

Self-motion in liquid sodium

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(Received 20 September 1972; revised manuscript received 17 September 1973)

The theory of Singwi and Sjölander for atomic motion in classical fluids is used to study the self-correlations in liquid sodium. The detailed numerical calculations have been done for the velocity-autocorrelation function and its frequency spectrum using two recently developed interatomic potentials. The results are compared with those obtained by Schiff and Rahman from molecular-dynamics experiments. The recent experimental results of Cocking for quasielastic scattering in liquid sodium at 388 °K are also analyzed using the results obtained from the above two model potentials.

I. INTRODUCTION

In recent years a great deal of information on the time-dependent correlation functions in classical fluids has been obtained by the neutron scattering experiments and molecular-dynamics calculations. Recently¹ it has been found that the velocity autocorrelation decays asymptotically as $t^{-3/2}$ leading to a cusp at the origin in the frequency-distribution function. Since then, there has been renewed interest in the study of self-correlations in classical fluids. The quantity of main interest in the study of self-motion is the velocity-autocorrelation function which satisfies an integrodifferential equation of the form

$$\frac{d\phi(t)}{dt} + \int_0^t d\tau K(t-\tau)\phi(\tau) = 0, \quad (1)$$

where $\phi(t)$ is the normalized velocity-autocorrelation function and the kernel $K(t)$ is the associated memory function. In the past, several functional²⁻⁶ forms of $K(t)$ were used, which gave good accounts of atomic motion in liquid argon. But all these forms are phenomenological and have no theoretical justification. A satisfactory theory will be to obtain the memory function from a first-principles calculation based on the knowledge of the interparticle potential $V(r)$ and the pair-distribution function $g(r)$. Such an approach has been adopted by Singwi and Sjölander⁷ (SS) and more recently by Gaskell.⁸ In all these theories, calculations have been done exclusively for liquid argon and no attempt has been made so far to apply these theories to liquid metals.

The main problem in liquid metals lies in the knowledge of the interatomic potentials. In recent years there has been some progress in this field. Shyu *et al.*⁹ have obtained the interatomic potential for liquid metals using the Ashcroft pseudopotential

and the self-consistent dielectric function of Singwi *et al.*¹⁰ The potential so developed has been found to give good agreement with the phonon dispersion curves in crystalline sodium, and has also given good results for the equilibrium properties of liquid sodium.¹¹ Another potential is a "model potential" constructed by Schiff,¹² which gives a good description of the thermodynamic properties and the static structure factor for liquid sodium. Since molecular-dynamics^{12,13} results for both the potentials are now available, we thought it worthwhile to use these potentials in the calculation of atomic motion in liquid sodium. Thus the purpose of the present paper is to apply the theory of atomic motion developed by SS to the calculation of the memory function for liquid sodium using both the above model potentials. In the SS theory the memory function is expressed in terms of the Van Hove self-correlation function $G_s(r, t)$ which in Gaussian approximation is related to $\phi(t)$. Therefore, a self-consistent solution for $\phi(t)$ is needed. This has been done in the present paper.

In Sec. II we introduce the relevant expressions of the SS theory which are used in the present calculations. In Sec. III, various results obtained with both the potentials are discussed. In Sec. IV we have analyzed the recent experimental results of Cocking¹⁴ for quasielastic scattering in liquid sodium at 388 °K using the Gaussian approximation and the velocity-autocorrelation function obtained by Schiff and Rahman from molecular-dynamics experiments.

II. FORMALISM

The equation of motion of a "blue" particle, moving in the field of the surroundings, has been obtained by SS by solving the kinetic equation for

the one-particle distribution function. This leads to, for the normalized velocity-autocorrelation function $\phi(t)$, the following integrodifferential equation

$$\frac{d\phi(t)}{dt} + \int_0^t \Gamma(t-t')\phi(t') dt' + \int_0^t \Gamma_1(t-t') dt' \int_{t'}^t \phi(\tau) d\tau = 0. \quad (2)$$

Björkman *et al.*¹⁵ have shown in liquid argon that $\Gamma_1(t)$ has only negligible contribution. We assume this contribution to be negligible for liquid sodium as well. Thus neglecting the third term, Eq. (2) reduces to the general form of the integrodifferential equation (1), where now the memory function has the form

$$\Gamma(t) = \left(-\frac{1}{3m} \int \nabla g(x) \cdot \nabla V_{\text{eff}}(x, t) d\vec{x} \right) e^{-t/\tau}, \quad (3)$$

where

$$\nabla V_{\text{eff}}(x, t) = \int \nabla \bar{V}(\vec{x} - \vec{x}', t) G_s(x', t) d\vec{x}' \quad (4)$$

and

$$\nabla \bar{V}(x, t) = \frac{\int \nabla V(\vec{x} - \vec{y}) \alpha(\vec{x} - \vec{y}) G_s(y, t) d\vec{y}}{\int \alpha(\vec{x} - \vec{y}') G_s(y', t) d\vec{y}'}. \quad (5)$$

