

Velocity Correlation and Relative Diffusion in Simple Liquids

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A method of calculating the velocity correlation function in monatomic classical liquids is developed essentially from first principles. The interaction between an atom in a liquid and the density fluctuation around it is formulated in the framework of a generalized Langevin equation. It is shown that the memory function can be rigorously expressed in terms of the interatomic potential $v(\mathbf{r})$, static pair correlation function $g(\mathbf{r})$ and a Green function of a certain linear operator \mathcal{L} . With the use of sum-rule arguments and an approximation on the static structure of liquid, the operator \mathcal{L} is shown to be reduced to a (non-Markoffian) Smoluchowski operator which has been used in studying relative diffusion in liquid. This gives a prescription for calculating the velocity autocorrelation function in terms of $v(\mathbf{r})$ and $g(\mathbf{r})$. Frequency spectrum and the memory function are calculated numerically both for soft core and long-range-oscillatory systems. The results have been compared with those obtained by machine computations.

§ 1. Introduction

Recently machine computations by the use of the molecular dynamics method have provided detailed information on atomic motion in simple classical liquids. For example the velocity autocorrelation function (v.a.f.) is computed for various model systems with a Lennard-Jones,¹⁾ a soft^{2),3)} and a hard⁴⁾ core and a long-range-oscillatory (LRO-II) interatomic potential.⁵⁾ Many theoretical attempts have also been made to reproduce the v.a.f. Observing that the motion of an atom has both vibratory and diffusive components, some proposed several stochastic models, e.g., the itinerant oscillator model and its modifications.⁶⁾ Since the two modes of motion can be easily incorporated in the memory function, others proposed plausible functional forms of the memory function.^{3),7)} In these approaches, parameters are introduced in a rather ad hoc manner, which are hardly related to microscopic quantities.

Singwi and Sjölander,⁸⁾ starting from first principles, developed a theory to calculate the v.a.f. They considered one atom, marked blue, in the liquid to be an external driving agent on the other atoms and calculated the response of the other atoms to the blue atom from a simplified kinetic equation. With this and a further series of approximations,⁸⁾ they derived an expression for the memory function which involves a Green function of the kinetic equation. Later Gaskell,⁹⁾ using a statistical decoupling approximation, expressed the memory function in a similar form to that of Singwi-Sjölander. One characteristic of these theories is

that the v.a.f. or the memory function is obtained with the use of the interatomic potential $v(\mathbf{r})$, the static pair correlation function $g(\mathbf{r})$ and the self-part of the Van Hove correlation function $G_s(\mathbf{r}, t)$. It is to be noted, however, that in the Gaussian approximation, $G_s(\mathbf{r}, t)$ is a functional of the v.a.f. and that the $G_s(\mathbf{r}, t)$ used in these theories was calculated with the v.a.f. obtained by machine computations.

In this paper, we discuss atomic motion in liquids and develop a method of calculating the v.a.f. without making use of the knowledge of $G_s(\mathbf{r}, t)$. First we formulate the interaction between the blue atom and the other atoms in the framework of a generalized Langevin equation choosing the momentum of the blue atom and the fluctuation of the density field of the other atoms as the set of dynamical variables. The damping function $\phi(\mathbf{r}, \mathbf{r}', t)$ or the damping operator \mathcal{L} which appears in this equation plays the central role in our theory. It is shown that the memory function can be rigorously expressed in the same form as Gaskell's, in terms of $v(\mathbf{r})$, $g(\mathbf{r})$ and a function $G(\mathbf{r}, t|\mathbf{r}')$. $G(\mathbf{r}, t|\mathbf{r}')$ is the Green function of the damping operator \mathcal{L} and plays a similar role to $G_s(\mathbf{r}, t)$ does in the theories of Singwi-Sjölander and of Gaskell. Secondly we introduce two approximations to obtain a concrete expression of \mathcal{L} . One is on the static structure of liquid. That is, three-body equilibrium distribution function is replaced by a product of two static pair correlation functions. The other which is essentially a short time approximation is based on sum rule arguments. Then it can be shown that the operator \mathcal{L} is reduced to a (non-Markoffian) Smoluchowski one which has been derived and used in the investigation of transport phenomena in fluids.^{15-18, 17)} Thus it is possible to calculate the v.a.f. or the memory function from $v(\mathbf{r})$ and $g(\mathbf{r})$. We notice that $G(\mathbf{r}, t|\mathbf{r}')$ can be interpreted as the transition probability of an other atom from \mathbf{r}' to \mathbf{r} in a time interval t , where \mathbf{r} and \mathbf{r}' represent the position of the other atom relative to the blue atom.

In §2 a generalized Langevin equation is set up and the expression for the memory function mentioned above is derived. In §3 some approximations are introduced to give the operator an explicit form. Frequency spectra for Soft core and LRO-II systems are calculated numerically in §4. Section 5 contains some remarks.

§ 2. Formal development

We consider a system of $N+1$ atoms, each with mass m , in a box of volume v . Atom 0 will be called the blue atom and atoms 1, ..., N will be called the other atoms. The position and momentum of the i -th atom are denoted by $\hat{\mathbf{r}}_i(t)$ and $\hat{\mathbf{p}}_i(t)$, respectively. The caret on a indicates that a is a dynamical variable. The deviation of the number density of other atoms around the blue atom from its equilibrium value is expressed microscopically as

$$\delta\hat{g}(\mathbf{r}, t) = \sum_{i=1}^N \delta(\mathbf{r} + \hat{\mathbf{r}}_0(t) - \hat{\mathbf{r}}_i(t)) - ng(\mathbf{r}) \equiv \hat{g}(\mathbf{r}, t) - ng(\mathbf{r}), \quad (2.1)$$

where n and $g(\mathbf{r})$ are the number density and the static pair correlation function, respectively.

