &= \frac{a}{2x^2} \int_0^\infty dy \bar{V}'_s(y, t) \left\{ \left( \frac{2xy}{a} - 1 \right) \frac{\partial \bar{G}_s(y-x, t)}{\partial t} \right. \\ &\quad \left. + \left( \frac{2xy}{a} + 1 \right) \frac{\partial \bar{G}_s(y+x, t)}{\partial t} \right\}. \quad (64)\end{aligned}$$

We can here neglect the second term within the curly bracket as long as  $a \ll \sigma_0^2$ , remembering that only  $x \gtrsim \sigma_0$  is of interest. Furthermore, as above, we take  $\bar{V}'_s(y, t) = V'_s(y, t)$  out of the integration sign and write

$$\begin{aligned}\bar{V}'_{\text{eff}}^s(x, t) &= \frac{a}{2x^2} V'_s(x) \int_{-x}^\infty \left[ \frac{2x}{a}(y+x) - 1 \right] \\ &\quad \times \frac{\partial \bar{G}_s(y, t)}{\partial t} dy. \quad (65)\end{aligned}$$

Extending the lower integration limit to  $-\infty$ , the integral is easily evaluated and found to be zero. We thus conclude that for  $a \ll \sigma_0^2$ ,  $\bar{V}'_{\text{eff}}^s$  within the present approximation is equal to zero, and hence

$$\Gamma_1^s(t) = 0 \quad (66)$$

for all times of interest.

#### 4. MODEL CALCULATION

The formulas for the memory functions  $\Gamma_0(t)$  and  $\Gamma_1(t)$ , derived in Sec. 3, are quite general in the sense

that they do not depend on the precise form of the function  $\alpha(x)$ , about which we have no detailed knowledge. As far as the soft-part contribution is concerned, one need have no knowledge of this for all times of interest. On the other hand, for the hard-core part of the contribution, one is forced to assume some reasonable form for  $\alpha(x)$ , if one wants to obtain numerical results covering all times of interest. The interatomic potential has for mathematical simplicity been divided into a hard core and a soft part. A Gaussian form for the soft part is assumed, and the parameters were chosen so as to give a good fit for the major part of the attractive potential (see Fig. 1). The difference between the actual 6-12 Lennard-Jones potential and the soft Gaussian part was taken as the hard-core part. The main physical reason for making such a division is that the two parts give rise to very different time dependence for  $\Gamma_0(t)$  and  $\Gamma_1(t)$ .

Adopting the form given in Eq. (38), we have

$$\begin{aligned}\nabla\bar{V}_c(\mathbf{x}, t) &= \int \frac{\mathbf{x}-\mathbf{y}}{|\mathbf{x}-\mathbf{y}|} V'_c(\mathbf{x}-\mathbf{y})\alpha(\mathbf{x}-\mathbf{y}) \\ &\quad \times G_s(\mathbf{y}, t) d\mathbf{y} / \int \alpha(\mathbf{x}-\mathbf{y}')G_s(\mathbf{y}', t) d\mathbf{y}', \quad (67)\end{aligned}$$

which after angular integration can be written as

$$\begin{aligned}\bar{V}'_c(x, t) &= \frac{a}{2x} \left[ \int_0^\infty V'_c(y)\alpha(y) \left\{ \left( \frac{2xy}{a} - 1 \right) \bar{G}_s(y-x, t) \right. \right. \\ &\quad \left. \left. + \left( \frac{2xy}{a} + 1 \right) \bar{G}_s(y+x, t) \right\} dy / \int_0^\infty y\alpha(y) \right. \\ &\quad \left. \times \{ \bar{G}_s(y-x, t) - \bar{G}_s(y+x, t) \} dy \right]. \quad (68)\end{aligned}$$

As stated earlier,  $V'_c(y)\alpha(y)$  has a sharp peak around  $y = \sigma_0$  with halfwidth  $\sqrt{\Delta}$ . We shall choose the following form:

$$V'_c(y)\alpha(y) = -C(\pi\Delta)^{-1/2} \exp[-(y-\sigma_0)^2/\Delta], \quad (69)$$

which has the correct width and whose area is  $C$ .