Here the function $\alpha(\vec{x} - \vec{y})$ is such that it drops sharply to zero for $|\vec{x} - \vec{y}| < \sigma_0$, σ_0 being the hard-core radius, and is of the order of unity whenever $|\vec{x} - \vec{y}| > \sigma_0$. It plays the role of excluding a certain volume corresponding to the hard-core radius around y . $G_s(y, t)$ is the Van Hove self-correlation function and can be written in the Gaussian approximation as

$$G_s(y, t) = [\pi a(t)]^{-3/2} e^{-y^2/a(t)}, \quad (6)$$

where the width function $a(t)$ is given by

$$a(t) = \frac{4}{3} \int_0^t (t-t') \langle \vec{V}(0) \cdot \vec{V}(t') \rangle_{\tau} dt'. \quad (7)$$

At $t=0$, the expression for the memory function, i.e., Eq. (3), reduces to

$$\Gamma(0) = -\frac{1}{3m} \int \nabla V(x) \cdot \nabla g(x) d\vec{x}, \quad (8)$$

which is an exact result and can be calculated directly.

It is physically reasonable to distinguish the effect of the core and soft parts of the potential on the memory function. However, there is no unique way of separating the core and soft parts of the potential. Singwi and Sjölander⁷ and Barker and Gaskell⁸ have used different prescriptions suited to their convenience. In the present paper for simplicity we have separated the Schiff model

potential,

$$V(r) = \frac{\cos 2K_F r}{r^3} \left(A + \frac{B}{r^2} \right) + \frac{\sin 2K_F r}{r^4} \times \left(C + \frac{D}{r^2} \right) + E e^{F-Gr/r_0}, \quad (9)$$

where constants have the same meaning as that of Schiff, into core and soft parts as shown in Fig. 1. That is,

$$V_c(r) = V(r) + \epsilon, \quad r < \sigma' \\ = 0, \quad r \geq \sigma' \quad (10)$$

and

$$V_s(r) = -\epsilon, \quad r < \sigma' \\ = V(r), \quad r \geq \sigma'.$$

where σ' is the distance at which the minimum of the interaction potential occurs.

A. Core-part contribution

At $t=0$, the expression for the core part of the memory function reduces to

$$\Gamma_c(0) = -\frac{1}{3m} \int \nabla V_c(x) \cdot \nabla g(x) d\vec{x}, \quad (11)$$

where $V_c(x)$ is the core potential. The above separation of the potential introduces a discontinuity in the gradient of the potential at $r = \sigma'$. Therefore, to avoid the second derivative of the potential, we use Eq. (11) for the evaluation of the $\Gamma_c(0)$.

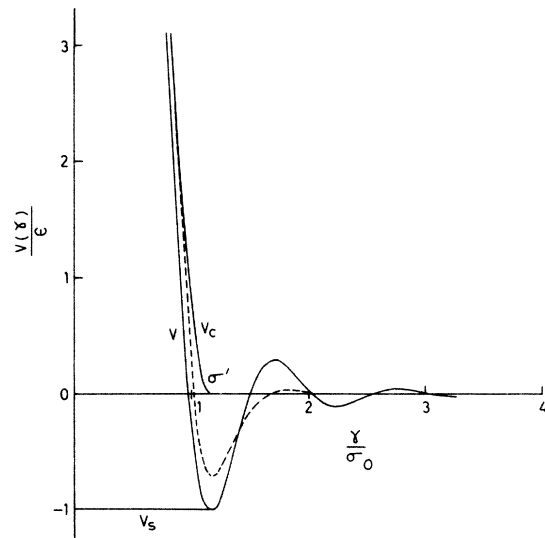


FIG. 1. Interatomic potentials for liquid sodium: Schiff (solid line) and Shyu *et al.* (dashed line). The units of length and energy are $\sigma_0 = 3.24 \text{ \AA}$, $\epsilon = 599 \text{ }^\circ\text{K}$.