The interaction between the blue atom and the other atoms is now formulated with the use of a generalized Langevin equation¹⁰ (2.2) for the set of dynamical variables $A^*(t) = \{\hat{p}_0(t), \delta\hat{g}(\mathbf{r}, t)\}$, where A^* is the row vector adjoint to A and \mathbf{r} plays the role of a continuous suffix:

$$\frac{d}{dt}A(t) - i\omega \cdot A(t) + \int_0^t \phi(t-s) \cdot A(s) ds = f(t). \quad (2.2)$$

First let us calculate the collective frequency matrix $i\omega \equiv (\dot{A}, A) \cdot (A, A)^{-1}$, where the dot on A denotes the time derivative, i.e., $\dot{A} = \{A, H\}_{\text{P.B.}} \equiv iLA$, $\{\dots, \dots\}_{\text{P.B.}}$ and L being a Poisson bracket and a Liouville operator, respectively. The inner-product (A, B) of two dynamical variables A, B is defined as a canonical ensemble average of AB^* , that is, $(A, B) = z^{-1} \int AB^* \exp\{-\beta H\} d\Gamma \equiv \langle AB^* \rangle$ where $\beta = (kT)^{-1}$, k and T being the Boltzmann constant and the temperature of the system, respectively. It is a straightforward task to show that

$$(\dot{A}, A) = \left(\begin{array}{c|c} 0 & -kTn\nabla'g(\mathbf{r}') \\ \hline kTn\nabla g(\mathbf{r}) & 0 \end{array} \right), \quad (A, A) = \left(\begin{array}{c|c} mkTI & 0 \\ \hline 0 & (\hat{g}(\mathbf{r}), \hat{g}(\mathbf{r}')) - n^2g(\mathbf{r})g(\mathbf{r}') \end{array} \right), \quad (2.3)$$

where I denotes a 3×3 unit matrix. From Eq. (2.1),

$$(\hat{g}(\mathbf{r}), \hat{g}(\mathbf{r}')) = ng(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}') + n^2n(\mathbf{r}, \mathbf{r}'), \quad (2.4)$$

where $n(\mathbf{r}, \mathbf{r}')$ is connected with the three-body generic distribution function $n_{N+1}^{(3)}(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{r}, \mathbf{r}_0 + \mathbf{r}')$ through $n_{N+1}^{(3)}(\mathbf{r}_0, \mathbf{r}_0 + \mathbf{r}, \mathbf{r}_0 + \mathbf{r}') = n^3n(\mathbf{r}, \mathbf{r}')$. For later use, we write two relations between $g(\mathbf{r})$ and $n(\mathbf{r}, \mathbf{r}')$:

$$\nabla g(\mathbf{r}) + \beta g(\mathbf{r})\nabla v(\mathbf{r}) + n\beta \int n(\mathbf{r}, \mathbf{r}')\nabla'v(\mathbf{r}') d\mathbf{r}' = 0, \quad (2.5)$$

$$\nabla g(\mathbf{r}) + \beta g(\mathbf{r})\nabla v(\mathbf{r}) + n\beta \int \{n(\mathbf{r}, \mathbf{r}') - g(\mathbf{r})g(\mathbf{r}')\}\nabla'v(\mathbf{r}') d\mathbf{r}' = 0, \quad (2.6)$$

where we have taken the thermodynamic limit $v \rightarrow \infty$, $N+1 \rightarrow \infty$ with $n = (N+1)/v$ held fixed. $v(\mathbf{r})$ denotes the interatomic potential and Eq. (2.5) is the first of the B-B-G-K-Y- hierarchy equation. Equation (2.6) is derived from Eq. (2.5) by noticing that $g(\mathbf{r})$ and $v(\mathbf{r})$ depend only on $|\mathbf{r}|$. If we write $(A, A)^{-1}$ as

$$(A, A)^{-1} = \left(\begin{array}{c|c} (mkT)^{-1}I & 0 \\ \hline 0 & \Phi(\mathbf{r}, \mathbf{r}') \end{array} \right), \quad (2.7)$$

$\Phi(\mathbf{r}, \mathbf{r}')$ satisfies the following integral equation from Eq. (2.4) and the definition of the inverse matrix, $\int (\delta\hat{g}(\mathbf{r}), \delta\hat{g}(\mathbf{r}'))\Phi(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}'')$:

$$ng(\mathbf{r})\Phi(\mathbf{r}, \mathbf{r}'') + n^2 \int \{n(\mathbf{r}, \mathbf{r}') - g(\mathbf{r})g(\mathbf{r}')\}\Phi(\mathbf{r}', \mathbf{r}'') d\mathbf{r}' = \delta(\mathbf{r}-\mathbf{r}''). \quad (2.8)$$

From Eqs. (2.3) and (2.7), we obtain

$$\begin{aligned}
 i\omega \cdot A &= \begin{pmatrix} 0 & -kTn\nabla'g(\mathbf{r}') \\ kTn\nabla g(\mathbf{r}) & 0 \end{pmatrix} \begin{pmatrix} (mkT)^{-1}I & 0 \\ 0 & \Phi(\mathbf{r}', \mathbf{r}'') \end{pmatrix} \begin{pmatrix} \hat{\mathbf{p}}_0 \\ \delta\hat{g}(\mathbf{r}'') \end{pmatrix} \\
 &= \begin{pmatrix} -kTn \int \nabla'g(\mathbf{r}') \Phi(\mathbf{r}', \mathbf{r}'') \delta\hat{g}(\mathbf{r}'') d\mathbf{r}' d\mathbf{r}'' \\ n\nabla g(\mathbf{r}) \cdot \hat{\mathbf{p}}_0/m \end{pmatrix}. \tag{2.9}
 \end{aligned}$$