We expect intuitively that  $\alpha(y) = \exp[-V_c(y)/k_B T]$  or some other similar function of  $V_c(y)$ . Adopting this assumption, it follows that

$$-k_B T \alpha'(y) = V'_c(y)\alpha(y), \quad (70)$$

where now  $k_B T$  is the area which was denoted by  $C$  above. Integrating Eq. (70), we have

$$\alpha(y) = -(1/k_B T) \int_0^y V'_c(y')\alpha(y') dy'. \quad (71)$$

Guided by this, we write for  $\alpha(y)$ ,

$$\alpha(y) = (\pi\Delta)^{-1/2} \int_0^y \exp[-(y'-\sigma_0)^2/\Delta] dy'. \quad (72)$$

From our reasoning here, we should expect  $C$  to be of the order  $k_B T$  and the width  $\Delta^{1/2}$  to be rather close to the width, given by the function  $\{V_e'(y) \exp[-V_e(y)/k_B T]\}$ , which was found to be  $0.20 \text{ \AA}$  for liquid argon at  $T=85.9^\circ\text{K}$ .

For  $a \ll \sigma_0$  and  $x \gtrsim \sigma_0$ , which are the only  $x$  values entering in our final expression, Eq. (68), can be written as

$$\bar{V}_e'(x,t) = -C \exp[-(x-\sigma_0)^2/(a+\Delta)] / \int_{-\infty}^{x-\sigma_0} \exp[-x'^2/(a+\Delta)] dx'. \quad (73)$$

For a detailed derivation of Eq. (73), we refer to the Appendix.

Substituting the above expression for  $\bar{V}_e'$  in Eqs. (51a) or (51b) and proceeding as in Sec. 3, we get

$$\exp\left(\frac{t}{\tau}\right) \Gamma_0^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \int_{-\infty}^{\infty} dy f(y) \int_{-\infty}^{\infty} \exp(-x^2) \times g'[\sigma_0 + y(a+\Delta)^{1/2} + x\sqrt{a}] dx, \quad (74)$$

where, as before,

$$f(y) = \left[ \exp(y^2) \int_{-\infty}^y \exp(-u^2) du \right]^{-1}. \quad (75)$$

We are reminded that Eq. (74) is derived under the assumption that  $a \ll \sigma_0^2$ . The above expression should be compared with Eq. (53). We see that it reduces to the latter for  $a \gg \Delta$ .

Using the form for  $g'(x)$  given in Eq. (54) and performing the integration over  $x$ , we have finally

$$\exp\left(\frac{t}{\tau}\right) \Gamma_0^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \left\{ \frac{A_0}{(a+\Delta_0)^{1/2}} \int_{-\infty}^{\infty} f(y) \times \exp[-y^2(a+\Delta)/(a+\Delta_0)] dy - \frac{A_1}{(a+\Delta_1)^{1/2}} \int_{-\infty}^{\infty} f(y) \exp[-(y-\eta_1)^2 \times (a+\Delta)/(a+\Delta_1)] dy \right\}, \quad (76)$$

where  $\eta_1 = (x_1 - x_0)/(a+\Delta)^{1/2}$ . This is analogous to Eq. (55) and reduces to the latter for  $a \gg \Delta$ .

With proper choice of  $\alpha(y)$  we should get the correct value for  $\Gamma_0^e(0)$ , which is also given by Eq. (45). Hence we should choose the constants  $C$  and  $\Delta$  such that

$$\Gamma_0^e(0) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \frac{A_0}{\sqrt{\Delta_0}} \int_{-\infty}^{\infty} f(y) \exp\left(\frac{-y^2\Delta}{\Delta_0}\right) dy. \quad (77)$$

The last term in Eq. (76) has been dropped, for it turns out to be small. With our lack of knowledge of the function  $\alpha(y)$ , one parameter is left undetermined

besides the relaxation time  $\tau$ , which has to be fixed in some other way.

For  $\Gamma_1^e(t)$  we have from the expression for  $\bar{V}'_{\text{eff}} e$  [see Eqs. (51a) and (51b) and the remarks below] and Eqs. (58) and (37), in analogy with Eq. (74),

$$\exp\left(\frac{t}{\tau}\right) \Gamma_1^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \int_{-\infty}^{\infty} dy f(y) \int_{-\infty}^{\infty} dx (2x^2-1) \times \exp(-x^2) g'[\sigma_0 + y(a+\Delta)^{1/2} + x\sqrt{a}] \dot{a}/2a. \quad (78)$$

