

## Density fluctuations in classical liquids: Self-consistent-field method†

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An analysis of the coherent scattering function  $S(q, \omega)$  for simple classical liquids is presented. The analysis is based on a generalization of the modified theory of Singwi, Tosi, Land, and Sjölander involving the polarization potential  $\psi(q)$  and the response function corresponding to the true self-motion of the atoms. The polarization potential has been determined through the modified self-consistent scheme proposed recently by Ailawadi, Miller, and Naghizadeh, thereby implying that both the static structure and dynamics of classical liquids can be understood in one single framework. The first two moments of  $S(q, \omega)$  are automatically satisfied, whereas the fourth moment is only approximately satisfied. Numerical predictions for  $S(q, \omega)$ , the full width at half maximum, and other related functions in liquid rubidium are compared with the neutron scattering measurements of Copley and Rowe. The theory yields agreement with the data for momentum transfers  $q \geq 1.5 \text{ \AA}^{-1}$ . Possible improvements for  $q \leq 1.5 \text{ \AA}^{-1}$  and in the hydrodynamic regime are discussed.

### I. INTRODUCTION

The structure and dynamics of simple liquids has been extensively studied over the last several years both experimentally as well as theoretically. An exhaustive and sufficiently reliable data for the static and dynamic structure of simple liquids is now available from both neutron inelastic scattering experiments<sup>1-3</sup> and molecular dynamics calculations.<sup>4-6</sup> However, a theoretical description of both the static and dynamic structure of liquids within one single framework is still lacking.

Various studies of the collective motions in liquids made so far can be grouped into three categories. First of these is the formalism of Kadanoff and Martin<sup>7</sup> or the Zwanzig-Mori<sup>8</sup> projection-operator technique. Both of these techniques involve memory functions which can either be modeled<sup>9-11</sup> or else calculated in an approximate way.<sup>12</sup> Second is the polarization-potential approach,<sup>13-18</sup> commonly known as the generalized mean-field approximation developed by Singwi *et al.*<sup>15</sup> The third approach to the problem is kinetic theory, where one starts from first principles and tries to use proper equations of motion to extract  $S(q, \omega)$ .<sup>19-23</sup> Unfortunately, this approach usually becomes very formal, and it is not easy to apply its results for numerical calculations. Exceptions are the recent papers of Jhon and Forster<sup>22</sup> and Sjögren and Sjölander.<sup>23</sup>

In all these studies, *a priori* knowledge of the static structure factor of liquids is required, which is obtained from molecular dynamics, Monte Carlo calculations, or x-ray and neutron-diffraction ex-

periments. Theoretically, the static structure factor is typically obtained by the well-known Percus-Yevick hard-core sphere equation<sup>24</sup> or by the more successful Weeks, Chandler, and Andersen (WCA)<sup>25</sup> perturbation theory.

Recently, Ailawadi *et al.* (AMN)<sup>26</sup> have suitably modified the theory of Singwi *et al.* (STLS)<sup>27</sup> for calculating the density response function of an interacting electron gas to take into account the fact that the pair correlation function  $g(r)$  vanishes in the highly repulsive hard-core region of the pair potential for classical liquids. They applied this modified self-consistent iterative scheme to calculate the structure factor of liquid sodium and rubidium. Their results for both these liquid metals were in good agreement with the data<sup>4, 28</sup> and were somewhat better than the predictions of the WCA theory.<sup>25</sup> In this respect, one has, therefore, a fully closed theory, where one does not have to get the structure factor from some other source.

In this paper, we report the results of our calculations for the density fluctuation spectrum in liquid rubidium on the basis of the modified STLS theory. The polarization potential  $\psi(q)$  is determined through the self-consistent-field method discussed by AMN.<sup>26</sup> Based on the physical argument that for a strongly interacting system, such as liquid, there is still a residual interaction left even after collective aspects are taken into account through  $\psi(q)$ , it is proposed that  $\chi_0(q, \omega)$ , the free-particle response function appearing in the STLS theory (as well as in its modified form), should be replaced by  $\chi_s(q, \omega)$ , the response function corresponding to self-motion of the atoms. Two different models

are considered for  $S_s(q, \omega)$ , the incoherent scattering law needed to calculate  $\chi_s(q, \omega)$ . We find that an overall good agreement with the data is obtained, except for wave vectors  $q \leq 1.25 \text{ \AA}^{-1}$ , where the theory is not yet applicable. Further, it is noted that for the intermediate range of momentum transfers ( $1.5\text{--}2.75 \text{ \AA}^{-1}$ ), the present results are much better as compared to the results obtained by Bansal and Pathak<sup>17</sup> using the Pathak and Singwi (PS)<sup>16</sup> theory, which almost failed in this region even though this theory is successful for liquid argon.

The outline of the paper is as follows. Theoretical formulation of the problem is discussed in Sec. II. In Sec. III, numerical results are compared with the neutron-scattering measurements of Copley and Rowe.<sup>3</sup> Connection with the recent first-principles theory of Sjögren and Sjölander<sup>23</sup> and possible improvements to extend the theory for  $q < 1.5 \text{ \AA}^{-1}$  and in the hydrodynamic region is discussed in Sec. IV. In the Appendix, we describe briefly the results of our calculations using a phenomenological mean-field expression proposed recently by Aldrich<sup>29</sup> and Aldrich *et al.*<sup>29</sup> for  $^4\text{He}$  and  $^3\text{He}$ . We find that this theory, even though it includes backflow, shows almost no effect on  $S(q, \omega)$  for liquid rubidium in the investigated range of momentum transfers ( $1.5 \leq q \leq 5.5 \text{ \AA}^{-1}$ ).