For all times of interest, the function $V'_c(y)\alpha(y)$ (V'_c denoting the derivative of V_c) has a sharp peak around $y=\sigma_0$ with a width $\sqrt{\Delta_c}$ and has an area C equal to

$$\int_0^\infty V'_c(y)\alpha(y) dy = -C. \quad (12)$$

Following SS we shall choose for the above function the form

$$V'_c(y)\alpha(y) = -C(\pi\Delta_c)^{-1/2} \exp[-(y-\sigma_0)^2/\Delta_c], \quad (13)$$

which has the correct width and whose area is C . Further we assume the form of $\alpha(y) = \exp[-V_c(y)/k_B T]$, k_B being Boltzmann's constant, which when substituted in (12) gives the area C equivalent to $k_B T$. With this form of $\alpha(y)$ we are left with only two unknown parameters $\sqrt{\Delta_c}$ and τ which can be fixed from the knowledge of $\Gamma_c(0)$ and the diffusion coefficient. Substituting Eq. (13) into (5), and after angular integration using $C = k_B T$, we have

$$\bar{V}'_c(x, t) = \frac{-k_B T \exp[-(x-\sigma_0)^2/(a+\Delta_c)]}{\int_{-\infty}^{\infty} \exp[-x'^2/(a+\Delta_c)] dx'}, \quad (14)$$

where a 's dependence on time is implicit. Now substituting Eq. (14) into (4) and performing angular integration, one obtains after some simplification the expression for the memory function

$$e^{t/\tau} \Gamma_c(t) = \frac{4(\sqrt{\pi})k_B T \sigma_0^2}{3m} \int_{-\infty}^{\infty} dy f(y) \times \int_{-\infty}^{\infty} dx e^{-x^2} g'(\sigma_0 + y(a+\Delta_c)^{1/2} + xa^{1/2}), \quad (15)$$

where

$$f(y) = \left(e^{y^2} \int_{-\infty}^y e^{-u^2} du \right)^{-1}.$$

Therefore at $t=0$, we should choose the constant $\sqrt{\Delta_c}$ such that

$$\Gamma_c(0) = \frac{4\pi k_B T \sigma_0^2}{3m} \int_{-\infty}^{\infty} dy f(y) g'(\sigma_0 + y\sqrt{\Delta_c}) \quad (16)$$

is equivalent to the value given by Eq. (11).

B. Soft-part contribution

The calculation of the soft-part contribution of the potential to the memory function $\Gamma(t)$ proceeds in an analogous way as to the core part. In this case one need have no knowledge of the function $\alpha(x)$ since it is of the order of unity for $x > \sigma'$. Using Eqs. (3)–(5) after angular integrations, we have the expression for the soft part of the memory function

$$e^{t/\tau} \Gamma_s(t) = -\frac{4\pi\rho\epsilon\sigma_0}{3m} \int_0^\infty dx x g'(x) \int_0^\infty dx' x' \times \bar{G}_s(\vec{x} - \vec{x}', t) \frac{\int_1^\infty d\mu \mu V'_s(\mu) \bar{G}_s(\vec{\mu} - \vec{x}', t)}{\int_1^\infty \mu' \bar{G}_s(\vec{\mu}' - \vec{x}', t) d\mu'}, \quad (17)$$

where $\bar{G}_s(x, t)$ is the one-dimensional Gaussian function,

$$\bar{G}_s(x, t) = [\pi a(t)]^{-1/2} e^{-x^2/a(t)}, \quad (18)$$

and V'_s is the derivative of the soft potential V_s .

In Secs. II A and II B we have obtained the expressions for the core and soft parts of the memory function. Since the computer results for the memory function are not available, we shall calculate the velocity-autocorrelation function and its frequency spectrum $f(\omega)$. The frequency distribution function can be obtained by solving Eq. (2) by the Laplace transforms, which gives

$$f(\omega) = \frac{\text{Re}\Gamma(\omega)}{[\text{Re}\Gamma(\omega)]^2 + [\omega - \text{Im}\Gamma(\omega)]^2}, \quad (19)$$

where $\text{Re}\Gamma(\omega)$ and $\text{Im}\Gamma(\omega)$ are, respectively, the cosine and sine transforms of $\Gamma(t)$. The velocity-autocorrelation function is related to the frequency distribution function as

$$\phi(t) = \frac{2}{\pi} \int_0^\infty f(\omega) \cos\omega t d\omega. \quad (20)$$

III. CALCULATION AND RESULTS

In order to perform the calculation of the memory function for liquid sodium, we need to know the interatomic potential and the static pair-correlation function. We use two different interatomic potentials and corresponding pair-correlation functions obtained by Schiff¹² and Rahman¹³ from the molecular-dynamics experiments. Schiff¹² has constructed a model potential by fitting the long-range ion-ion interaction part by an oscillatory function and the repulsive core by a Born-Mayer-type function. Using this potential, he has obtained from molecular-dynamics calculations the static pair-correlation function, velocity-autocorrelation function, and its frequency spectrum at 383 °K and density of $2.43 \times 10^{22} \text{ cm}^{-3}$. The second potential we use is that of Shyu *et al.*,⁹ who have obtained the interatomic potential for alkali metals using the Ashcroft pseudopotential and the self-consistent dielectric function of Singwi *et al.*¹⁰ For the potential of Shyu *et al.*, Rahman¹³ has done the molecular-dynamics calculations and has obtained the static pair-correlation function, the velocity-autocorrelation function, and its frequency spectrum at the above

density and a temperature of 394 °K. Thus we have two sets of "experimental data" for "our purpose" to compare with the results obtained for the velocity-autocorrelation function and its spectral function obtained from the theory of Singwi and Sjölander. In the following we present details of such calculations and results obtained.