After evaluating the second integral, using Eq. (54) we get finally

$$\exp\left(\frac{t}{\tau}\right) \Gamma_1^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m} \left\{ \frac{a}{a+\Delta_0} \frac{A_0}{(a+\Delta_0)^{1/2}} \int_{-\infty}^{\infty} \left\{ 2 \frac{a+\Delta}{a+\Delta_0} y^2 - 1 \right\} \times f(y) \exp[-y^2(a+\Delta)/(a+\Delta_0)] dy - \frac{a}{a+\Delta_1} \frac{A_1}{(a+\Delta_1)^{1/2}} \int_{-\infty}^{\infty} \left\{ 2 \frac{a+\Delta}{a+\Delta_1} (y-\eta_1)^2 - 1 \right\} f(y) \times \exp[-(y-\eta_1)^2(a+\Delta)/(a+\Delta_1)] dy \right\} \dot{a}/2a, \quad (79)$$

with, as before,  $\eta_1 = (x_1 - x_0)/(a+\Delta)^{1/2}$ .

## 5. NUMERICAL RESULTS

Equation (76) can be written in the following form, which is more convenient for numerical calculations;

$$\exp\left(\frac{t}{\tau}\right) \Gamma_0^e(t) = \frac{4(\sqrt{\pi})C\sigma_0^2}{3m\sqrt{\Delta_0}} \frac{A_0}{(1+\zeta)^{1/2}} \int_{-\infty}^{\infty} dy f(y) \times \exp(-\xi y^2) [1 - F(\zeta)], \quad (80)$$

where

$$F(\zeta) = \frac{A_1}{A_0} \left( \frac{\zeta+1}{\zeta+\Delta_1/\Delta_0} \right)^{1/2} \left\{ \int_{-\infty}^{\infty} dy f(y) \times \exp[-\xi'(y-\eta_1)^2] / \int_{-\infty}^{\infty} dy f(y) \exp(-\xi y^2) \right\} \quad (81)$$

and

$$\begin{aligned} \zeta &= a/\Delta_0, & \xi &= (\zeta+\Delta/\Delta_0)/(\zeta+1), \\ \xi' &= (\zeta+\Delta/\Delta_0)/(\zeta+\Delta_1/\Delta_0), \\ \eta_1 &= (\zeta+\Delta/\Delta_0)^{-1/2} (x_1-x_0)/\sqrt{\Delta_0}. \end{aligned} \quad (82)$$

For liquid argon at  $T=85.9^\circ\text{K}$ , we have chosen

$$A_1/A_0 = \frac{2}{3}, \quad \Delta_1/\Delta_0 = 4, \quad (x_1-x_0)/\sqrt{\Delta_0} = 3 \quad (83)$$

and

$$\begin{aligned} \sqrt{\Delta_0} &= 0.05 \text{ (0.19 \AA)}, & \sqrt{\Delta_1} &= 0.10 \text{ (0.38 \AA)}, \\ x_0 &= 0.90 \text{ (3.4 \AA)}, & x_1 &= 1.05 \text{ (4.0 \AA)}, \end{aligned} \quad (84)$$

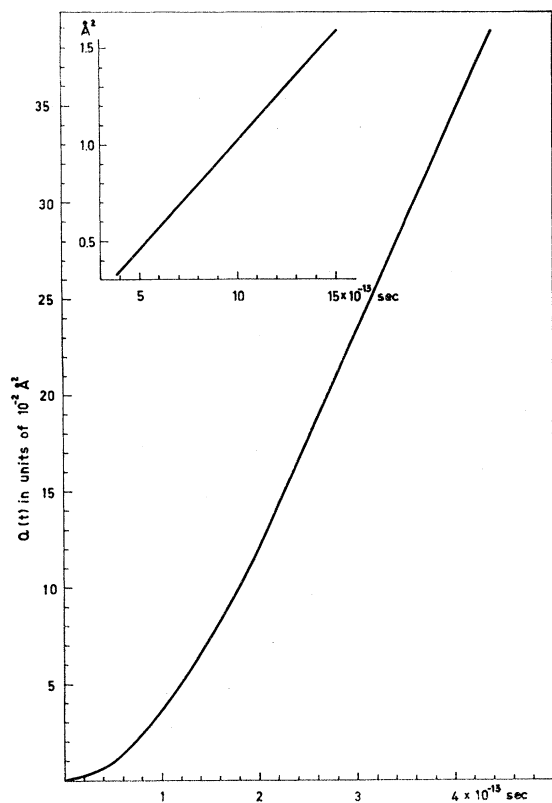


FIG. 3. The width  $a(t)$  (in units of  $10^{-2} \text{Å}^2$  and  $\text{Å}^2$  for the insert) of  $G_s(\mathbf{r}, t)$  versus time for liquid argon at  $T=85.9^\circ\text{K}$  based on Rahman's machine computations.

when expressed in units of  $\sigma'=3.817 \text{Å}$ , which is the distance to the minimum of the interaction potential. With slight adjustments of the above parameters, one could obtain a somewhat better fit to Rahman's  $g'(r)$  (see Fig. 2). Since it would have no significant effect on our final results, we did not attempt to do this.