## II. FORMULATION

### A. General theory

The dynamical density response function in the STLS theory is given by

$$\chi(q, \omega) = \frac{\chi_0(q, \omega)}{1 - \psi(q)\chi_0(q, \omega)}, \quad (1)$$

where  $\chi_0(q, \omega)$  is the dynamical density-response function of a free-particle system and  $\psi(q)$  is the Fourier transform of the polarization potential  $\psi(r)$ , defined by

$$\frac{d\psi(r)}{dr} = g(r) \frac{d\phi(r)}{dr}. \quad (2)$$

Here  $\phi(r)$  is the pair potential of the system and  $g(r)$  is the well-known radial distribution function. The dynamical structure factor  $S(q, \omega)$  is related to the imaginary part  $\chi''(q, \omega)$  of the dynamical density-response function by the fluctuation-dissipation theorem, which in the classical limit ( $\hbar\omega \ll k_B T$ ) reads as

$$S(q, \omega) = -(k_B T / \pi n \omega) \chi''(q, \omega). \quad (3)$$

The symbols  $k_B$ ,  $T$ , and  $n$  have their usual meaning. Using the Kramers-Kronig relation

$$\chi(q, \omega) = \int_{-\infty}^{\infty} \frac{d\omega'}{\pi} \frac{\chi''(q, \omega')}{\omega' - \omega - i\eta}, \quad \eta \rightarrow 0^+, \quad (4)$$

we can write the zeroth moment of  $S(q, \omega)$ , the static structure factor  $S(q)$ , as

$$S(q) = -(k_B T / n) \chi(q, \omega = 0). \quad (5)$$

Substituting (1), this becomes

$$S(q) = (k_B T / n) \{ \psi(q) - [\chi_0(q, \omega)]^{-1} \}^{-1}. \quad (6)$$

Since

$$\chi_0(q, \omega = 0) = -n / k_B T, \quad (7)$$

Eq. (6) can be expressed as

$$S(q) = \frac{1}{1 + (n/k_B T)\psi(q)}. \quad (8)$$

Given a pair potential, the effective-field  $\psi(q)$  can, in principle, be determined by solving Eqs. (2) and (8) in a self-consistent manner. However, such an iterative procedure for simple liquids leads to computational difficulties because of the highly repulsive nature of the pair potential in the hard-core region. This difficulty has been surmounted by AMN, and the modified STLS scheme has been applied to calculate  $S(q)$  for liquid sodium and rubidium. This modified scheme has been even more successfully applied by Block<sup>30</sup> to analyze the neutron-diffraction measurements of  $S(q)$  in liquid rubidium at various temperatures (450–1400 °K) and pressures, performed at Grenoble.<sup>30</sup> For the details of the modified STLS scheme, the reader is referred to the original AMN paper.

In order to study the dynamics of simple liquids, Ailawadi<sup>31</sup> has calculated the dynamical-structure factor for liquid rubidium using this self-consistent scheme for calculating  $S(q)$ . As compared to the neutron-scattering measurements<sup>3</sup> of  $S(q, \omega)$ , the results obtained by him were not very good except at large values of  $q$  and  $\omega$ , where  $S(q, \omega)$  approaches the free-particle behavior.

Since in the normal mean-field approach<sup>15</sup>  $\chi_0(q, \omega)$  is presumed to represent the residual behavior of the density response function other than the collective aspects, it would be physically more reasonable to replace  $\chi_0(q, \omega)$  by  $\chi_s(q, \omega)$ , representing the true self-motion of the particles in a strongly interacting system, such as liquid. Only in the large-wave-vector limit does the single-particle motion approach the free-particle behavior. At all other wave vectors, this motion is rather complicated and has both diffusive and vibratory aspects. Furthermore,

$$\chi_s''(q, \omega) = -(\pi n \omega / k_B T) S_s(q, \omega), \quad (9)$$

where  $S_s(q, \omega)$  is the usual incoherent scattering law. It should be pointed out that  $\chi_s(q, \omega)$  representing the self-motion has also been used by Singwi *et al.*<sup>15</sup> in their analysis of liquid-argon data.<sup>4</sup>

Note that Eqs. (9) and (4) preserve Eq. (8) for

$S(q)$ . Assuming that the polarization potential  $\psi(r)$  is still given by Eq. (2), the modified STLS scheme can be used to calculate  $S(q)$  and hence  $\psi(q)$  from Eqs. (2) and (8) leading to a closed theory of liquids. A theoretical justification of replacing  $\chi_0(q, \omega)$  by  $\chi_s(q, \omega)$  can be given by a general and more formal approach due to Kerr,<sup>14</sup> who modified earlier expressions of Nelkin and co-workers.<sup>13</sup> The recent first-principles kinetic theory of Sjögren and Sjölander<sup>23</sup> provides further justification for this replacement. In this theory,<sup>23</sup> the polarization potential  $\psi(q)$  and the static-structure factor  $S(q)$  are still related through Eq. (8). The expression for the dynamic-response function, i.e., Eq. (1), is, however, modified by the inclusion of an  $\omega$ -dependent backflow term [see Eq. (31)]. A phenomenological form of the backflow term proposed recently by Aldrich<sup>29</sup> and Aldrich *et al.*<sup>29</sup> is, however, studied in the Appendix.

### B. Moments

In the classical limit, the odd moments of  $S(q, \omega)$  vanish and even moments are defined by

$$\begin{aligned} \langle \omega^{2l} \rangle &= \int_{-\infty}^{\infty} d\omega \omega^{2l} S(q, \omega) \\ &= -\frac{k_B T}{\pi n} \int_{-\infty}^{\infty} d\omega \omega^{2l-1} \chi''(q, \omega), \end{aligned} \quad (10)$$

which follows from the relation (3). Large  $\omega$  expansion of  $\chi(q, \omega)$  can be obtained from Eq. (4), which using Eq. (10) can be written as

$$\chi(q, \omega) = \frac{n}{k_B T} \sum_{l=1}^{\infty} \frac{\langle \omega^{2l} \rangle}{\omega^{2l}}. \quad (11)$$

We can write a similar expression for  $\chi_s(q, \omega)$ :

$$\chi_s(q, \omega) = \sum_{l=1}^{\infty} \frac{\langle \omega_s^{2l-1} \rangle}{\omega_s^{2l}}, \quad (12)$$

where we define

$$\langle \omega_s^{2l-1} \rangle = - \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{2l-1} \chi_s''(q, \omega). \quad (13)$$