The effect of core and soft parts of the model potential of Schiff on the memory function has been seen separately. To calculate the contribution to the memory function from core and soft parts separately, we write Eq. (8) as

$$\Gamma(0) = \Gamma_c(0) + \Gamma_s(0), \quad (21)$$

where c and s refer to the core and soft parts, respectively. The values of $\Gamma_c(0)$ and $\Gamma_s(0)$, which are obtainable from Eq. (8) through the replacement of V with V_c and V_s , respectively, turns out to be $1.507 \times 10^{26} \text{ sec}^{-2}$ and $0.753 \times 10^{26} \text{ sec}^{-2}$, respectively. Having known the value of $\Gamma_c(0)$, the parameter $\sqrt{\Delta_c}$ can be obtained from (16) which gives $\sqrt{\Delta_c} = 0.35$ when expressed in unit of $\sigma_0 = 3.24 \text{ \AA}$. As we have pointed out earlier, there is no unique way of separating a potential into core and soft parts. We have, therefore, studied the effect of different separations of the potential on the memory function and compare the results with the corresponding separation in liquid argon. For the separation shown in Fig. 1 the respective values of $\Gamma_c(0)$ and $\Gamma_s(0)$ in liquid argon are $51.01 \times 10^{24} \text{ sec}^{-2}$ and $2.60 \times 10^{24} \text{ sec}^{-2}$. On the other hand, if one divides the potential into hard and soft cores at the point where it is zero (i.e., $r = \sigma_0$) then the corresponding values of $\Gamma_c(0)$ and $\Gamma_s(0)$ in sodium are $0.918 \times 10^{26} \text{ sec}^{-2}$ and $1.342 \times 10^{26} \text{ sec}^{-2}$, and in argon⁸ $35 \times 10^{24} \text{ sec}^{-2}$ and $25 \times 10^{24} \text{ sec}^{-2}$, respectively. These results show that for the same corresponding separation the ratio $\Gamma_c(0)/\Gamma_s(0)$ in argon is much higher than in sodium, indicating that the potential for argon is much harder than in sodium as expected. We have also seen the effect of various ways of fitting the soft part of the potential in the region $r < \sigma'$. For liquid argon SS have approximated it by a Gaussian function which gives the value of $\Gamma_s(0) = -2.25 \times 10^{24} \text{ sec}^{-2}$, whereas for the case (as shown in Fig. 1) the value of $\Gamma_s(0)$ is $2.60 \times 10^{24} \text{ sec}^{-2}$. These results show that if one fits the soft part of the potential by some function such that it fits the potential well in the region $r > \sigma'$, then the value of $\Gamma_s(0)$ depends on how this function goes in the region $r < \sigma'$. From what has been said above, we conclude that the values of $\Gamma_c(0)$ and $\Gamma_s(0)$ are dependent on the way one separates the potential.

In calculating the ratio $\Gamma(t)/\Gamma(0)$, for the mo-

ment we disregard the factors $e^{t/\tau}$ in (15) and (17). Since $a(t)$ is given in terms of velocity-autocorrelation function, which in turn is related to $\Gamma(t)$ through Eq. (2), a self-consistent solution for $\phi(t)$ is needed. To start with, we have used Schiff's numerical values for $\phi(t)$ and have calculated the right-hand sides of Eqs. (15) and (17). The relaxation time has been fixed from the diffusion coefficient which is related to $\Gamma(t)$ through the relation

$$D = \frac{k_B T}{m} \left(\int_0^\infty \Gamma(t) dt \right)^{-1}, \quad (22)$$

with $D = 4.4 \times 10^{-5} \text{ cm}^2/\text{sec}$ obtained by Schiff from molecular dynamics. Having thus obtained the result of the memory function, after the first iteration we calculate the width function $a(t)$ from Eq. (7) using Eqs. (19) and (20), and repeat the iteration till the self-consistency is achieved. For $\tau = 2.10 \times 10^{-13} \text{ sec}$ our self-consistently calculated $\Gamma(t)$ gives $D = 4.43 \times 10^{-5} \text{ cm}^2/\text{sec}$. The normalized self-consistent memory function along with its core and soft parts is shown in Fig. 2(a). In Fig. 2(a) we have also shown the memory func-