We shall for the moment disregard the factor  $\exp(-t/\tau)$ . In calculating the ratio  $\Gamma_0^e(t)/\Gamma_0^e(0)$ , the only unknown quantity is then the width  $\sqrt{\Delta}$  of the function  $V_e'(x)\alpha(x)$ . Using Rahman's numerical values for the velocity autocorrelation function for liquid argon at  $T=85.9^\circ\text{K}$ , we have calculated  $a(t)$  as a function of time (see Fig. 3). Rahman solved on a computer Newton's equations for 864 argon atoms corresponding to a density of 1.407 g/cc and a temperature  $85.9^\circ\text{K}$ , and it is his numerical results for  $\Phi(t)$ ,  $g(x)$ , and  $\Gamma(t)$  that we have been referring to. The integrals in Eqs. (79) and (80) were evaluated for a few values of  $\Delta/\Delta_0$ , which then enabled us to calculate the corresponding ratio  $\Gamma_0^e(t)/\Gamma_0^e(0)$ .

The choice  $\Delta/\Delta_0=0.5$  gave a reasonable over-all fit to Rahman's curve.

We have seen in Sec. 3 that for all times of interest  $\exp(t/\tau)\Gamma_0^e(t)$  is constant and is given by Eq. (63). The soft part of the potential was taken to be a Gaussian

function (see Fig. 1)

$$V_s(x) = -A \exp(-x^2/\Delta_s), \quad (85)$$

with  $A=4.9\epsilon$  ( $\epsilon=120k_B$ ) and  $\sqrt{\Delta_s}=0.80$  ( $3.1 \text{Å}$ ) in units of  $\sigma'=3.817 \text{Å}$ . Using Rahman's  $g(x)$  and  $V_s(x)$  above, we have evaluated the integral in Eq. (63) and the result is

$$\Gamma_0^e(0) = -2.3 \times 10^{24} \text{ sec}^{-2}. \quad (86)$$

In  $\mathbf{q}$  space, Eq. (63) can be written as

$$\Gamma_0^e(0) = [A\Delta_s^{3/2}/6(\sqrt{\pi}m)] \times \int_0^\infty q^4 \exp(-\frac{1}{4}q^2\Delta_s)g(q)dq, \quad (87)$$

where  $g(\mathbf{q})$  is the Fourier transform of  $g(\mathbf{r})$ . In order to get an estimate of  $\Gamma_0^e(0)$ , which does not depend on Rahman's calculations, we shall evaluate  $\Gamma_0^e(0)$  from Eq. (87). We first remark that the main contribution to the integral arises from values of  $q^2 \lesssim 4/\Delta_s = 0.5 \text{Å}^{-2}$ . In this region of  $q$  values,  $g(q)$  lies between  $-1$  and  $-0.8$  (from x-ray scattering experiments).<sup>14</sup> Taking  $g(q) = -0.9$  and integrating, we obtain

$$\Gamma_0^e(0) = -0.9(2A/m\Delta_s) = -2.25 \times 10^{24} \text{ sec}^{-2}, \quad (88)$$

which is in good agreement with the value given in Eq. (86).

In Fig. 4, we have plotted the resultant  $\Gamma_0(t)/\Gamma_0(0)$  for  $\Delta/\Delta_0=0.5$  and  $\tau=\infty$  (full curve) and have compared our curve with that of Rahman, obtained from his computer calculations (dashed curve). For  $\Delta/\Delta_0=0.7$ , our calculations gave a nearly perfect fit for  $t \lesssim 10^{-13}$  sec, but it gave a significant increase in the height of the tail. On the other hand, for  $\Delta/\Delta_0 < 0.5$ , the height of the tail became less and the peak for small times became narrower.

