Collective motions in classical liquids. IV. Liquid rubidium*

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The coherent scattering function is calculated for liquid rubidium at its melting point on the basis of the theory developed in paper II of this series and using the static structure factor obtained by Rahman from computer simulation with a potential determined by Price *et al.* It is noted that for q up to 1 Å^{-1}, the theory indicates the existence of propagating density waves unlike liquid argon, but the shape of $S(q,\omega)$ is found to disagree with the experimental observations. For intermediate values of q, the agreement between the theoretical and experimental results is not so good, but the disagreement is always less than 40%. However, for $q \geq 3$ Å^{-1}, the theoretical results for $S(q,\omega)$ are quantitatively in good agreement with the recent neutron inelastic-scattering measurements on liquid rubidium.

I. INTRODUCTION

Recently, the coherent scattering function of liquid rubidium has been extensively investigated by both the neutron-scattering experiments[1] and the molecular-dynamics calculations[2] within the range $0.174 \leq q \leq 5.5$ Å^{-1}, giving a clear indication of the existence of propagating density waves for $q < 1.2$ Å^{-1}. We analyze here these data on the basis of the theory of Pathak and Singwi,[3] developed in paper II of this series. This theory has successfully explained the behavior of $S(q,\omega)$ in liquid argon[3] for wave vector $q > 0.5$ Å^{-1}. Neutron-scattering results of Randolph[4] on liquid sodium have also been analyzed fairly well by this theory.

Since the details of the theory have already been discussed by Pathak and Singwi, we quote here only relevant expressions. In the classical limit, $S(q,\omega)$ is related to the imaginary part of the density response function $\chi(q,\omega)$ according to

$$S(q,\omega) = -(\pi n\omega)^{-1} k_B T \,\mathrm{Im}\chi(q,\omega), \tag{1}$$

which in the generalized mean-field approach is given by

$$\chi(q,\omega) = \frac{\chi_{sc}(q,\omega)}{1 - \Psi(q)\,\chi_{sc}(q,\omega)}, \tag{2}$$

where $\Psi(q)$ and $\chi_{sc}(q,\omega)$ are the effective mean field and the screened response function, respectively. In II, the imaginary part of the screened response function was related to a dressed-particle response function in which the damping of the free-particle motion has been taken into account. This can be written

$$\mathrm{Im}\chi_{sc}(q,\omega) = -\frac{2n\omega q^2}{2q^2 k_B T + m\Gamma(q)} \left(\frac{m\omega^2}{2q^2 k_B T + m\Gamma(q)}\right)^{1/2} \times \exp\left(-\frac{m\omega^2}{2q^2 k_B T + m\Gamma(q)}\right), \tag{3}$$

and the real part of $\chi_{sc}(q,\omega)$ can be obtained by using Kramers-Krönig relation. The unknowns $\Psi(q)$ and $\Gamma(q)$ were determined by requiring that the zeroth- and fourth-moment sum rules of $S(q,\omega)$ are exactly satisfied. These are given by

$$\Psi(q) = \frac{3k_B T}{2n}\left(\frac{1}{S(q)} - 1\right) - \tfrac{1}{2}P_4(q) \tag{4}$$

and

$$\Gamma(q) = \frac{q^2}{m}\left[nP_4(q) - k_B T\left(\frac{1}{S(q)} - 1\right)\right], \tag{5}$$

where

$$P_4(q) = \int d\vec{r}\, g(r) \frac{1 - \cos(\vec{q}\cdot\vec{r})}{q^2} (\hat{q}\cdot\vec{\nabla})^2 v(r). \tag{6}$$

The second moment of $S(q,\omega)$ is automatically satisfied in this theory. We have estimated[5] the sixth and eighth frequency moments of $S(q,\omega)$ for liquid argon using various models of $S(q,\omega)$. We have also estimated[5] these moments using the molecular-dynamics data of Rahman and we find that for $q > 0.5$ Å^{-1}, the results of the theory of Pathak and Singwi are in favorably good agreement with those obtained using molecular-dynamics data. We feel that higher moments are not violated significantly.