Operating $-\beta^{-1}n\int \Phi(\mathbf{r}, \mathbf{r}') \dots d\mathbf{r}$ on Eq. (2.6) and using Eq. (2.8), we get

$$-\beta^{-1}n \int \nabla g(\mathbf{r}) \Phi(\mathbf{r}, \mathbf{r}') d\mathbf{r} = \nabla'v(\mathbf{r}'), \tag{2.10}$$

where the symmetry $n(\mathbf{r}, \mathbf{r}') = n(\mathbf{r}', \mathbf{r})$ is used. Thus the first line on the r.h.s. of Eq. (2.9) is reduced to $\int \nabla v(\mathbf{r}) \delta\hat{g}(\mathbf{r}) d\mathbf{r}$ where the symmetry $\Phi(\mathbf{r}, \mathbf{r}') = \Phi(\mathbf{r}', \mathbf{r})$ is used. The random force f in Eq. (2.2), defined to be $\hat{A} - i\omega \cdot A$, becomes

$$f = \begin{pmatrix} 0 \\ \hat{\mathbf{p}}_0 \cdot \nabla \{ \hat{g}(\mathbf{r}) - ng(\mathbf{r}) \} / m - \nabla \cdot \sum \hat{\mathbf{p}}_i \delta(\hat{\mathbf{r}}_0 + \mathbf{r} - \hat{\mathbf{r}}_i) / m \end{pmatrix} = \begin{pmatrix} 0 \\ f_{\mathbf{r}} \end{pmatrix}. \tag{2.11}$$

From the above discussion and the definition of the damping matrix $\phi = (f(t), f) \cdot (A, A)^{-1}$, we finally arrive at the following Langevin equation:

$$\frac{d}{dt} \hat{\mathbf{p}}_0(t) = \int \nabla v(\mathbf{r}) \delta\hat{g}(\mathbf{r}, t) d\mathbf{r}, \tag{2.12}$$

$$\begin{aligned}
 \frac{\partial}{\partial t} \delta\hat{g}(\mathbf{r}, t) &= n\nabla g(\mathbf{r}) \cdot \hat{\mathbf{p}}_0(t) / m - \int d\mathbf{r}' \int_0^t ds \phi(\mathbf{r}, \mathbf{r}', s) \delta\hat{g}(\mathbf{r}', t-s) + f_{\mathbf{r}}(t) \\
 &\equiv n\nabla g(\mathbf{r}) \cdot \hat{\mathbf{p}}_0(t) / m + \mathcal{L} \delta\hat{g}(\mathbf{r}, t) + f_{\mathbf{r}}(t), \tag{2.13}
 \end{aligned}$$

where

$$\phi(\mathbf{r}, \mathbf{r}', t) = \int d\mathbf{r}'' (f_{\mathbf{r}}(t), f_{\mathbf{r}'}(0)) \Phi(\mathbf{r}'', \mathbf{r}') d\mathbf{r}'', \tag{2.14}$$

and $f_{\mathbf{r}}(t) = \exp\{i(1-\mathcal{P})Lt\}f_{\mathbf{r}}$, \mathcal{P} denoting a projection operator defined by its action on an arbitrary dynamical variable G as $\mathcal{P}G = (G, A) \cdot (A, A)^{-1} \cdot A$. Equation (2.12) is the Newtonian equation of motion for the blue atom. $\phi(\mathbf{r}, \mathbf{r}', t)$ and the linear operator \mathcal{L} defined by Eq. (2.13) we call as the damping function and the damping operator, respectively.

The memory function $K(t)$ corresponding to the v.a.f. $\psi(t) \equiv \langle \hat{\mathbf{p}}_0(t) \cdot \hat{\mathbf{p}}_0(0) \rangle / \langle \hat{\mathbf{p}}_0(0) \cdot \hat{\mathbf{p}}_0(0) \rangle$ is defined by

$$\frac{d}{dt} \psi(t) = - \int_0^t K(t-s) \psi(s) ds. \tag{2.15}$$

As is shown in the Appendix, $K(t)$ can be expressed as follows:

$$K(t) = - (n/m) \int \partial v(\mathbf{r}) / \partial x \cdot \partial g(\mathbf{r}') / \partial x' \cdot G(\mathbf{r}, t | \mathbf{r}') d\mathbf{r} d\mathbf{r}', \tag{2.16}$$

where $x(x')$ denotes an arbitrary Cartesian component of $\mathbf{r}(\mathbf{r}')$. The Green function $G(\mathbf{r}, t|\mathbf{r}')$ satisfies the equation

$$\frac{\partial}{\partial t}G(\mathbf{r}, t|\mathbf{r}') = \mathcal{L}G(\mathbf{r}, t|\mathbf{r}'), \tag{2.17}$$

with the initial condition

$$G(\mathbf{r}, 0|\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}'). \tag{2.18}$$

As is well known, if one neglects $f(t)$, a generalized Langevin equation (2.2) describes the most probable path of $A(t)$, $\langle A(t) \rangle_{av}$ in the linear approximation.¹⁰ Thus $\langle \delta\hat{g}(\mathbf{r}, t) \rangle_{av}$ satisfies

$$\frac{D}{Dt}\langle \delta\hat{g}(\mathbf{r}, t) \rangle_{av} = \mathcal{L}\langle \delta\hat{g}(\mathbf{r}, t) \rangle_{av}, \tag{2.19}$$

where $D/Dt (\equiv \partial/\partial t - n\nabla g(\mathbf{r}) \cdot \langle \hat{\mathbf{p}}_0(t) \rangle_{av}/m)$ denotes a Lagrangian-like derivative. From Eqs. (2.17), (2.18) and (2.19), $G(\mathbf{r}, t|\mathbf{r}')$ can be regarded as a transition probability of another atom from \mathbf{r}' to \mathbf{r} in the time interval t . The expression of the memory function (2.16) is similar to those derived by Singwi-Sjölander and Gaskell,^{9,9} but it is to be noted that Eq. (2.16) is exact.