It is unreasonable to expect  $\tau=\infty$ . For illustration, we have also plotted (dotted curve) in Fig. 4 the results obtained for  $\tau=10^{-12}$  sec, which we believe is a reasonable value. The calculated curve is now in much better agreement with that of Rahman.

The diffusion constant of the liquid in terms of  $\Gamma_0(t)$  is given by<sup>4,5</sup>

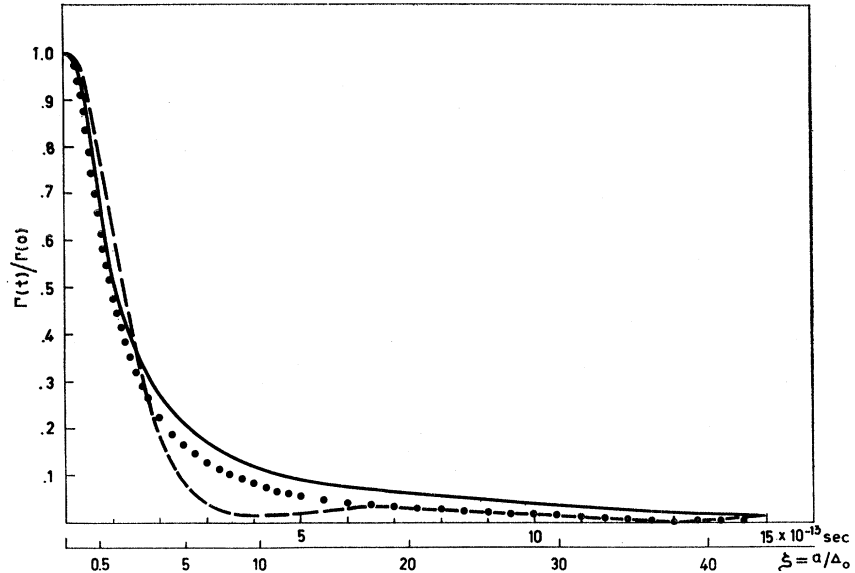
$$D = \frac{k_B T}{m} \int_0^\infty \Gamma_0(t) dt, \quad (89)$$

which, for  $\tau=10^{-12}$  sec and using our calculated  $\Gamma_0(t)$  for  $\Delta/\Delta_0=0.5$ , gave  $D=2.2 \times 10^{-5} \text{ cm}^2/\text{sec}$ , whereas the value of  $D$  obtained from Rahman's  $\Gamma_0(t)$  is  $2.10 \times 10^{-5} \text{ cm}^2/\text{sec}$ .

Also, the calculated value for the constant  $C$  which we have obtained from Eq. (77) using Rahman's value for  $\Gamma_0(0)=\Gamma_0^e(0)+\Gamma_0^s(0)=53.5 \times 10^{24} \text{ sec}^{-2}$  and our  $\Gamma_0^s(0) = -2.3 \times 10^{24} \text{ sec}^{-2}$ , is, within a few percent, equal

<sup>14</sup> N. S. Gingrich and C. W. Tompson, J. Chem. Phys. 36, 2398 (1962).

FIG. 4. Ratio  $\Gamma_0(t)/\Gamma_0(0)$  versus time and versus the parameter  $\xi = a/\Delta_0$ . The solid curve represents our calculations for  $\tau = \infty$  and the corresponding dotted curve is for  $\tau = 1.0 \times 10^{-12}$  sec. The dashed curve represents Rahman's machine computations for liquid argon at  $T = 85.9^\circ\text{K}$ .



to  $k_B T$ . We remark that the half-width, chosen for  $V_c'(x)\alpha(x)$ ,  $\sqrt{\Delta} = 0.036$ , is not very far from that of  $V_c'(x) \exp[-V_c(x)/k_B T]$ , which is  $0.052$  ( $0.20 \text{ \AA}$ ) in our units.

We have in the comparison above disregarded the influence of  $\Gamma_1(t)$ . Before we make the numerical estimate of  $\Gamma_1(t)$ , let us rewrite Eq. (28) in the form

$$\frac{d\Phi}{dt} + \int_0^t \Gamma_0(t-t')\Phi(t')dt' + \int_0^t \Gamma_1(t-t')(t-t')\bar{\Phi}(t,t')dt' = 0, \quad (90)$$

where

$$\bar{\Phi}(t,t') = \frac{1}{t-t'} \int_{t'}^t \Phi(\tau)d\tau \quad (91)$$

is the average value of  $\Phi(t)$  in the interval  $(t, t')$ . It is evident from Eq. (90) that we should compare  $t\Gamma_1(t)$  with  $\Gamma_0(t)$  to get an idea of the magnitude of the correction term.