The neutron-scattering results presented by Copley and Rowe[1] are available for the symmetrized scattering function $\tilde{S}(q,\omega)$ (for $0.3 \leq q \leq 5.5$ Å^{-1}) which is defined as

$$\tilde{S}(q,\omega) = e^{-\hbar\omega/2k_B T} S(q,\omega). \tag{7}$$

II. CALCULATIONS AND RESULTS

We now describe the results of our calculations for liquid rubidium at 319°K and for a density of 1.502 g/cm^3. For this temperature and density, the results for $S(q)$ and $P_4(q)$ have been obtained by Rahman from the molecular-dynamics calcula-

tions using the potential obtained by Price *et al.*[6] Using these results we calculate $\Psi(q)$ and $\Gamma(q)$ from Eqs. (4) and (5). Like liquid argon, $\Gamma(q)$ is found to be positive and has a damped oscillatory behavior. On the other hand, $\Psi(q)$, unlike liquid argon, has been found to be positive for $q < 1.2$ Å^{-1}. It is large for very small q and decreases with q, so that at $q = 1.2$ Å^{-1} it becomes negative.

Having calculated $\Psi(q)$ and $\Gamma(q)$, we have calculated $S(q, \omega)$ and $\tilde{S}(q, \omega)$ as a function of ω for q in the range $0.174 \leq q \leq 5.5$ Å^{-1}. It has been found that the theoretically calculated $S(q, \omega)$ has a peak at finite ω up to $q = 1$ Å^{-1}. Thus the model also indicates the existence of propagating density fluctuations up to $q = 1$ Å^{-1}, but the shape of $S(q, \omega)$ is bad. After $q = 1$ Å^{-1}, $\Psi(q)$ becomes negative and