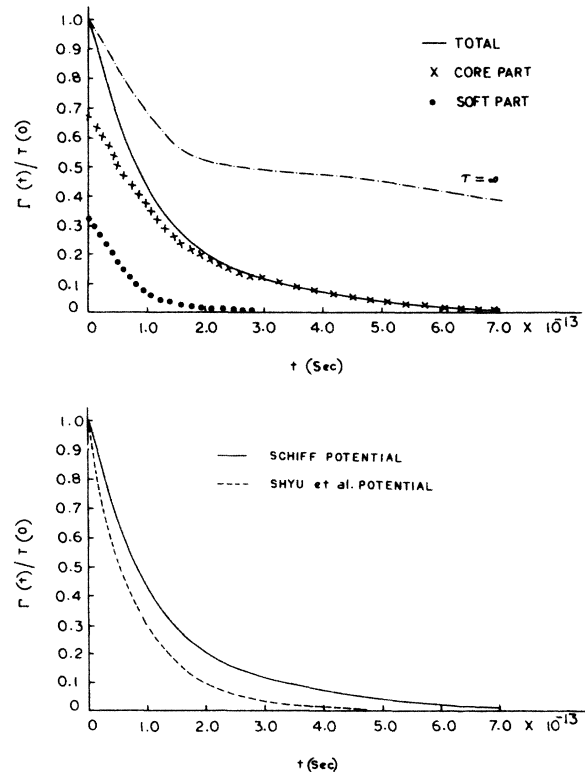


FIG. 2. (a) Separate contributions of the soft and core parts of the Schiff model potential to the memory function. (b) Comparison of the memory function obtained from the potentials of Schiff and Shyu *et al.*

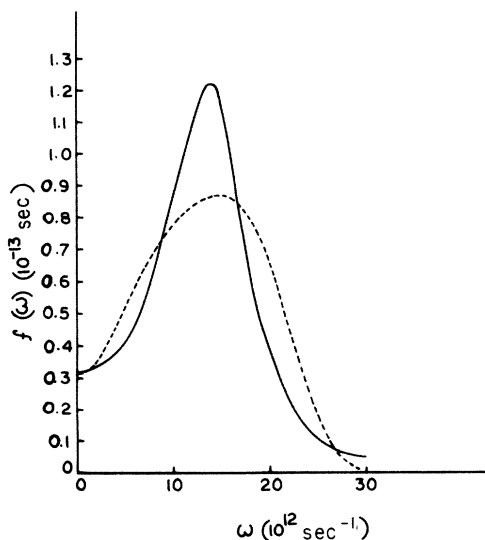


FIG. 3. Frequency spectrum obtained with the Schiff potential (solid line) and Schiff's molecular dynamics (dashed line). The area under the curve is normalized to $\frac{1}{2}\pi$.

tion for $\tau = \infty$. From this figure we notice that the memory function for $\tau = \infty$ decreases from its value at $t = 0$ to half of its value during the interval $(0-2) \times 10^{-13}$ sec and has a higher long tail. However, to obtain the correct value of the diffusion constant, it is necessary to choose the value of the relaxation time $\tau = 2.1 \times 10^{-13}$ sec. This is of the same order of magnitude as the decay time of the memory function. Therefore, the decay of the actual memory function shown in Fig. 2(a) is due mainly to the factor $e^{-t/\tau}$. This exponential factor

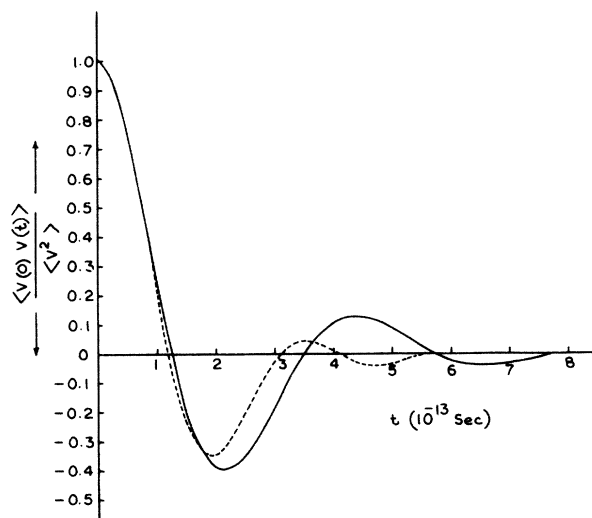


FIG. 4. Velocity-autocorrelation function obtained with the Schiff potential (solid line) and Schiff's molecular dynamics (dashed line).

was phenomenologically put into SS theory to approximate the complicated interaction terms that could not be treated in a satisfactory way. In fact, this interaction term gives rise to the effect of collective motions on the motion of the blue particle. In liquid-argon calculations τ came out to be much larger than the decay time of the memory function, and one could then identify the microscopic origin of the decay as owing to hard-core collisions. In the present liquid-sodium calculations, the smaller value of τ indicates that the collective effects are more significant. Therefore, one may not be justified in approximating the interaction terms through a single relaxation-time approximation.