In the time region where  $a(t) \propto t^2$ , the factor  $\dot{a}/2a$  in Eq. (79) is equal to  $1/t$ , whereas in the region where  $a(t) \propto t$ , this factor is equal to  $1/2t$ . We have estimated the ratio  $t\Gamma_1(t)/\Gamma_0(t)$  from Eqs. (79) and (76) and found its value to be less than  $0.3$  in the time interval of interest and most probably much less. For the soft part we have earlier [Eq. (66)] found that  $\Gamma_1^s(t) \approx 0$  throughout the whole time region of interest. Thus we expect the error we make in the equation for the velocity autocorrelation function not to be very significant for our conclusions (certainly less than  $30\%$ ), when we neglect the term containing  $\Gamma_1(t)$ . In that case our equation is of the same form as Eq. (1). However, we cannot exclude the possibility that the correction is larger in certain time regions, particularly where  $\Phi(t) \approx 0$ . At the present stage of the theory we have not

considered this point to be essential, but we intend to investigate it further, among others.

## 6. CRITIQUE AND CONCLUSIONS

From an inspection of Fig. 4 it is evident that the calculated memory function  $\Gamma(t)$  has two important characteristic features: (1), it decreases sharply from its value at  $t=0$  to a value which is one order of magnitude less in a very short time interval  $0-4 \times 10^{-13}$  sec; and (2), it has a long tail. Both these features are in general agreement with Rahman's numerical computations. In the region of the tail and for  $\tau$  very large, a quantitative agreement with Rahman's  $\Gamma(t)$  is lacking, but this can be easily achieved by a suitable choice for the value of the relaxation time parameter. For instance, in the present case with  $\tau = 10^{-12}$  sec, which as we know from other considerations is not an unreasonable value, a quantitative agreement has indeed been achieved (see dotted curve in Fig. 4). In the time region  $2-4 \times 10^{-13}$  sec, our calculated values are much higher than those given by Rahman. This discrepancy could possibly be due to our neglect of the  $\Gamma_1(t)$  term, which may not be justifiable in the region where  $\Phi(t) \approx 0$ . Whether this is so could only be checked by a proper numerical solution for  $\Phi(t)$  of our basic integrodifferential equation [Eq. (28)]. At the present stage of the development of the theory, we did not think it worthwhile to undertake such an elaborate numerical task.

A weak point of the present theory is our lack of precise knowledge of the function  $\alpha(x)$  and the relaxation time  $\tau$ . This lack of knowledge results in our introducing three parameters, the half-width  $\sqrt{\Delta}$  and the area  $C$  of the assumed Gaussian function  $V_c'(x)\alpha(x)$  and  $\tau$ . Unfortunately, to fix the values of these parameters we have only two relations, one involving  $\Gamma_0(0)$  and the other involving the diffusion constant. The

former is known, if one has a precise knowledge of the static pair correlation function and the interatomic potential. In practice, the situation regarding the choice for the values of the parameters seems to be fairly restrictive. We have made the observation in Sec. 3 that the area  $C$  is very nearly equal to  $k_B T$ . If this is generally true, the half-width  $\sqrt{\Delta}$  is determined from our knowledge of  $\Gamma_0(0)$ . The parameter  $\tau$  can then be uniquely fixed through the relation for the diffusion constant. These ideas need further confirmation by doing numerical computations of the kind Rahman has done for liquids with various interatomic potentials and at various temperatures. We should mention here that at present even inelastic neutron-scattering experiments, which of the various experimental techniques give the most detailed information on the motion of atoms in solids and liquids, do not furnish enough details to make a comparison between our theoretical results and experiments very useful.

In our numerical evaluation of  $\Gamma_0(t)$ , which depends on  $\Phi(t)$  through  $a(t)$ , we have used the values of  $a(t)$  obtained from Rahman's computed  $\Phi(t)$ . The justification for doing this is that the former, being an integrated quantity, does not depend significantly on the detailed shape of the latter. Nevertheless, a self-consistent solution of Eq. (28) is desirable and should be undertaken.