Using Eq. (13), large  $\omega$  expansion of (1) can be written as

$$\begin{aligned} \chi(q, \omega) &= \langle \omega_s \rangle / \omega^2 + (1/\omega^4) [\langle \omega_s^3 \rangle + \psi(q) \langle \omega_s \rangle^2] \\ &\quad + O(1/\omega^6). \end{aligned} \quad (14)$$

Comparing Eqs. (11) and (14), we have

$$(n/k_B T) \langle \omega^2 \rangle = \langle \omega_s \rangle, \quad (15)$$

$$(n/k_B T) \langle \omega^4 \rangle = \langle \omega_s^3 \rangle + \psi(q) \langle \omega_s \rangle^2. \quad (16)$$

Using Eq. (9), one immediately finds that

$$\langle \omega_s \rangle = nq^2/m. \quad (17)$$

This relation retains its form if we replace  $\chi_s(q, \omega)$

by  $\chi_0(q, \omega)$ . Therefore it is clear that for both these choices, the second frequency moment of  $S(q, \omega)$  is automatically satisfied. Furthermore, from Eqs. (9) and (13), one finds that

$$\langle \omega_s^3 \rangle = \frac{nq^2}{m} \left( \frac{3q^2 k_B T}{m} + \Omega_0^2 \right), \quad (18)$$

where

$$\Omega_0^2 = \frac{n}{m} \int d\vec{r} g(r) \frac{\partial^2 \phi(r)}{\partial x^2}. \quad (19)$$

Substituting (17) and (18) in (16), we notice that

$$\langle \omega^4 \rangle = \frac{q^2 k_B T}{m} \left[ \frac{3q^2 k_B T}{m} + \frac{nq^2}{m} \psi(q) + \Omega_0^2 \right]. \quad (20)$$

Note that the third term on the right-hand side of Eq. (20) representing the potential contribution would be absent if  $\chi_0(q, \omega)$  were used instead of  $\chi_s(q, \omega)$ . Both these choices violate the fourth-moment relation of  $S(q, \omega)$ . However, we find in our calculations that the choice of  $\chi_s(q, \omega)$  leads to marked improvement in  $\langle \omega^4 \rangle$  as compared to that of  $\chi_0(q, \omega)$ .

### C. Computation

The expression for the dynamical-structure factor can be written in a form suitable for numerical calculations,

$$S(q, \omega) = -\frac{k_B T}{\pi n \omega} \frac{\chi_s''(q, \omega)}{[1 - \psi(q) \chi_s'(q, \omega)]^2 + [\psi(q) \chi_s''(q, \omega)]^2}. \quad (21)$$

$\chi_s'(q, \omega)$ , the real part of  $\chi_s(q, \omega)$ , is related to its imaginary part  $\chi_s''(q, \omega)$  through the Kramers-Kronig relation, Eq. (4).  $S(q, \omega)$  can be computed only if both  $\psi(q)$  and  $\chi_s(q, \omega)$  are given. As mentioned earlier, we follow AMN for calculating  $\psi(q)$ . However, a knowledge of the incoherent scattering function  $S_s(q, \omega)$  is still needed to calculate  $\chi_s(q, \omega)$  from Eqs. (9) and (4).

In the memory-function formalism of Zwanzig-Mori,<sup>8</sup> the intermediate scattering function  $F_s(q, t)$  satisfies an integrodifferential equation of the form

$$\frac{dF_s(q, t)}{dt} + \int_0^t dt' M_1(q, t-t') F_s(q, t') = 0. \quad (22)$$

The kernel  $M_1(q, t)$  is the memory function associated with  $F_s(q, t)$ .  $M_1(q, t)$  also satisfies an equation similar to (22) with a "higher-order" memory function  $M_2(q, t)$  as the kernel, and so on. In terms of Laplace transforms, this chain of equations can be written as

$$\begin{aligned} \tilde{F}_s(q, p) &= \frac{F_s(q, t=0)}{p + \tilde{M}_1(q, p)}, \\ \tilde{M}_k(q, p) &= \frac{\delta_k}{p + \tilde{M}_{k+1}(q, p)}, \end{aligned} \quad (23)$$

where  $\delta_k = M_k(q, t=0)$ .

In order to calculate  $S_s(q, \omega)$ , the spectral function of  $F_s(q, t)$ , it is necessary to truncate the hierarchy of Eqs. (23) at some suitable stage. We truncate it at the third stage by assuming that  $M_3(q, t)$  decays much faster than  $M_2(q, t)$  and obtain

$$\pi S_s(q, \omega) = \frac{\tau(q)\delta_1\delta_2}{[\omega\tau(q)(\omega^2 - \delta_1 - \delta_2)]^2 + [\omega^2 - \delta_1]^2}, \quad (24)$$

where

$$\delta_1 = (k_B T/n) \langle \omega_s \rangle, \quad \delta_1(\delta_1 + \delta_2) = (k_B T/n) \langle \omega_s^3 \rangle. \quad (25)$$

$(k_B T/n) \langle \omega_s \rangle$  and  $(k_B T/n) \langle \omega_s^3 \rangle$  are just the second and fourth moments of  $S_s(q, \omega)$  and are defined by Eqs. (17) and (18), respectively. Furthermore,

$$\tau^{-1}(q) = \tilde{M}_3(q, 0) = \int_0^\infty dt M_3(q, t). \quad (26)$$

To determine  $\tau(q)$ , we follow Lovesey<sup>10</sup> and relate  $\tilde{M}_3(q, 0)$  to  $\tilde{M}_1(q, 0)$  through the chain of equations (23) and assume  $M_1(q, t)$  to be a function of  $\delta_2 t^2$ , which reproduces the first two terms in the short-time expansion of  $M_1(q, t)$ . We thus obtain

$$\tau^{-1}(q) = \xi \sqrt{\delta_2}, \quad (27)$$

where  $\xi$  is the proportionality constant which is determined by requiring  $S_s(q, 0)$  to coincide with the ideal-gas result for large  $q$ . This gives  $\xi = 2/\sqrt{\pi}$ .