With these values of the parameters and $\Gamma(t)$ we have calculated the frequency distribution $f(\omega)$ and the velocity-autocorrelation function through Eqs. (19) and (20). The theoretical results, with those of Schiff, are shown in Figs. 3 and 4, respectively. The results are in qualitative agreement with molecular-dynamics calculations.

We have only numerical values of the potential of Shyu *et al.* Therefore, we have calculated the total $\Gamma(t)$ without separating it into the core and soft parts. Using their potential and $g'(x)$ in Eq. (8), the value of $\Gamma(0)$ comes out to be $\Gamma(0) = 2.28 \times 10^{26} \text{ sec}^{-2}$. Since the amplitude of the long-range oscillation in the potential of Shyu *et al.* is negligibly small, we assume that $V'(y)\alpha(y)$ (V' denoting the derivative of V) is a

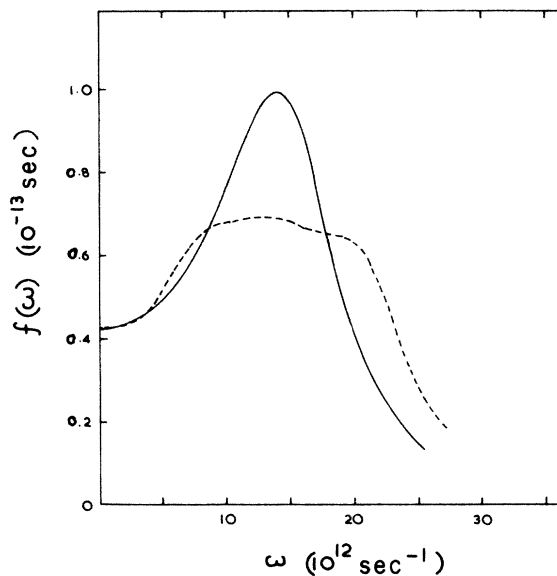


FIG. 5. Frequency spectrum obtained with the potential of Shyu *et al.* (solid line) and Rahman's molecular dynamics (dashed line). The area under the curve is normalized to $\frac{1}{2}\pi$.

single-peaked function at $y = \sigma_0$. The half-width $\sqrt{\Delta}$ of the function $V'(y)\alpha(y)$ can be determined in the way described previously, and we obtain $\sqrt{\Delta} = 0.30$ when expressed in units of $\sigma_0 = 3.30 \text{ \AA}$. From the potential of Shyu *et al.*, Rahman has obtained the diffusion coefficient $D = 5.8 \times 10^{-5} \text{ cm}^2/\text{sec}$. To fit this value of diffusion coefficient we need the value of relaxation time $\tau = 1.1 \times 10^{-13} \text{ sec}$. Again a self-consistent solution for $\phi(t)$ is obtained and is shown in Fig. 2(b). This figure shows the comparison of the memory functions obtained from the potentials of Schiff and Shyu *et al.* The results for the velocity-autocorrelation function and its spectral function are shown in Figs. 5 and 6, respectively. The results with both the potentials of Schiff and Shyu *et al.* show similar qualitative behavior and are in fairly good agreement with the molecular-dynamics results.

IV. QUASIELASTIC SCATTERING

So far we have compared the results obtained from the theory of Singwi and Sjölander only with the molecular-dynamics calculations. Recently Cocking¹⁴ has reported the results for the quasi-elastic scattering for liquid sodium at 388 °K from neutron scattering experiments. Therefore, we thought it worthwhile to compare the results obtained from the potentials of Shyu *et al.* and Schiff

with the experimental results of Cocking.

To study the atomic motion in liquid sodium, Cocking has performed the neutron scattering experiment for different scattering angles using the incident neutrons of 6.1 Å. The scattering cross section of sodium is, in general, a mixture of both coherent- and incoherent-scattering components ($\sigma_{\text{inc}} = 1.85 \text{ b}$, $\sigma_{\text{coh}} = 1.55 \text{ b}$). However, in the region of momentum transfer $Q < 1 \text{ \AA}^{-1}$ the scattered intensity is predominantly incoherent. This is due to the fact that the coherent-scattered intensity integrated over all energies varies as the static structure factor $S(Q)$ which falls to a very small value for $Q < 1 \text{ \AA}^{-1}$. The Gaussian approximation is perfectly valid in this region. Therefore, there is no theoretical uncertainty of any kind in comparing the theoretical results with the experimentally observed cross section. The calculations of total cross section for larger Q values have been done by Pathak *et al.*¹⁶ using the theory of Pathak and Singwi¹⁷ for the coherent part.