§ 3. The damping function and a modified Smoluchowski equation

We make two crude approximations on the damping function $\phi(\mathbf{r}, \mathbf{r}', t)$ without using its microscopic definition, (2.14). This will elucidate some aspects of the Langevin equations (2.12) and (2.13). First we put $\phi(\mathbf{r}, \mathbf{r}', t) = 0$. Then from Eqs. (2.17) and (2.18), $G(\mathbf{r}, t|\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$ and the memory function $K(t)$ becomes a constant $\langle \omega^2 \rangle$ which is defined by

$$\langle \omega^2 \rangle = (n/3m) \int \nabla^2 v(\mathbf{r}) g(\mathbf{r}) d\mathbf{r}. \tag{3.1}$$

The constancy of $K(t)$ leads to the sinusoidal v.a.f. $\psi(t) = \cos \sqrt{\langle \omega^2 \rangle} t$. If the number density $\hat{g}(\mathbf{r}, t)$ is fixed to its average, $ng(\mathbf{r})$ and the blue atom is displaced by $\Delta\mathbf{r}$ from its equilibrium point, the force on the blue atom is given by

$$F(\Delta\mathbf{r}) = n \int \nabla v(\mathbf{r}) g(\mathbf{r} + \Delta\mathbf{r}) d\mathbf{r} \simeq n \int \nabla v(\mathbf{r}) \nabla g(\mathbf{r}) \cdot \Delta\mathbf{r} d\mathbf{r} = -m\langle \omega^2 \rangle \Delta\mathbf{r}. \tag{3.2}$$

Thus $\sqrt{\langle \omega^2 \rangle}$ may be considered to be an Einstein frequency of an atom in fluid. It is seen that neglect of the damping function corresponds to that of the density fluctuation around the blue atom. Secondly, let us assume that $\phi(\mathbf{r}, \mathbf{r}', t) = \tau_r^{-1} \cdot \delta(\mathbf{r}-\mathbf{r}')\delta(t)$. From Eqs. (2.16), (2.17) and (2.18), we have an exponential memory function

$$K(t) = \langle \omega^2 \rangle \exp(-t/\tau_r). \tag{3.3}$$

This memory function was first derived by Gray¹⁰ and later used by Berne et al.⁷

in their calculation of correlation functions. It is readily seen from $\mathcal{L}\delta\hat{g}(\mathbf{r}, t) = -\tau_r^{-1}\delta\hat{g}(\mathbf{r}, t)$ that τ_r represents a relaxation time of the density fluctuation of the other atoms.

We now calculate $\phi(\mathbf{r}, \mathbf{r}', t)$ starting from its microscopic definition (2.14), by putting the following two approximations: (I) $\phi(\mathbf{r}, \mathbf{r}', t) \simeq \phi(\mathbf{r}, \mathbf{r}', 0)m(t)$, where $m(0)=1$, (II) $n(\mathbf{r}, \mathbf{r}') \simeq g(\mathbf{r})g(\mathbf{r}')$. The decaying feature of $\phi(\mathbf{r}, \mathbf{r}', t)$ in time is assumed to be described by a representative function $m(t)$ and it is readily seen that with simple forms for $m(t)$ we can satisfy all frequency moment sum rules for $G(\omega)$ (cf. Eq. (4.1)) up to sixth. Thus (I) is essentially a short time approximation and has been used in deriving kinetic equations approximately.¹⁰ We notice that (II) is cruder than the superposition approximation¹⁰ $n(\mathbf{r}, \mathbf{r}') \simeq g(\mathbf{r})g(\mathbf{r}')g(\mathbf{r}-\mathbf{r}')$. To calculate $\phi(\mathbf{r}, \mathbf{r}', 0)$, we first consider $(f_{\mathbf{r}}(0), f_{\mathbf{r}'}(0))$. From Eq. (2.11) it is obtained that

$$(f_{\mathbf{r}}(0), f_{\mathbf{r}'}(0)) = 2(kT/m)(\nabla \cdot \nabla') \{ng(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\} + n^2(kT/m)(\nabla \cdot \nabla') \times \{n(\mathbf{r}, \mathbf{r}') - g(\mathbf{r})g(\mathbf{r}')\}. \quad (3.4)$$

With (II) we obtain

$$(f_{\mathbf{r}}(0), f_{\mathbf{r}'}(0)) \simeq (2kT/m)(\nabla \cdot \nabla') \{ng(\mathbf{r})\delta(\mathbf{r}-\mathbf{r}')\}. \quad (3.5)$$

From Eq. (2.8) and with (II), it is seen that

$$\Phi(\mathbf{r}, \mathbf{r}') \simeq \delta(\mathbf{r}-\mathbf{r}') / \{ng(\mathbf{r})\}. \quad (3.6)$$

The approximate expression for $\Phi(\mathbf{r}, \mathbf{r}')$, (3.6) is also obtained by retaining the first term of the iterative solution to the integral equation (2.8). Using Eqs. (3.5), (3.6) and (2.14), we obtain

$$\Phi(\mathbf{r}, \mathbf{r}', 0) \simeq -\{2kT/mg(\mathbf{r}')\}\nabla \cdot \{g(\mathbf{r})\nabla\delta(\mathbf{r}-\mathbf{r}')\}. \quad (3.7)$$

From Eq. (3.7) and with (I), the generalized Langevin equation (2.13) becomes as follows:

$$\frac{\partial}{\partial t}\delta\hat{g}(\mathbf{r}, t) = (n/m)\nabla g(\mathbf{r}) \cdot \hat{\mathbf{p}}_0(t) + D'\nabla \cdot \{\nabla\delta\hat{g}(\mathbf{r}, t) - \delta\hat{g}(\mathbf{r}, t)\nabla \ln g(\mathbf{r})\} + f_{\mathbf{r}}(t), \quad (3.8)$$

where $D' \equiv 2kT\tau/m$, τ being $\int_0^\infty m(t)dt$ and

$$\bar{\delta\hat{g}}(\mathbf{r}, t) \equiv (1/\tau) \int_0^t m(s)\delta\hat{g}(\mathbf{r}, t-s)ds. \quad (3.9)$$