The second model used in the calculation of  $S_s(q, \omega)$  is the well-known Gaussian approximation for  $F_s(q, t)$ ,

$$F_s(q, t) = \exp[-q^2 \langle r^2(t) \rangle / 6]. \quad (28)$$

Here  $\langle r^2(t) \rangle$  is the mean-square displacement of the particle and is defined as

$$\langle r^2(t) \rangle = 2 \int_0^t dt' (t-t') \langle \vec{v}(0) \cdot \vec{v}(t') \rangle. \quad (29)$$

The Gaussian approximation is useful because in the limits of large as well as small time, the exact behavior of  $F_s(q, t)$  is recovered. Further, it has been shown for liquid argon that for intermediate times, the non-Gaussian corrections to  $F_s(q, t)$  are of the order of 10–15%.<sup>32</sup> The approximation, however, requires the velocity autocorrelation function  $\langle \vec{v}(0) \cdot \vec{v}(t) \rangle$  as input.

In Sec. III, we present the results of our numerical computation for  $S(q, \omega)$  for liquid rubidium using both these models for the spectral function  $S_s(q, \omega)$ .

### III. RESULTS AND DISCUSSION

We describe now the results of our calculations for liquid rubidium at a temperature of 319 °K and for a density of 1.502 g/cm<sup>3</sup>. For this system, AMN have already calculated  $S(q)$  from Eqs. (2) and

(8) using the modified STLS self-consistent scheme. The Price *et al.*<sup>33</sup> potential was used as input for this calculation, because this potential was used by Rahman<sup>6</sup> in the molecular dynamics simulation of a liquid-rubidium-like system of 500 particles. Also corresponding to these conditions of temperature and density, Copley and Rowe<sup>3</sup> performed neutron-scattering measurements for liquid rubidium. They measured the dynamical-structure factor  $S(q, \omega)$  for different energies in the range of momentum transfers  $0.3 \leq q \leq 5.5 \text{ \AA}^{-1}$ .

In order to study the closed theory discussed in Sec. II, we use as input the static-structure factor  $S(q)$  calculated by AMN. However, for  $\Omega_0^2$  [defined by Eq. (19)] needed in the memory-function model for  $S_s(q, \omega)$ , the value provided by Rahman<sup>6</sup> is used. We find that the value of  $\Omega_0^2$  as calculated from the AMN results for  $S(q)$  is different from Rahman's result by less than 12%. The effect of changes in  $S(q)$  is studied by repeating the calculations using neutron scattering as well as Rahman's data for  $S(q)$ . Since neutron-scattering data is available for the symmetrized scattering function defined as

$$\tilde{S}(q, \omega) = \exp(-\hbar \omega / 2k_B T) S(q, \omega), \quad (30)$$

we calculate  $\tilde{S}(q, \omega)$  and compare our results with the neutron-scattering data.<sup>3</sup>

Using the AMN data for  $S(q)$ , the effective-mean-field  $\psi(q)$  given by Eq. (8) is plotted in Fig. 1. We

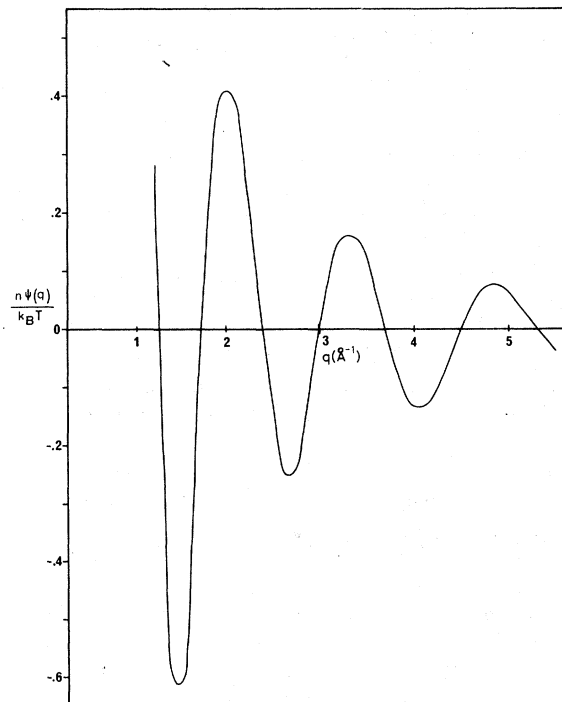


FIG. 1. Effective potential  $\psi(q)$  versus the wave vector  $q$ .