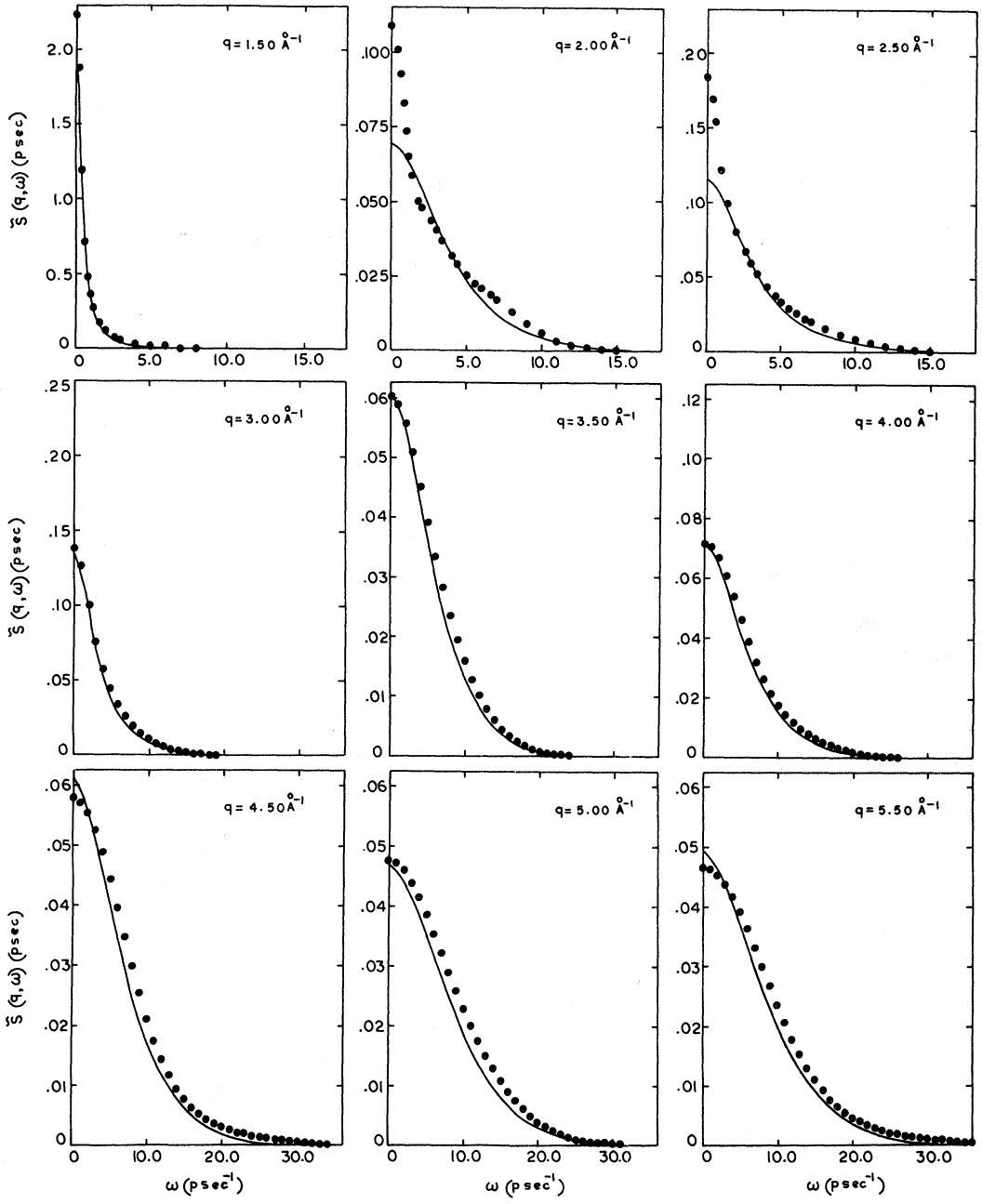

FIG. 1. Symmetrized scattering function $\tilde{S}(q,\omega)$ as a function of frequency ω for nine values of the wave vector q ($1.5 \leq q \leq 5.5$ Å^{-1}). Solid circles: results from neutron-inelastic-scattering experiments.