We notice that $\delta\hat{g}(\mathbf{r}, t)$ and $\bar{\delta\hat{g}}(\mathbf{r}, t)$ in Eq. (3.9) can be replaced by $\hat{g}(\mathbf{r}, t)$ and $\bar{g}(\mathbf{r}, t)$, respectively. The damping operator \mathcal{L} becomes

$$\mathcal{L}G(\mathbf{r}, t) = D'\nabla \cdot \{\nabla\bar{G}(\mathbf{r}, t) - \bar{G}(\mathbf{r}, t)\nabla \ln g(\mathbf{r})\}, \quad (3.10)$$

τ represents the correlation time of the random force $f_{\mathbf{r}}(t)$ and the bar on $\delta\hat{g}(\mathbf{r}, t)$ or $G(\mathbf{r}, t)$ denotes the time average with the weight function $m(t)$. If we put

$m(t) = \tau \delta(t)$, $\overline{\delta \hat{g}}(\mathbf{r}, t)$ in Eq. (3.8) is replaced by $\delta \hat{g}(\mathbf{r}, t)$ and we obtain a Markoffian kinetic equation. Equation (3.8) or its Markoffian equation has a clear physical meaning. The first term on the r.h.s. of Eq. (3.8) express the "linear part" of the streaming term $\nabla \hat{g}(\mathbf{r}, t) \cdot \hat{\mathbf{p}}_0(t)/m$. The first term in the bracket denotes the current due to diffusion and the second term represents the current induced by the effective force exerted by the blue atom.¹²⁾ Thus D' , defined to be $2kT\tau/m$ may be identified with the relative diffusion constant and it is usually set about $2D$,^{12), 13)} where D is the self-diffusion constant. If we neglect the random force $f_r(t)$ in Eq. (3.8), we obtain a modified Smoluchowski equation (S-eq). which is non-Markoff and contains a streaming term.

§ 4. Numerical calculation

Using the Markoffian and the non-Markoffian Smoluchowski operator derived in § 3 as the damping operator \mathcal{L} , we calculate $K(t)$, $\psi(t)$ and the normalized frequency spectrum $f(\omega) \equiv G(\omega)/G(0)$, where

$$G(\omega) = \int_0^\infty \psi(t) \cos \omega t dt. \tag{4.1}$$

It is well known that the self-diffusion constant D is given by

$$D = (kT/m) \int_0^\infty \psi(t) dt = (kT/m) G(0). \tag{4.2}$$

Two model systems are investigated, one with a soft-core interatomic potential $v(r) = \varepsilon(\sigma/r)^{12}$ and the other with a Long-range-oscillatory one $v(r) = \varepsilon\phi(r/\sigma)$,⁵⁾ where

$$\phi(x) = Ax^{-8} \cos\{2k_r\sigma x + B\} + E \exp\{F - G(\sigma/r_0)x\}. \tag{4.3}$$

The equilibrium state of the soft-core system is specified by one parameter,²⁾ the reduced density ρ^* defined to be $(\varepsilon/kT)^{1/4}\rho$, $\rho \equiv (N+1)\sigma^3/v$. We investigate the state $\rho^* = 1.144$ which is very close to the freezing point, $\rho^* = 1.15$. By molecular dynamics nondimensional diffusion constant is given to be $\tilde{D}_{m.d.} = 0.026$. The state of LRO-II system we investigate is at $T = 377^\circ\text{K}$ with the density $\rho = 0.927\text{g/cc}$ and $D = 6.18 \times 10^5 \text{cm}^2/\text{sec}$. This state is considered to represent liquid sodium just above the melting point.⁵⁾ The parameters in Eq. (4.3) are given in Ref. 5).

We list here the set of equations (A.8), (A.9), (A.10) and (3.11), used in the calculation of $K(t)$:

$$\frac{\partial}{\partial t} K(\mathbf{r}, t) = D' \{ \nabla^2 \bar{K}(\mathbf{r}, t) - \nabla \cdot \bar{K}(\mathbf{r}, t) \nabla \ln g(\mathbf{r}) \}, \tag{4.4}$$

$$K(\mathbf{r}, 0) = (n/m) \partial g(\mathbf{r}) / \partial x, \tag{4.5}$$

$$K(t) = - \int (\partial v(\mathbf{r}) / \partial x) K(\mathbf{r}, t) d\mathbf{r}. \tag{4.6}$$

In a polar coordinate system, the initial condition (4.5) becomes

$$K(r, 0) = (n/m) dg(r)/dr \cdot \cos \theta. \quad (4.7)$$

We assume a solution to the S-eq. of the form

$$K(r, t) = u(r, t) \cos \theta, \quad (4.8)$$

and insert it into Eq. (4.4) to obtain

$$\frac{\partial u(r, t)}{\partial t} = D' \left\{ \frac{\partial^2 \bar{u}(r, t)}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{u}(r, t)}{\partial r} - \frac{2}{r^2} \bar{u}(r, t) - \frac{1}{r^2} \frac{d}{dr} \left(\frac{d}{dr} \ln g(r) \cdot r^2 \bar{u}(r, t) \right) \right\}. \quad (4.9)$$

The initial condition for Eq. (4.9) is, from Eqs. (4.7) and (4.8)

$$u(r, 0) = (n/m) dg(r)/dr. \quad (4.10)$$

and from Eqs. (4.6) and (4.8),

$$K(t) = - (4\pi/3) \int_0^\infty dv(r)/dr u(r, t) r^2 dr. \quad (4.11)$$

$g(r)$ is given numerically by machine computations^{2b,5b} and application of iterative numerical techniques (six-point symmetric method^{18b}) permits solution to Eqs. (4.9) and (4.10). With the use of this solution, we calculate $K(t)$ from Eq. (4.11), $\psi(t)$ from Eq. (2.15), $f(\omega)$ from Eq. (4.1) and D from Eq. (4.2). We attach a suffix s to quantities thus obtained and m.d. to those obtained by molecular dynamics.