The Fourier transform of the intermediate self-correlation function in the Gaussian approximation can be written as

$$S_s(Q, \omega) = \frac{1}{\pi} \int_0^{\infty} dt e^{-Q^2 a(t)/4} \cos \omega t, \quad (23)$$

where $a(t)$ is the width function defined earlier.

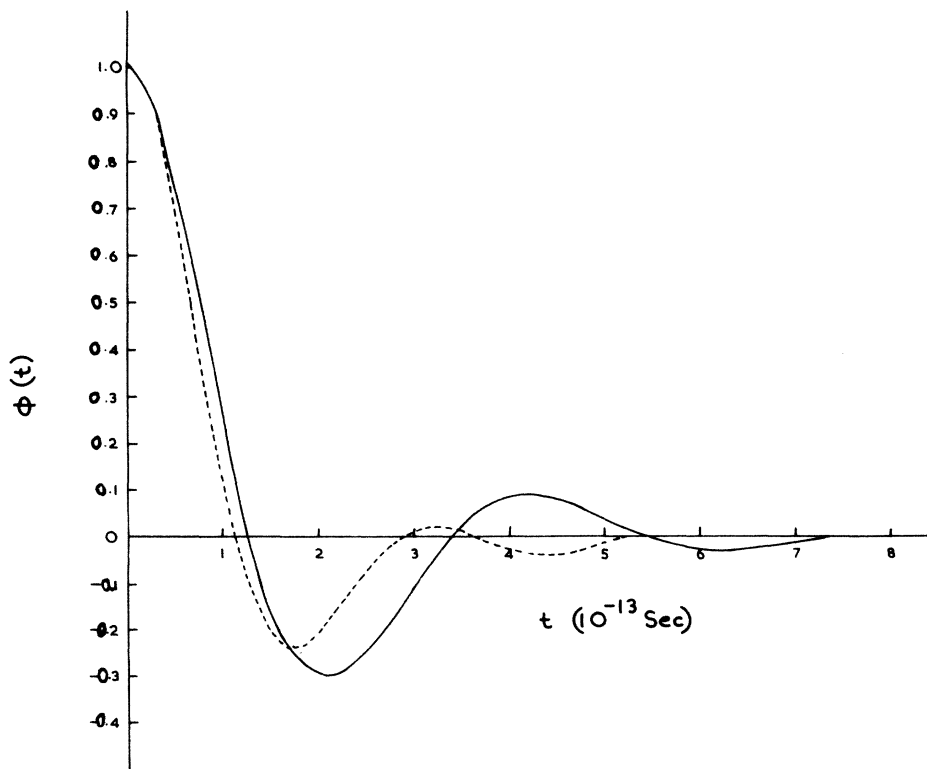


FIG. 6. Velocity-autocorrelation function obtained with the potential of Shyu *et al.* (solid line) and Rahman's molecular dynamics (dashed line).

The width function has been calculated using the velocity-autocorrelation functions obtained by Schiff and Rahman from molecular-dynamics experiments. For the numerical integration Eq. (23) can be split into two parts as

$$S_s(Q, \omega) = \frac{1}{\pi} \left(\int_0^{t_m} dt e^{-Q^2 a(t)/4} \cos \omega t + \int_{t_m}^{\infty} dt e^{-Q^2 a(t)/4} \cos \omega t \right), \quad (24)$$

where t_m is some value of t from which $a(t)$ attains its asymptotic value $Dt + C$; C is a constant. Equation (24) further simplifies to

$$S_s(Q, \omega) = \frac{1}{\pi} \int_0^{t_m} dt (e^{-Q^2 a(t)/4} - e^{-Q^2(Dt+C)}) \cos \omega t + \frac{1}{\pi} e^{-Q^2 C} \frac{DQ^2}{(DQ^2)^2 + \omega^2}. \quad (25)$$

We have used the above equation along with the calculated values of $a(t)$ obtained from molecular dynamics, to calculate the $S_s(Q, \omega)$. The results obtained from both the potentials are plotted in Fig. 7. Cocking has presented his experimental data without applying the resolution correction. Since we do not have the knowledge of his resolution function, we compare our results with his uncorrected data which are shown with solid circles. It has been observed that for the range of momentum transfers considered here the first term in Eq. (25) is negligibly small compared to the second term. The consequence of this is that results obtained here are only slightly different from those which one obtains from the simple diffusion model. One can notice that this seems to fit quite well for most of Q and ω values. The discrepancy in peak heights for the scattering angles of 20° and 30° may be due to resolution correction which has not been applied in the present calculation. It would not be unusual for resolution correction to reduce the peak height by half. The difference between two theoretical curves is due to different values of diffusion coefficients for the two potentials. Therefore it appears that the scattering cross section is not at all sensitive to the details of interatomic potentials. On the other hand, the velocity autocorrelation and its spectral function seems to be more sensitive to the interatomic potential.

