him the technique for making oriented gallium crystals in a mold.

[9]A. Tyler, J. Phys. C: Proc. Phys. Soc., London 4, 1479 (1971).

[10]D. F. Brewer *et al.*, in *Monolayer and Submonolayer Helium Films*, edited by J. G. Daunt and E. Lerner (Plenum, New York, 1973); R. J. Rollefson, *ibid.*; D. L. Husa *et al.*, *ibid.*

Short-Wavelength Collective Excitations in Liquid Rubidium Observed by Coherent Neutron Scattering*

J. R. D. Copley†
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439

and

J. M. Rowe
Solid State Science Division, Argonne National Laboratory, Argonne, Illinois 60439, and Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234

(Received 12 November 1973)

The short-wavelength collective excitations in liquid rubidium at 320 K have been studied by coherent neutron scattering. For values of $\kappa = 2\pi/\lambda$ up to 1.0 Å^{-1}, clear evidence of propagating modes was found from the shape of the scattering function $S(\kappa,\omega)$ at constant values of κ. This result shows that the existence of such modes does not depend upon either quantum effects or low thermal population of the modes.

The existence of propagating collective modes of finite wavelengths in simple liquids is a subject of intense, continuing interest. Recent neutron-scattering studies[1] of liquid parahydrogen near its freezing point established the existence of such modes for values of $\kappa = 2\pi/\lambda$ as large as 3.1 Å^{-1}, and suggested the existence of transverse excitations. Since the first peak in the structure factor $S(\kappa)$ occurs at $\kappa = 2.0$ Å^{-1}, this implies that the wavelengths of these modes are smaller than typical interatomic spacings. Earlier measurements[2] on liquid lead near the freezing point were interpreted as evidence for the existence of both longitudinal and transverse modes with wavelengths comparable to two interatomic spacings. Recent molecular-dynamics studies[3] of a Lennard-Jones fluid with parameters chosen to simulate liquid argon show evidence of such excitations, but only for κ's smaller than 0.3 Å^{-1}, implying wavelengths greater than 5–7 interatomic spacings. Neutron-scattering studies[4] on liquid argon at 85.2 K show no evidence of peaks for values of $\kappa \geq 1.0$ Å^{-1}. In this Letter we present neutron-scattering results for liquid Rb at 320 K which show evidence of "longitudinal" modes for $\kappa \leq 1.0$ Å^{-1}, but no evidence of "transverse" modes.

The lattice dynamics of Rb have been extensively studied,[5] and the results have been used to derive a volume-dependent effective two-body potential.[6] Molecular-dynamics calculations[7] with this potential have been compared in detail to neutron-scattering results[8] in the range $1.25 < \kappa < 5.50$ Å^{-1} and good agreement found. Further computations[9] at wave vectors $\kappa < 1.0$ Å^{-1} predicted the existence of well-defined propagating modes in the spectrum of density fluctuations. Since the ratio of coherent[10] to incoherent[11] neutron-scattering cross sections is high ($\sigma_{\text{coh}}/\sigma_{\text{inc}} \geq 1800$), liquid rubidium is an excellent choice for experimental study.

The experiments were performed at the thermal-neutron time-of-flight spectrometer[12] at the Argonne National Laboratory CP-5 reactor. The incident energy was 33.0 meV, with an overall energy resolution of approximately 1.0 meV (full width at half-maximum). As has been discussed in Ref. 2, large incident energies are required in order to make measurements at small momentum transfers over a useful range of energy transfers. Using the computer code MSCAT,[13] the sample container was designed to maximize the ratio of first scattering to multiple scattering, while maintaining a large first-scattering probability. The final sample container consisted of 32 slabs of liquid, each 2.54 cm wide by 0.22 cm high by 10.16 cm long, separated from each other by horizontal boron-nitride spacers 0.10 cm thick. Even with this large a sample (182 cm^3 of Rb) 32 days of running time were required. The alumi-

num walls of the sample container were 0.012 cm thick. The sample was heated to 320 K in the evacuated flight path. The temperature was maintained to within ± 1 K over the sample as measured by two iron-Constantan thermocouples. Measurements were made at 14 scattering angles between 2.4° and 14.4°.

Separate runs were made with the empty sample container and with a V slab (for absolute normalization of each detector). Corrections were made to the data for empty-container scattering, for sample self-shielding, and for the effective volume of sample seen by the detectors. The data were reduced to the symmetrized scattering function $\tilde{S}(\kappa, \omega)$ of van Hove[14] using the programs detailed by Copley, Price, and Rowe.[15] No correction was made for energy resolution. At this stage, the data were normalized absolutely except for one factor which could not be computed reliably—the vertical collimation of the incident beam introduced by the shape of the sample container. Estimates of this effect suggested that it should reduce the intensity by a factor of the order of 2. Since a reliable multiple-scattering correction can only be made to properly normalized data, the following procedure was adopted: First, the multiple scattering was calculated by MSCAT,[15] using the results of Rahman[7,9] as an input kernel. Then, the data were multiplied by a constant α and the multiple scattering was subtracted. The results were interpolated to 15 values of κ between 0.3 and 1.0 Å^{-1}, so that the second moment $\langle\omega^2\rangle = \int\omega^2\tilde{S}(\kappa, \omega)\,d\omega$ could be calculated. The exact classical value for this moment is $\langle\omega^2\rangle_E = \kappa^2 kT/M$, and the constant α was chosen (by trial and error) so that the average of the ratio $\langle\omega^2\rangle/\langle\omega^2\rangle_E$ for all 15 values of κ was equal to unity. The final value of α found from this procedure was 2.0.