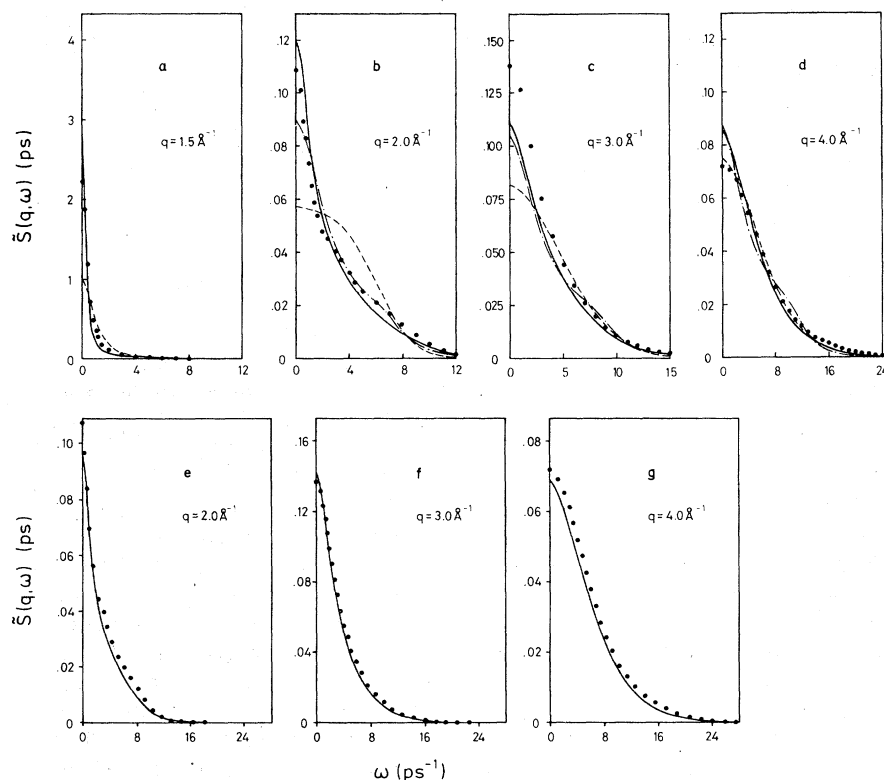


FIG. 2. Symmetrized scattering function  $\tilde{S}(q, \omega)$  as a function of frequency  $\omega$  for some selected values of the wave vector  $q$ . Solid circles: results of neutron inelastic scattering measurements of Copley and Rowe; dashed circle: results obtained by Ailawadi using Eq. (1); dash-dot curve: present calculation using memory function model for  $S_s(q, \omega)$ ; solid curve: present calculation using Gaussian approximation for  $F_s(q, t)$ . In the first four cases (a, b, c, d), AMN data for  $S(q)$  have been used in the present calculations, whereas in the last three cases (e, f, g), Rahman's data for  $S(q)$  has been used.

then compute  $S(q, \omega)$  from Eq. (21), using these results for  $\psi(q)$  and Eq. (9) for  $\chi_s''(q, \omega)$ . For  $S_s(q, \omega)$ , we first use the memory-function model described by Eqs. (24) and (27). These results for  $\tilde{S}(q, \omega)$  have been displayed in Fig. 2 for three different values of  $q$  (2, 3, and  $4 \text{ \AA}^{-1}$ ). These results for  $\tilde{S}(q, \omega)$  have a kink which becomes more pronounced with increasing  $q$ . It is found that the memory-function model used for  $\tilde{S}_s(q, \omega)$  is responsible for this unphysical behavior of  $S(q, \omega)$ . In fact, Eq. (24) for  $S_s(q, \omega)$  gives a three-peak structure for particular values of  $\delta_1$ ,  $\delta_2$ , and  $\tau(q)$ . The resultant  $S_s(q, \omega)$  for these values of  $q$  is shown in Fig. 3 by dashed curves and possesses a definite shoulder.

In view of this drawback of the memory-function model, we use the Gaussian approximation [Eq. (28)] for  $S_s(q, \omega)$ . The velocity autocorrelation function needed in the calculation of the mean-square displacement  $\langle r^2(t) \rangle$  is taken from Rahman's molecular-dynamics data.<sup>34</sup> For  $t \approx 2.2257 \times 10^{-12}$  sec,  $\langle r^2(t) \rangle$  approaches its diffusion limit, i.e.,  $\langle r^2(t) \rangle = 6Dt + C$ , where  $D = 2.458 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  and  $C = 0.819 \text{ \AA}^2$ . The corresponding results for  $S_s(q, \omega)$  are also shown in Fig. 3 for the sake of comparison and are free from any kink or shoulder.

A complete analysis of  $\tilde{S}(q, \omega)$  has been done using the Gaussian approximation for  $S_s(q, \omega)$ . For selected values of  $q$  in the range  $1.25$ – $5.5 \text{ \AA}^{-1}$ , we

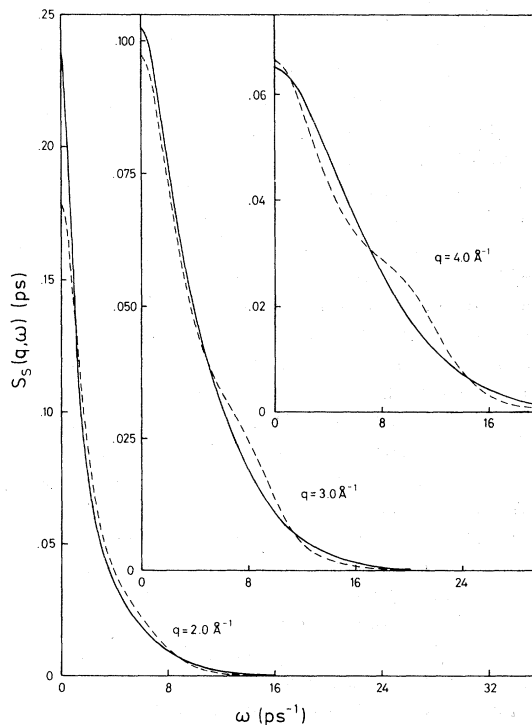


FIG. 3. Incoherent scattering function  $S_s(q, \omega)$  vs  $\omega$  for three selected values of  $q$ . Dashed curve: calculated using memory-function model; solid curve: calculated using Gaussian approximation for  $F_s(q, t)$ .

compare our results in Fig. 2 with the neutron-scattering data of Copley and Rowe.<sup>3</sup> Here, the results obtained by Ailawadi<sup>31</sup> using Eq. (1) directly [i.e.,  $\chi_0(q, \omega)$  instead of  $\chi_s(q, \omega)$ ] are also shown for completeness. We find that for  $q$  between 1.5 and  $3.5 \text{ \AA}^{-1}$ , the present results show a marked improvement over the previous results,<sup>31</sup> thereby showing the importance of replacing  $\chi_0(q, \omega)$  by  $\chi_s(q, \omega)$  in this range of momentum transfers. Furthermore, for  $q > 3.5 \text{ \AA}^{-1}$ , the present results tend to coincide with those of Ailawadi and agree quite well with the experimental data. This is not surprising because at such large  $q$  values, single-particle motion approaches the free-particle behavior.