First we use the Markoffian S-eq., replacing $\bar{u}(r, t)$ by $u(r, t)$. Since D' ($\equiv 2kT\tau/m$) may be considered to be a relative diffusion constant, we take the ratio $\alpha \equiv D'/D_{m.d.}$ as a parameter and change it around 2. As α increases D_s increases (Table I) and the maximum of $f_s(\omega)$, $f_s^{\max}(\omega)$ decreases monotonically. Comparing D_s and $f_s^{\max}(\omega)$ with $D_{m.d.}$ and $f_{m.d.}^{\max}(\omega)$, we choose $\alpha = 2.4$ for both systems. Frequency spectrum is shown in Fig. 1 for soft-core system and in Fig. 2 for LRO-II system. Next we turn to the non-Markoffian S-eq. If we choose an α , the correlation time τ is determined by $\tau \equiv mD'/2kT = D_{m.d.}m/2kT$. For the LRO-II system, τ is about 4×10^{-14} sec and for the soft-core system, the non-dimensional τ , in the time unit $\tau_0 = 1\sqrt{m/kT}$, 1 being $n^{-1/3}$, is about 0.025. We choose the time mesh Δt of our difference scheme equal to $\tau/4$ and replace $u(r, t)$

Table I. Calculated (with the use of Markoffian S-eq.) diffusion constant D_s and maximum of frequency spectrum, $f_s^{\max}(\omega)$. $\delta \equiv D_s/D_{m.d.}$. $\tau \equiv f_s^{\max}(\omega)/f_{m.d.}^{\max}(\omega)$.

α	1.8	2.0	2.2	2.4
δ (S-C)	0.82	0.91	1.01	1.10
τ (S-C)	1.83	1.65	1.47	1.33
δ (LRO-II)	0.96	1.01	1.04	1.13
τ (LRO-II)	1.45	1.39	1.19	1.05

$\equiv (1/\tau) \int_0^\infty m(s) u(r, t-s) ds$ by $\sum_{i=0}^{\infty} a_i u(r, t-idt)$ where $\sum_{i=0}^{\infty} a_i = 1$ because of $\int_0^\infty m(s) ds = \tau$. Since the detailed feature of the correlation function $m(t)$ is left unknown, we choose as $\{a_i\}$ two sets $\{0.5, 0.25, 0.125, 0.125\}$ and $\{0.5, 0.3, 0.15, 0.05\}$ and find that the two sets make no appreciable difference in the resulting $f_s(\omega)$. In Figs. 1 and 2, frequency spectra obtained by setting $\alpha=2.5$ and $\{a_i\} = \{0.5, 0.25, 0.125, 0.125\}$ for both systems are drawn. Memory function of the Soft-core system and v.a.f. of the LRO-II system are also shown in Fig. 3 and Fig. 4, respectively. In these figures, $f(\omega)$, $K(t)$ and $\psi(t)$ from the exponential memory function (3.3) with $\tau_r = kT/mD\langle\omega^2\rangle$ are also shown for comparison. τ_r is determined so as to give a correct diffusion constant. The approach to v.a.f. with the use of S-eq. is seen to give better agreement with experiments than that with the use of the exponential memory function.^{7,15} It is readily shown that S-eq. makes the relaxation time τ_r wave-number dependent (§ 5). Frequency spectrum $f_s(\omega)$ is similar in shape to $f_\sigma(\omega)$ obtained by Gaskell who investigated liquid argon just above the melting point.⁹ Comparing ratios $\gamma \equiv f^{\max}(\omega)/f_{\text{m.d.}}^{\max}(\omega)$ and $\delta \equiv D/D_{\text{m.d.}}$ between Gaskell's and ours, it is seen that γ_σ is a little larger than ours, i.e., $\gamma_\sigma = 1.27$, $\gamma_s = 1.18$ (Soft-core) and $\gamma_s = 1.0$ (LRO-II) and δ_σ is a little smaller, i.e., $\delta_\sigma = 0.8$, $\delta_s = 1.08$ (Soft-core) and $\delta_s = 1.08$ (LRO-II). Connection of our method with that of Gaskell is discussed in detail in § 5.

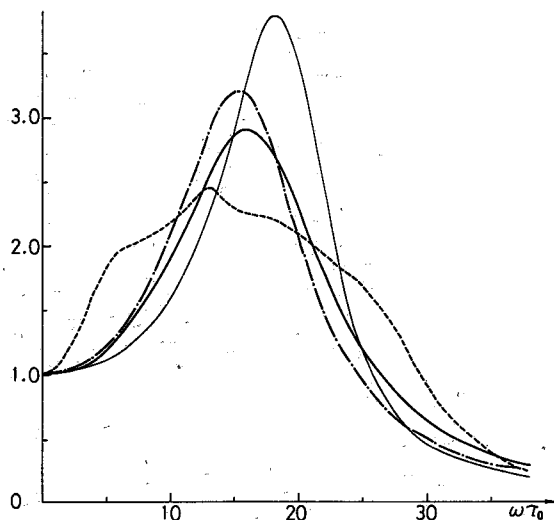


Fig. 1. Normalized frequency spectrum $f(\omega)$ of Soft-core system calculated from a Markoffian S-eq. with $\alpha=2.4$ (dotted curve), a non-Markoffian S-eq. with $\alpha=2.5$ (thick curve) and the exponential memory function (thin curve). The dashed curve represents experimental results.⁸⁾

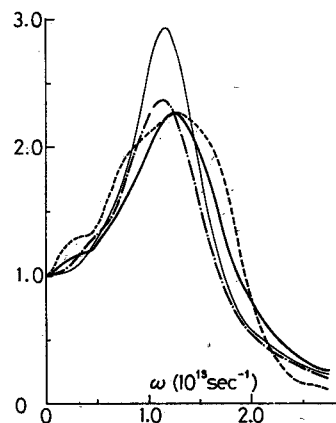


Fig. 2. Normalized frequency spectrum $f(\omega)$ of LRO-II system calculated from a Markoffian S-eq. with $\alpha=2.4$ (dotted curve), a non-Markoffian S-eq. with $\alpha=2.5$ (thick curve) and the exponential memory function (thin curve). The dashed curve represents experimental results.²⁰⁾