V. CONCLUSION

In this paper we have studied in detail the atomic self-correlations in liquid sodium using the theory of Singwi and Sjölander. We have used in the calculations two different interatomic potentials and corresponding static pair-correlation functions obtained by Schiff and Rahman from molecular-

dynamics techniques. For the Schiff model potential the effect of the core and soft parts of the potential on the memory function has been studied separately. It has been found that the initial values of Γ_c and Γ_s depend very much on the way of separating the core and soft parts of the potential. It has also been observed that for the same separation of the potential the ratio $\Gamma_c(0)/\Gamma_s(0)$ in argon is much larger than in sodium, indicating that the

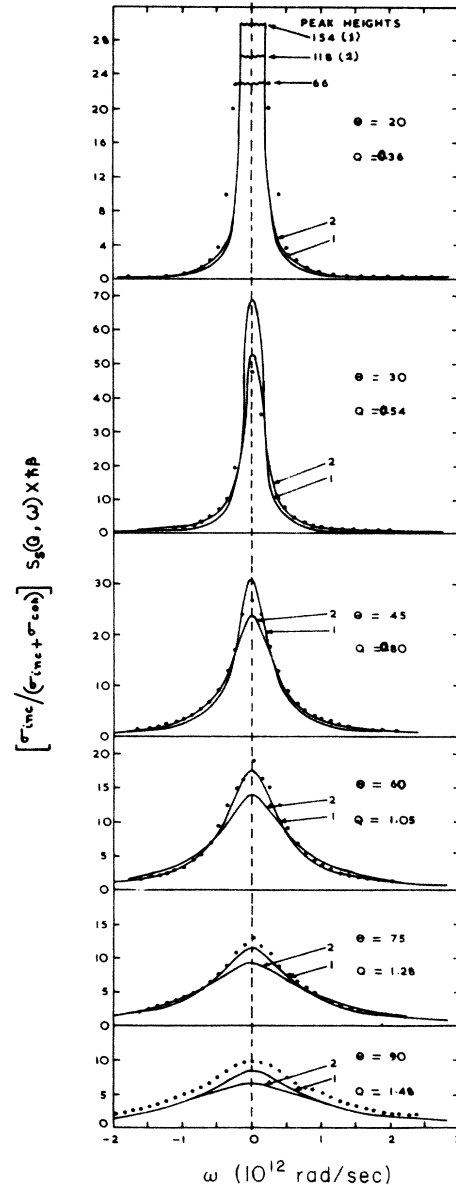


FIG. 7. Measured quasielastic spectra for liquid sodium at a temperature of 388°K with incident neutrons of 6.1 \AA (points) compared with the results of the potentials of Schiff (curve 1) and Shyu *et al.* (curve 2). The indicated Q 's (in \AA^{-1}) refer to the values for $\omega = 0$ at each angle.

potential is much harder in argon than in sodium. We find the relaxation time τ to be of the same order of magnitude as the decay time of the memory function in contrast to liquid argon. This may be an indication of the inapplicability of SS theory to liquid sodium. In this case it will be worthwhile to use an approach similar to Kerr¹⁸ who has solved the Liouville equation for the N -particle system to obtain an expression for the memory function which differs from SS by having a total correlation function instead of the self-correlation one.

We have used the molecular-dynamics results of velocity-autocorrelation function obtained from the potentials of Shyu *et al.* and Schiff to calculate the quasielastic neutron scattering cross sections in the Gaussian approximation. The results are compared with the experimental results recently

obtained by Cocking for liquid sodium at 388 °K. It can be seen from Fig. 7 that the neutron scattering cross sections are not sensitive to the interatomic potentials. The two curves for the cross sections are only slightly different from those which one obtains from the simple diffusion model with the respective diffusion coefficients. For example, the maximum difference in the simple diffusion model and curve 1 is about 15% for the scattering angle of 90°. The maximum difference between the simple diffusion model with the experimental diffusion coefficient (4.78×10^{-5} at 388 °K) and experimental results of Cocking is about 10% for most of the Q and ω values except for the peak heights at scattering angles of 20° and 30°. The discrepancy in these peak heights is due to the fact that we have not convoluted the experimental resolution function with the theoretical expression.

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