Figure 2 also illustrates the effect of using Rahman's data for  $S(q)$  in our calculations. The same data for  $S(q)$ , along with the fourth moment of  $S(q, \omega)$ , have been used by Bansal and Pathak<sup>17</sup> to analyze the neutron-scattering results for  $\tilde{S}(q, \omega)$  using the PS<sup>16</sup> theory. The results obtained by Bansal and Pathak are not included here, but it should be pointed out that for  $q \geq 3 \text{ \AA}^{-1}$ , the present results are at least as good as those obtained by these authors. However, for intermediate momentum transfers,  $q \approx 2 \text{ \AA}^{-1}$ , where the PS theory is found unsuccessful, the present results are much better. Note that the PS theory incorporates the first four frequency moments of  $S(q, \omega)$ , whereas the present approach involves only the first two moment relations. It seems suggestive that  $\chi_s(q, \omega)$  plays a more important role in determining the structure of  $S(q, \omega)$  than the fourth-moment sum-rule condition. Further, as seen from Fig. 2, different data for  $S(q)$  lead to perceptible changes in  $S(q, \omega = 0)$  for  $q = 3$  and  $4 \text{ \AA}^{-1}$ . This is caused by the fact that  $S(q, \omega = 0)$  is proportional to  $S^2(q)$  and that the AMN data for  $S(q)$  do not show a pointwise agreement with the molecular-dynamics data.<sup>6</sup> But to be consistent with the theory, we have used the AMN data in our calculations.

The wave-number dependence of the full width at half maximum (FWHM) of  $\tilde{S}(q, \omega)$  as obtained from the present calculations for  $q \geq 1.25 \text{ \AA}^{-1}$  is shown in Fig. 4. These results are compared with the neutron-scattering data.<sup>3</sup> Also represented by crosses in Fig. 4 are the results of the present calculations when the neutron-scattering data for  $S(q)$  is used as input. Clearly this quantity is not very sensitive to the input value of  $S(q)$ . The agreement between the theoretical values and the experimental data is very good for  $q$  between 1.5 and  $3.25 \text{ \AA}^{-1}$ . For  $q \geq 3.5 \text{ \AA}^{-1}$ , the theoretical curve lies somewhat below the experimental data but the  $q$  dependence is in agreement.

Figure 5 compares the fourth moment  $\langle \omega^4 \rangle$  of  $S(q, \omega)$ , obtained from Eq. (16) using  $\chi_s(q, \omega)$  as

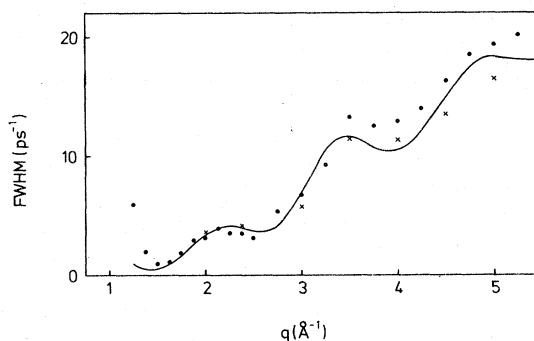


FIG. 4. Full width at half maximum (FWHM) of  $\tilde{S}(q, \omega)$  versus wave vector  $q$ . Notation is same as in Fig. 2 except that crosses represent the results of present calculation obtained by using  $S(q)$  from the neutron-scattering measurements of Copley and Rowe.

well as  $\chi_0(q, \omega)$  in the present calculations. The difference between the two curves is far from negligible in the region of wave vectors of interest. The results obtained using  $\chi_s(q, \omega)$  are in reasonable agreement with the molecular-dynamics data, also shown in Fig. 5. The maximum deviation appears to be at  $q = 1.5 \text{ \AA}^{-1}$ , but it is less than 13%. One is, therefore, led to conclude that  $\langle \omega^4 \rangle$  is not significantly altered, suggesting that the self part of the fourth moment, accounted for by Eq. (9), gives the most significant contribution in the region of wave vectors of interest.

#### IV. CONCLUSIONS

An analysis of the dynamics of density fluctuations in rubidium has been presented on the basis of a fully closed theory in which, unlike other calculations, an *a priori* knowledge of the static-structure factor  $S(q)$  is not demanded. In fact, as discussed by AMN,  $S(q)$ , and hence the polarization field  $\psi(q)$  from Eq. (8), is first calculated self-consistently by the modified STLS theory. This modi-

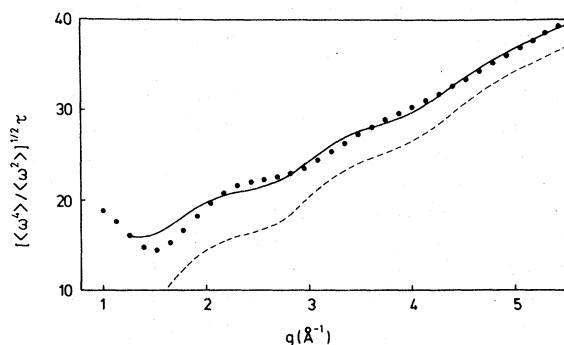


FIG. 5. Fourth moment of  $S(q, \omega)$  versus the wave vector  $q$  as calculated from Eq. (20) compared with the molecular-dynamics results of Rahman, shown as solid circles.

fied theory is then applied in the present calculations. We find that it is necessary to insert  $\chi_s(q, \omega)$ , the response function of the self-motion of the atoms, for  $\chi_0(q, \omega)$  in order to get any agreement with the data. Once this replacement is made, the theory goes a long way in explaining the experimental data. This is also found by Singwi *et al.*<sup>15</sup> for liquid argon. However, in their calculations, the polarization field  $\psi(q)$  is still a parameter.