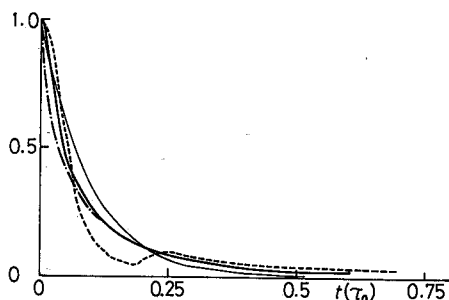


Fig. 3. Normalized memory function $K(t)/K(0)$ calculated from a Markoffian S-eq. with $\alpha=2.4$ (dotted curve) and a non-Markoffian S-eq. with $\alpha=2.5$ (thick curve) compared to the exponential memory function (thin curve) and experimental results.⁹⁾ Two curves (dotted curve and thick one) coincide after $t \approx 0.1\tau_0$.

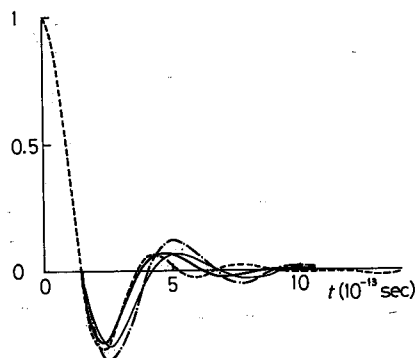


Fig. 4. Velocity autocorrelation function $\psi(t)$ calculated from a Markoffian S-eq. with $\alpha=2.4$ (thin curve), a non-Markoffian S-eq. with $\alpha=2.5$ (thick curve) and the exponential memory function (dotted curve) compare to experimental results⁹⁾ (dashed curve). Three theoretical curves do not deviate appreciably from experimental results for $t < t_0$ (the first zero of $\psi(t)$). Therefore only experimental results are shown for $t < t_0$.

§ 5. Some remarks

We have shown that the memory function $K(t)$ can be expressed rigorously as in Eq. (2.16) in terms of $v(r)$, $g(r)$ and the Green function $G(r, t|r')$ which can be regarded as the transition probability of another atom from r' to r in a time interval t . It is to be noted that r and r' denote positions relative to the blue atom. If we assume that the blue atom and the other atom move independently, $G(r, t|r')$ may be expressed as

$$G(r, t|r') = \int G_s(r'', t) G_s(r+r''-r', t) dr'', \quad (5.1)$$

where $G_s(r, t)$ denotes the self-part of the Van-Hove correlation function and r'' is the displacement of the blue atom in the time interval t . Under the Gaussian approximation to $G_s(r, t)$,¹⁰⁾ $G(r, t|r')$ becomes as follows:

$$G(r, t|r') = \{4\pi a(t)\}^{-3/2} \exp\{-|\mathbf{r}-\mathbf{r}'|^2/4a(t)\}, \quad (5.2)$$

where

$$a(t) = (kT/m^*) \int_0^t \psi(s) (t-s) ds, \quad (5.3)$$

and the effective mass m^* is equal to $m/2$. Inserting Eq. (5.2) to Eq. (2.16), we obtain the same expression for $K(t)$ as derived by Gaskell. Since $G(r, t|r')$ given by Eq. (5.2) has a finite non-zero value near $|\mathbf{r}| \approx 0$, which results from

neglect of correlations between the blue atom and others, $K(t)$ diverges for large t .⁹ To check this divergence Gaskell had to introduce further a rather intuitive approximation. In our approach, the effective force term in S-eq. prevents another atom from coming near the blue atom and assures the convergence of Eq. (2.16) for large t .

If we neglect the effective force term in the S-eq. for $G(\mathbf{r}, t|\mathbf{r}')$, we obtain

$$G_s'(\mathbf{r}, t|\mathbf{r}') = \{4\pi D' t\}^{-3/2} \exp\{-|\mathbf{r}-\mathbf{r}'|^2/4D' t\}, \tag{5.4}$$

as the fundamental solution of the diffusion equation. In order to take account of the effective force, we multiply Eq. (5.4) by a step function $\alpha(|\mathbf{r}|)$, which is zero for $|\mathbf{r}| < \sigma$ and 1 for $|\mathbf{r}| > \sigma$ where σ is some characteristic length of hard core repulsion. Inserting this into Eq. (2.16), we obtain

$$K(t) = -(n/3m) \int \nabla' g(\mathbf{r}') \cdot \nabla v^*(\mathbf{r}) G_s'(\mathbf{r}, t|\mathbf{r}') d\mathbf{r} d\mathbf{r}', \tag{5.5}$$

where $v^*(\mathbf{r}) = v(\mathbf{r})$ for $|\mathbf{r}| > \sigma$ and $v^*(\mathbf{r}) = 0$ for $|\mathbf{r}| < \sigma$. It is evident from Eqs. (5.2) and (5.4) that the appearance of the effective mass $m^* (= m/2)$ in the theory of Gaskell corresponds to that of the relative diffusion constant $D' \simeq 2D$ in our theory. Fourier and Laplace transforming Eq. (5.5), we obtain

$$\bar{K}(t) = -(1/8\pi^3) (n/3m) \int d^3k k^2 g(k) v^*(k) \exp(-D' k^2 t), \tag{5.6}$$

$$K(z) = -(1/8\pi^3) (n/3m) \int d^3k k^2 g(k) v^*(k) / (z + D' k^2). \tag{5.7}$$

If we put $D' k^2 = \tau_r$, Eq. (5.6) gives an exponential memory function. From Eq. (5.6), $K(t)$ has a leading term proportional to $t^{-3/2}$ at large t . However it has been shown recently that asymptotically $K(t) \sim t^{-3/2}$.¹⁹ Thus our S-eq. approach to v.a.f. cannot give a correct asymptotic form of v.a.f. The reason for this defect may be traced back to the assumption (I) introduced in § 3. The assumption (I) together with Eqs. (A.8), (A.9) and (A.10) permits one to satisfy all frequency moment sum rule up to fourth. Thus the time region covered by our theory is much smaller than that of hydrodynamics.