We would like to emphasize once more the fact that the width of the rapidly falling part of  $\Gamma_0(t)$  is determined by the half-width  $\sqrt{\Delta}$  of the function  $V_e'(x)\alpha(x)$ , whereas the width of the tail is essentially governed by the relaxation time  $\tau$ . The value of  $\Gamma_0(t)$  for  $t=0$  is determined precisely by the static pair correlation function and the interatomic potential. It is important to realize that the shape of  $\Gamma_0(t)$  depends sensitively on the detailed shape of the main peak of the static pair correlation function.

It is also worth remarking that the time expansion of  $\Gamma_0(t)$  is valid only as long as  $a(t) < \Delta$ , i.e., for  $t \lesssim 0.4 \times 10^{-13}$  sec. This is indeed an extremely small time region. The smallness of the radius of convergence is responsible for the failures<sup>15</sup> of recent attempts towards time expansion of the velocity autocorrelation function.

In conclusion, we might say that the present approach enables us to understand the main features of the memory function and, hence, of the velocity autocorrelation function in a classical monatomic liquid in terms of basic physical quantities like the interatomic potential and the static pair correlation function.

From the point of view of the present treatment, it would be highly desirable to have available machine computations of the memory function and the static pair correlation function for a hypothetical fluid at

liquid densities with only a hard-core interaction of the type considered here.

*Note added in proof.* Since this paper was sent for publication, a paper by J. P. Boon and S. A. Rice has appeared in *J. Chem. Phys.* **47**, 2480 (1967), dealing with the same questions as here. We have, therefore, not been able to comment on their paper, nor have we referred to it before. The reader should compare the results and the arguments given in the two papers. Also, since this work was finished, extensive numerical calculations have been taken up by G. Björkman, based on our general results here. It has been shown that  $[\Delta\Gamma_1(t)/\Gamma_0(t)]$  in our paper is for all times less than 0.1 for the case of liquid argon.

### ACKNOWLEDGMENTS

This work was done while one of the authors (K.S.S.) was on leave of absence from the Argonne National Laboratory and he wishes to thank NORDITA for sponsoring his visit and to U. S. Atomic Energy Commission for partial support. Thanks are also due to the Institute of Theoretical Physics, Chalmers Technical University, for its kind hospitality. We are particularly grateful to Dr. A. Rahman for sending us his recent unpublished results on liquid argon from machine computations. A discussion at an early stage of this work with Dr. P. Schofield is gratefully acknowledged. We also want to thank Professor P. Resibois and G. Björkman for critical remarks and for pointing out some mistakes in an earlier version of this paper.

### APPENDIX

In calculating the numerator in Eq. (68) we insert for  $V_e'(y)\alpha(y)$  the expression in Eq. (69). The two terms in the square bracket divide the integral in two parts. In the first part we change the integration variable to  $y' = y - x$ , whereas in the second part we change to  $y' = y + x$ . We then get for the numerator

$$\begin{aligned}
 & -C(\pi^2 a \Delta)^{-1/2} \left\{ \int_{-x}^{\infty} \exp\left[ \frac{-(y'-x-\sigma_0)^2}{\Delta} \right] \left\{ \frac{2x}{a}(y'+x) - 1 \right\} \right. \\
 & \quad \times \exp\left( \frac{-y'^2}{a} \right) dy' + \int_x^{\infty} \exp\left[ \frac{-(y'-x-\sigma_0)^2}{\Delta} \right] \\
 & \quad \left. \times \left\{ \frac{2x}{a}(y'-x) - 1 \right\} \exp\left( \frac{-y'^2}{a} \right) dy' \right\}. \quad (A1)
 \end{aligned}$$

Considering  $a \ll \sigma_0^2$  we can in the first integral approximate the curly brackets by  $2x^2/a$  and also extend the lower integration limit to  $-\infty$ . The whole second integral can be neglected, remembering that  $x \gtrsim \sigma_0$  and  $\Delta \ll \sigma_0^2$ . The numerator can then easily be evaluated

<sup>15</sup> B. R. A. Nijboer and A. Rahman, *Physica* **32**, 415 (1966); P. Schofield, in *Inelastic Scattering of Neutrons in Solids and Liquids* (International Atomic Energy Agency, Vienna, 1961), p. 39.

and gives

$$-(2Cx^2/a) \exp[-(x-\sigma_0)^2/(a+\Delta)]/[\pi(a+\Delta)]^{1/2}. \quad (\text{A2})$$