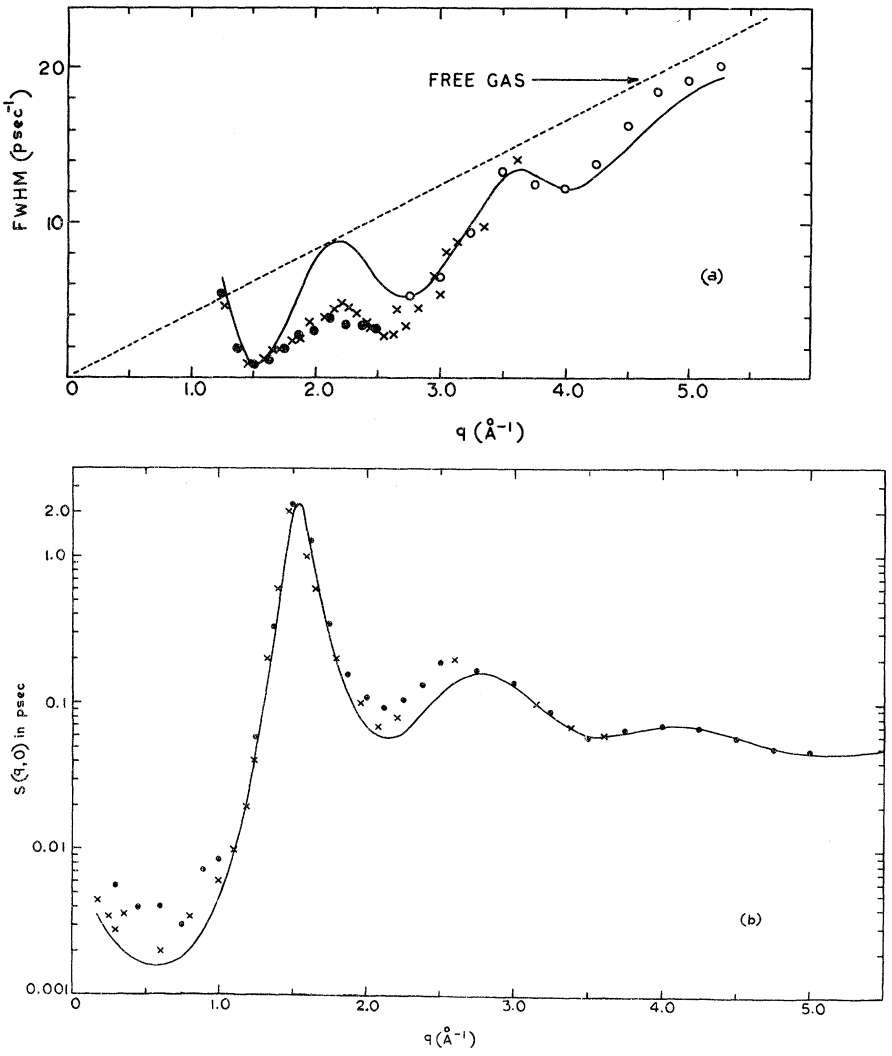

FIG. 2. (a) Full width at half-maximum (FWHM) of $S(q,\omega)$ vs wave vector q. (b) Coherent scattering function $S(q,\omega)$ at $\omega=0$ vs wave vector q. Circles: results from neutron-inelastic-scattering experiments; open (solid) circles: neutron energy loss (gain); crosses: results of the molecular-dynamics calculations of Rahman.

the peak in $S(q,\omega)$ disappears.

In Fig. 1, we have plotted the results of our calculations for the symmetrized scattering function $S(q,\omega)$ against ω for q in the range 1.5–5.5 Å^{-1}. We have compared our results with those measured through neutron-scattering experiments. For intermediate values of q (1.5–2.75 Å^{-1}), there are discrepancies between the two results, but these are always less than 40%. However, the agreement is quite good for $q \geq 3$ Å^{-1} and for all ω.

The full width at half-maximum (FWHM) of $S(q,\omega)$ as obtained from the calculations for $q > 1.2$ Å^{-1} is shown in Fig. 2(a). The positions of the minimum and maximum in FWHM are in phase with the maxima and minima of $S(q)$. The agreement between the theory and the experiment is not good in the region of first maximum in FWHM. At large q both the experiment and the theory approach the ideal-gas limit shown by the dashed line. In Fig. 2(b), the absolute value of the intensity for $\omega=0$, i.e., $S(q,\omega=0)$, is plotted as a function of q. Again around $q \sim 2$ Å^{-1}, the agreement is poor, but for $q \geq 3$ Å^{-1}, there is a good agreement between the theoretical and the experimental observations.

III. SUMMARY

In this paper we have presented the results of a detailed calculation for the coherent scattering function for liquid rubidium using the theory of Pathak and Singwi. The theory indicated the existence of a collective mode. We find that the effective mean field plays an important role for the existence of a collective mode. It must be positive and large for the occurrence of a peak in $S(q,\omega)$. The value of $\Psi(q)$ is, in effect, determined by the interatomic potential and the pair-correlation

function, which are the only inputs of the theory. In the case of liquid sodium,[7] $\Psi(q)$ was found to be positive but small, and a bump in $S(q,\omega)$ for $q \simeq 0.8$ Å^{-1} was noted which was not conclusive. However, for liquid argon, $\Psi(q)$ remained negative even up to $q = 0.23$ Å^{-1}, and no peak in $S(q,\omega)$ was seen. This is consistent with the result of the molecular-dynamics calculations of the Orsay group[8] that the propagating density waves disappear at wavelengths of about eight times the nearest-neighbor distance.

It has been found that the calculated $S(q,\omega)$ for wave vector $q < 1.2$ Å^{-1} is very bad. It does not show a bowl which is present in the experimental results.[1,2] This bowl is a consequence of the thermal-conduction effects which are not at all built in the model. It has already been mentioned in paper II of this series that the theory is not applicable in the hydrodynamic region. Also, the Kubo limit,[9] which relates the longitudinal viscosity to $S(q,\omega)$, does not exist in this model. This is why the shape of $S(q,\omega)$ for small q values has not been reproduced by this model. However, it has been noted that the form of the dispersion curve as predicted by the model is similar to the experimental curves; but it always lies below the experimental curves.

For the intermediate values of q (1.5–2.75 Å^{-1}) the various theoretical results have been found to disagree with the experimental observations within about 40%. It seems that the dynamics of waves around $q \sim 2$ Å^{-1} contains more information than is contained in the present model. It has been conjectured by Copley and Rowe[1] that for $q \sim 2$ Å^{-1}, a "two-relaxation-time" approach is indicated from the experimental observations. It may be that for this region the conjecture of Copley and Rowe is to some extent substantiated by the failure of present model which can be considered as a "one-relaxation-time" model.

It is hoped that, if the above-mentioned shortcomings of the model in the hydrodynamic and intermediate q regions are removed, the results could be improved. The failure of the model in these regions might encourage further efforts to try to make improvements.

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