If the assumption (II) in § 3 is replaced by the Superposition approximation, we would obtain a correction to S-eq. which takes into account of correlations among other atoms. This point will be discussed elsewhere. If we consider the blue atom to be a heavy isotope, our formalism developed in § 2 can be used to investigate Brownian motion from a new point of view. More elaborate analysis of Eqs. (2.12), (2.13) and (2.14) than those given in §§ 3, 4 is now in progress.

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Appendix

—Derivation of Eqs. (2.16) and (2.17)—

Laplace transforming Eqs. (2.12), (2.13) and (2.15), we obtain

$$z\hat{p}_0(z) = \hat{p}_0(0) + \nabla v(\mathbf{r})\delta\hat{g}(\mathbf{r}, z), \quad (\text{A}\cdot 1)$$

$$z\delta\hat{g}(\mathbf{r}, z) = (n/m)\nabla g(\mathbf{r}) \cdot \hat{p}_0(z) - \phi(\mathbf{r}, \mathbf{r}', z)\delta\hat{g}(\mathbf{r}', z) + \hat{F}, \quad (\text{A}\cdot 2)$$

$$z\psi(z) = 1 - K(z)\psi(z). \quad (\text{A}\cdot 3)$$

A convention is employed that if a space variable, say \mathbf{r} , appears twice in a term, the integration over the space, $\int d\mathbf{r}$, is performed. $\hat{F} (\equiv \hat{f}_r(z) + \delta\hat{g}(\mathbf{r}, t=0))$ is orthogonal to $\hat{p}_0(0)$ and may be set equal to zero when one calculates the correlation function $\psi(t)$ or $K(t)$. Thus we set $\hat{F}=0$ in what follows. We solve Eq. (A.2) for $\hat{g}(\mathbf{r}, z)$ by iteration and insert it into Eq. (A.1) to obtain

$$\begin{aligned} z\hat{p}_0(z) &= \hat{p}_0(0) + \frac{1}{z}(n/m)\nabla v(\mathbf{r})\nabla g(\mathbf{r}) \cdot \hat{p}_0(z) \\ &+ (n/m)\nabla v(\mathbf{r})\sum_{n=1}^{\infty}\{-1/(-z)^{n+1}\}\phi(\mathbf{r}, \mathbf{r}^{(1)}, z)\phi(\mathbf{r}^{(1)}, \mathbf{r}^{(2)}, z)\dots \\ &\times \phi(\mathbf{r}^{(n-1)}, \mathbf{r}^{(n)}, z)\nabla^{(n)}g(\mathbf{r}^{(n)}) \cdot \hat{p}_0(z). \end{aligned} \quad (\text{A}\cdot 4)$$

We take the innerproduct of (A.4) and $\hat{p}_0(0)$ and compare the resulting equation with Eq. (A.3) to obtain

$$\begin{aligned} K(z) &= -(n/3m)\nabla v(\mathbf{r}) \cdot \left[\frac{1}{z}\nabla g(\mathbf{r}) \right. \\ &\left. + \sum_{n=0}^{\infty}\{-1/(-z)^{n+1}\}\phi(\mathbf{r}, \mathbf{r}^{(1)}, z)\dots\phi(\mathbf{r}^{(n-1)}, \mathbf{r}^{(n)}, z)\nabla^{(n)}g(\mathbf{r}^{(n)}) \right]. \end{aligned} \quad (\text{A}\cdot 5)$$

If we define a vector $\mathbf{K}(\mathbf{r}, z)$ by

$$\mathbf{K}(\mathbf{r}, z) = (n/3m)\nabla g(\mathbf{r})/z - \phi(\mathbf{r}, \mathbf{r}', z)\mathbf{K}(\mathbf{r}', z)/z, \quad (\text{A}\cdot 6)$$

it is readily shown from Eq. (A.5) and the iterative solution to Eq. (A.6) that

$$K(z) = -\nabla v(\mathbf{r}) \cdot \mathbf{K}(\mathbf{r}, z). \quad (\text{A}\cdot 7)$$

From the isotropic property of the system, we finally obtain an equation for $K(t)$ as follows:

$$K(t) = -\int \partial v(\mathbf{r})/\partial x \mathbf{K}(\mathbf{r}, t) d\mathbf{r}. \quad (\text{A}\cdot 8)$$

where the scalar $K(\mathbf{r}, t)$ satisfies

$$\frac{\partial}{\partial t} K(\mathbf{r}, t) = - \int d\mathbf{r}' \int_0^t ds \phi(\mathbf{r}, \mathbf{r}', s) K(\mathbf{r}', t-s) = \mathcal{L}K(\mathbf{r}, t), \quad (\text{A}\cdot 9)$$

with the initial condition

$$K(\mathbf{r}, 0) = (n/m) \partial g(\mathbf{r}) / \partial x, \quad (\text{A}\cdot 10)$$

x denoting an arbitrary Cartesian component of the position vector \mathbf{r} . If we define a Green function $G(\mathbf{r}, t | \mathbf{r}')$ of the damping operator \mathcal{L} by requiring in to satisfy Eq. (A·9) with the initial condition $G(\mathbf{r}, t=0 | \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, $K(t)$ is expressed as

$$K(t) = - (n/m) \int \partial v(\mathbf{r}) / \partial x \partial g(\mathbf{r}') / \partial x' G(\mathbf{r}, t | \mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (\text{A}\cdot 11)$$

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