We proceed in a similar way to evaluate the denominator in Eq. (68), inserting for  $\alpha(y)$  the expression in Eq. (72). Neglecting as above the part containing  $\bar{G}_s(y+x, t)$  and changing the integration variable to  $y'=y-x$ , we have

$$(\pi^2 a \Delta)^{-1/2} \int_{-x}^{\infty} dy' \left\{ \int_0^{y'+x} \exp\left[\frac{-(y''-\sigma_0)^2}{\Delta}\right] dy'' \right\} \\ \times (y'+x) \exp\left(\frac{-y'^2}{a}\right). \quad (\text{A3})$$

The integral within the curly brackets can after change of integration variable be written

$$\int_{-\sigma_0}^{y'+x-\sigma_0} \exp(-y''^2/\Delta) dy''. \quad (\text{A4})$$

Here, we can extend the lower integration limit to  $-\infty$ , for  $\Delta \ll \sigma_0^2$ . Likewise, we change in Eq. (A3) the integration limits  $(-x, \infty)$  to  $(-\infty, \infty)$ , which is justified as long as  $a \ll \sigma_0^2$ . We further use the relation

$$y' \exp(-y'^2/a) = -(\frac{1}{2}a) (\partial/\partial y) \exp(-y'^2/a). \quad (\text{A5})$$

Equation (A3) can then be written

$$(\pi^2 a \Delta)^{-1/2} \int_{-\infty}^{\infty} dy' \left\{ \int_{-\infty}^{y'+x-\sigma_0} \exp\left(\frac{-y''^2}{\Delta}\right) dy'' \right\} \\ \times \left[ x \exp\left(\frac{-y'^2}{a}\right) - \left(\frac{1}{2}a\right) \frac{\partial}{\partial y'} \exp\left(\frac{-y'^2}{a}\right) \right], \quad (\text{A6})$$

which after partial integration of the second part of the integral and evaluation of that final integral

gives

$$x(\pi^2 a \Delta)^{-1/2} \int_{-\infty}^{\infty} dy' \exp\left(\frac{-y'^2}{a}\right) \\ \times \left[ \int_{-\infty}^{y'+x-\sigma_0} dy'' \exp\left(\frac{-y''^2}{\Delta}\right) \right] \\ + \frac{1}{2}a \exp\left[\frac{-(x-\sigma_0)^2}{(a+\Delta)}\right] / [\pi(a+\Delta)]^{1/2}. \quad (\text{A7})$$

When evaluating the first integral we first notice that

$$\frac{\partial}{\partial x} \left\{ \int_{-\infty}^{\infty} dy' \exp\left(\frac{-y'^2}{a}\right) \left[ \int_{-\infty}^{y'+x-\sigma_0} dy'' \exp\left(\frac{-y''^2}{\Delta}\right) \right] \right\} \\ = \int_{-\infty}^{\infty} dy' \exp\left(\frac{-y'^2}{a}\right) \exp[-(y'+x-\sigma_0)^2/\Delta] \\ = \{ (\pi^2 a \Delta)^{1/2} / [\pi(a+\Delta)]^{1/2} \} \\ \times \exp[-(x-\sigma_0)^2/(a+\Delta)], \quad (\text{A8})$$

which after integration with respect to  $x$  gives

$$\int_{-\infty}^{\infty} dy' \exp\left(\frac{-y'^2}{a}\right) \left[ \int_{-\infty}^{y'+x-\sigma_0} dy'' \exp\left(\frac{-y''^2}{\Delta}\right) \right] \\ = \left[ \frac{\pi a \Delta}{(a+\Delta)} \right]^{1/2} \int_{-\infty}^x \exp\left[\frac{-(x'-\sigma_0)^2}{(a+\Delta)}\right] dx' \\ = \left[ \frac{\pi a \Delta}{(a+\Delta)} \right]^{1/2} \int_{-\infty}^{x-\sigma_0} \exp[-x'^2/(a+\Delta)] dx'. \quad (\text{A9})$$

We can now neglect the second term in Eq. (A7) compared with the first one as long as  $a \ll x^2 (x > \sigma_0)$ . Finally, using Eqs. (A2), (A7), and (A9) we get from Eq. (68)

$$\bar{V}'_c(x, t) = -C \exp[-(x-\sigma_0)^2/(a+\Delta)] / \\ \int_{-\infty}^{x-\sigma_0} \exp[-x'^2/(a+\Delta)] dx'. \quad (\text{A10})$$