Our suggestion that  $\chi_0(q, \omega)$  be replaced by  $\chi_s(q, \omega)$  is reinforced from the recent first-principles kinetic theory of Sjögren and Sjölander.<sup>23</sup> If only density and longitudinal current are assumed to be coupled, the dynamic density-response function in their theory becomes

$$\chi(q, \omega) = \frac{\chi_s(q, \omega)}{1 - \psi(q)\chi_s(q, \omega) - (mi\omega/nq^2)\Gamma_{ii}(q, \omega)\chi_s(q, \omega)}, \quad (31)$$

where the third term in the denominator of Eq. (31) represents the motion of the surroundings around the labeled atom (backflow). That is, it corresponds to the motion of the correlation hole around the impurity. In the original STLS formulation, as well as its modification discussed by AMN, this correlation hole remains fixed around the impurity. Furthermore, the polarization field  $\psi(q)$  in Eq. (31) is given by the Ornstein-Zernike direct-correlation function, i.e.,  $\psi(q) = -k_B T c(q)$ .

If this backflow term is included, one would expect to see the propagating sound modes up to  $q \approx 1.25 \text{ \AA}^{-1}$  observed experimentally in liquid rubidium. The small kink in  $\tilde{S}(q, \omega)$  data for  $q \approx 2 \text{ \AA}^{-1}$  should also be reproduced, since the motion of the correlation hole or the backflow would correspond to a second relaxation time discussed by Copley and Rowe<sup>3</sup> and Kahol *et al.*<sup>9</sup> The phenomenological theory of Aldrich<sup>29</sup> and Aldrich *et al.*,<sup>29</sup> which includes backflow and explains the elementary excitations in <sup>4</sup>He and zero sound mode in <sup>3</sup>He, has been studied for this reason. It seems that the backflow term proposed by them is either too small for classical liquids or else the quantities  $\psi(q)$  and  $f(q)$  appearing in Eq. (A1) need to be determined quite differently. Indeed, a comparison of Eqs. (31) and (A1) seems to indicate that the backflow term of Eq. (A1) is the long-wavelength and low-frequency limit of  $\Gamma_{ii}(q, \omega)$  appearing in Eq. (31). Since we choose to fix  $f(q)$  [in Eq. (A1)] through the fourth moment of  $S(q, \omega)$ , it is plausible that a determination of  $f(q)$  in terms of hydrodynamic quantities would improve the results in the region  $q < 1.5 \text{ \AA}^{-1}$ . Also, temperature fluctuations need to be considered for studying the hydrodynamic regime.

Finally, while the use of molecular-dynamics or neutron-scattering data for  $S(q)$  in Eq. (8), rather than the  $S(q)$  calculated by AMN, leads to better agreement with the data at  $S(q, 0)$ , we believe that the  $S(q)$  results presented in AMN could be improved as shown recently by Block<sup>30</sup> so that a fully self-consistent theory can be used to study liquids for most of the  $q$  and  $\omega$  ranges.

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#### APPENDIX

In order to study elementary excitations in liquid helium-4, Aldrich<sup>29</sup> proposed that the generalized mean-field expression for the density-response function should be written as

$$\chi(q, \omega) = \frac{\chi_{sc}(q, \omega)}{1 - [\psi(q) + (\omega^2/q^2)f(q)]\chi_{sc}(q, \omega)}, \quad (A1)$$

where the self-consistent fields  $\psi(q)$  and  $f(q)$  are described by a scalar polarization potential,

$$\phi_{\text{pol}}(\vec{q}, \omega) = \psi(q) \langle \rho(\vec{q}, \omega) \rangle, \quad (A2)$$

and a vector polarization potential,

$$\vec{A}_{\text{pol}}(\vec{q}, \omega) = f(q) \langle \vec{J}(\vec{q}, \omega) \rangle. \quad (A3)$$

Here,  $\langle \rho(\vec{q}, \omega) \rangle$  and  $\langle \vec{J}(\vec{q}, \omega) \rangle$  are the particle- and current-density fluctuations induced by an external probe and  $\chi_{sc}(q, \omega)$  is the usual screened density-response function representing noncollective aspects of the atomic motion. The term involving  $f(q)$  represents the well-known backflow. Aldrich *et al.*<sup>29</sup> recently used Eq. (A1) to analyze liquid <sup>3</sup>He studied by Sköld *et al.*<sup>35</sup> by neutron-scattering technique.

In order to study the effect of this additional backflow term  $\omega^2 f(q)\chi_{sc}(q, \omega)/q^2$ , in the denominator of Eq. (A1), on the dynamics of classical liquids, we attempted to analyze liquid-rubidium data. Since the backflow term vanishes for  $\omega = 0$ , Eq. (6) for  $S(q)$  remains unchanged. The mean-field  $\psi(q)$  is still related to  $S(q)$  through Eq. (8) when  $\chi_{sc}(q, \omega)$  is assumed to be either  $\chi_0(q, \omega)$ , its free-particle value, or  $\chi_s(q, \omega)$  for self-motion of atoms. Having fixed  $\psi(q)$  from Eq. (8), we calculate the second

mean-field  $f(q)$  by demanding that the fourth moment of  $S(q, \omega)$  be satisfied; thus,

$$\langle \omega_{sc} \rangle f(q) / q^2 = 1 - \frac{1}{\omega_i(q)} \left( \frac{m}{nq^2} [\langle \omega_{sc}^3 \rangle + \langle \omega_{sc} \rangle^2 \psi(q)] \right)^{1/2}, \quad (\text{A4})$$

where

$$\langle \omega_{sc}^{2l-1} \rangle = - \int_{-\infty}^{\infty} \frac{d\omega}{\pi} \omega^{2l-1} \chi_{sc}''(q, \omega) \quad (\text{A5})$$

are the frequency moments of  $\chi_{sc}(q, \omega)$ , and

$$\omega_i^2(q) = \langle \omega^4 \rangle / \langle \omega^2 \rangle. \quad (\text{A6})$$

Further, the second moment relation yields

$$(n/k_B T) \langle \omega^2 \rangle = \langle \omega_{sc} \rangle [1 - \langle \omega_{sc} \rangle f(q) / q^2]^{-1}. \quad (\text{A7})$$

If  $\chi_{sc}(q, \omega)$  is replaced by  $\chi_0(q, \omega)$ , Eqs. (A4) and (A7) reduce to

$$\frac{n}{m} f(q) = 1 - \frac{1}{\omega_i(q)} \left[ \frac{q^2 k_B T}{m} \left( 3 + \frac{n}{k_B T} \psi(q) \right) \right]^{1/2} \quad (\text{A8})$$

and

$$\langle \omega^2 \rangle = \frac{q^2 k_B T}{m} \left( 1 - \frac{n}{m} f(q) \right)^{-1}. \quad (\text{A9})$$

However, if  $\chi_{sc}(q, \omega)$  is assumed to be the response function  $\chi_s(q, \omega)$ , Eq. (A4) gives

$$\frac{n}{m} f(q) = 1 - \frac{1}{\omega_i(q)} \left[ \frac{3q^2 k_B T}{m} + \frac{nq^2}{m} \psi(q) + \Omega_0^2 \right]^{1/2}, \quad (\text{A10})$$

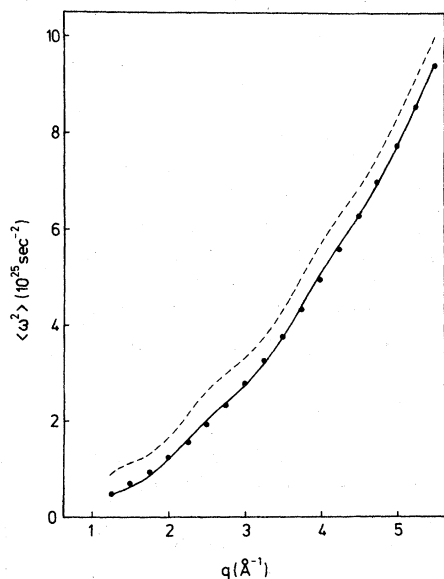


FIG. 6. Second moment of  $S(q, \omega)$  versus the wave vector  $q$ . Solid circles:  $q^2 k_B T / m$ ; solid curve: obtained from Eqs. (A9), (A10), and (8); dashed curve: obtained from Eqs. (A9), (A8), and (8).

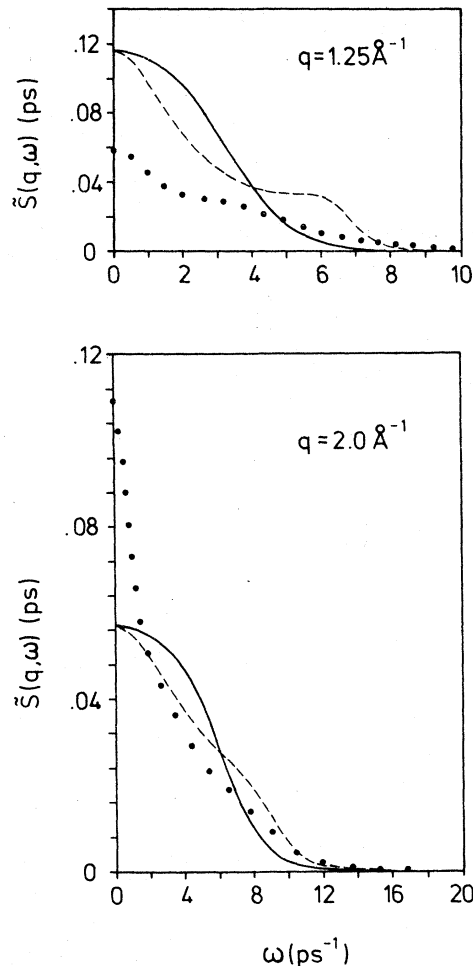


FIG. 7.  $\tilde{S}(q, \omega)$  vs  $\omega$  for  $q = 1.25$  and  $2.0 \text{\AA}^{-1}$ . Solid circles: neutron inelastic scattering data; solid curve: obtained by Ailawadi using Eq. (1); dashed curve: present calculation using Eq. (A1) and the free-particle approximation for the screened response function  $\chi_{sc}(q, \omega)$ .

where  $\Omega_0^2$  is defined through Eq. (19).  $\langle \omega^2 \rangle$  is still given by (A9). Thus if  $f(q)$  is determined through (A8) or (A10), the second moment of  $S(q, \omega)$  is violated.

In Fig. 6,  $\langle \omega^2 \rangle$  is plotted as a function of  $q$  using Eqs. (A8) and (A9) and compared with the exact result as well as with that obtained from Eqs. (A10) and (A9). In this calculation, the AMN data for  $S(q)$  is used. Note that use of  $\chi_s(q, \omega)$  for  $\chi_{sc}(q, \omega)$  through Eq. (9) satisfies the second moment  $\langle \omega^2 \rangle$  for all practical purposes.

The dynamical-structure factor  $S(q, \omega)$  is now computed from Eqs. (A1) and (3). For  $1.25 \leq q \leq 5.5 \text{\AA}^{-1}$  investigated in this paper, the effect of the backflow term involving  $f(q)$  is negligible when  $\chi_s(q, \omega)$  calculated from Eq. (9) is used in Eq. (A1).



However, this term has a definite effect in the structure of  $S(q, \omega)$  if  $\chi_0(q, \omega)$  is used for  $\chi_{sc}(q, \omega)$  in Eq. (A1). This is shown in Fig. 7 for  $q = 1.25$  and  $2.0 \text{ \AA}^{-1}$ , where  $\tilde{S}(q, \omega)$  calculated in this way is compared with the result of Eq. (1) in the absence of the backflow term.  $\tilde{S}(q, \omega)$  calculated

from (A1) seems to have a three-peak structure reminiscent of its behavior in the hydrodynamic region, which persists here up to  $q \approx 2.5 \text{ \AA}^{-1}$ . However, an inspection of Fig. 7 shows that this peak (or shoulder) does not bear any relationship to the structure observed experimentally.

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