Using this normalization, the structure factor $S(\kappa)$, which is the zeroth moment of $S(\kappa, \omega)$, was computed for each κ value and the extrapolation of this result to $\kappa = 0$ was compared to the known compressibility limit $S(\kappa \to 0) = 0.021$. This comparison showed that the experimental values were too high as $\kappa \to 0$. Comparison of the present result at $\kappa = 1.0$ Å^{-1} to measurements[8] taken with a different configuration showed clearly that the extra intensity seen in the present result was due to excess scattering at zero energy transfer ($\hbar\omega = 0$). This observation was consistent with the fact that the width of the central peak was almost completely independent of κ and was equal to the resolution width of the spectrometer. In an attempt to correct for this effect, we have subtracted an elastic component having the shape of the measured resolution function. The magnitude of this component was chosen (by trial and error) to yield a result in reasonable agreement with the earlier result at $\kappa = 1.0$ and with the $\kappa = 0$ limit of $S(\kappa)$ at $\kappa = 0.3$. Complete agreement could not be obtained without introducing clearly unreasonable shapes of $\tilde{S}(\kappa, \omega)$ near $\omega = 0$ at small values of κ. The final correction to $S(\kappa)$ ranged linearly from -0.022 to -0.018 for $\kappa = 0.3$ and 1.0 Å^{-1}, respectively. The origin of this extra scattering is not understood, and the final results obtained for $\tilde{S}(\kappa, \omega)$ near $\omega = 0$ must be considered suspect. However, this procedure did not affect the scattering at larger values of ω, and we believe that the results obtained for $\tilde{S}(\kappa, \omega)$ for $\omega > 1.5$ psec^{-1} are reliable.

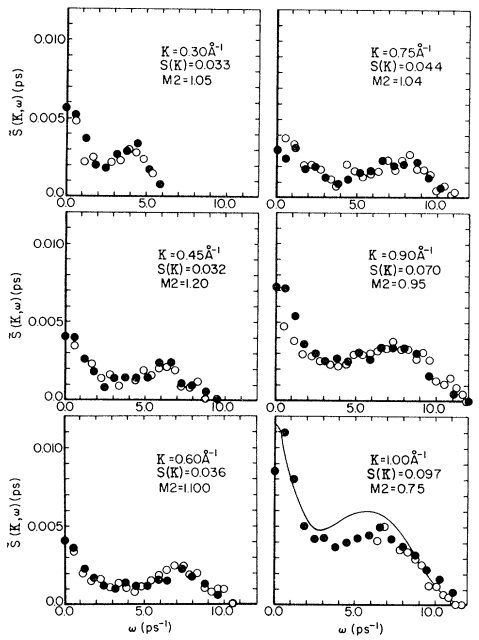

FIG. 1. Representative results for the symmetrized scattering $\tilde{S}(\kappa, \omega)$ of liquid rubidium at constant values of κ. Open (closed) circles represent neutron energy loss (gain). The statistical errors are smaller than the points; estimates of systematic errors are given by the scatter of the points. Note the large scatter near $\omega = 0$ which arises from a correction described in the text. Solid line for $\kappa = 1.0$ Å^{-1}, results obtained from another experiment (Ref. 8). Also shown, the zeroth moment $S(\kappa)$ and the ratio of the measured to the exact second moment $M2$ for each κ.

These results are shown for selected values of κ in Fig. 1. The large scatter in the points near $\omega = 0$ for several of the plots reflects both the in-

adequacy of the corrections described above and systematic errors in the interpolation procedure. For $\kappa = 1.0$ Å^{-1}, the solid line represents the smoothed result obtained from the earlier experiment using a different sample container. It is clear from this figure that the scattering function $\tilde{S}(\kappa, \omega)$ consists of a three-peak structure reminiscent of the known behavior in the hydrodynamic regime. (Note that energy loss and energy gain are both plotted on the positive-ω side of the graph.) This shape of $\tilde{S}(\kappa, \omega)$ implies the existence of propagating collective modes in liquid Rb for values of κ up to 1.0 Å^{-1} (the first peak in the structure factor occurs at $\kappa = 1.53$ Å^{-1}). The position of the peak in $\tilde{S}(\kappa, \omega)$ for finite ω has been extracted as a function of κ, with the result shown in Fig. 2. Other experimental data[8] show that *no* such excitations exist in the liquid for $\kappa > 1.25$ Å^{-1}, although as discussed in Ref. 8, there is evidence for the existence of two characteristic relaxation times in the density fluctuation spectrum near $\kappa = 2.0$ Å^{-1}. The present results are in good agreement with molecular-dynamics calculations discussed in Ref. 7.

We stress that the "dispersion curve" presented in Fig. 2 is derived from data *at constant* κ and is not to be confused with "dispersion curves" derived from time-of-flight spectra or from constant-energy plots. This point is discussed in detail in Refs. 4 and 8. The small-κ dispersion relation implied by the measured velocity-of-sound techniques[16] (1.37×10^5 cm sec^{-1}) is shown in Fig. 2 as a solid line. The apparent systematic discrepancy between the neutron and ultrasonic results may be related to the distinction between first sound and zero sound as discussed by Egelstaff.[17] However, the large errors in the neutron results which are directly related to the width of the observed peaks preclude definitive statements in this regard.

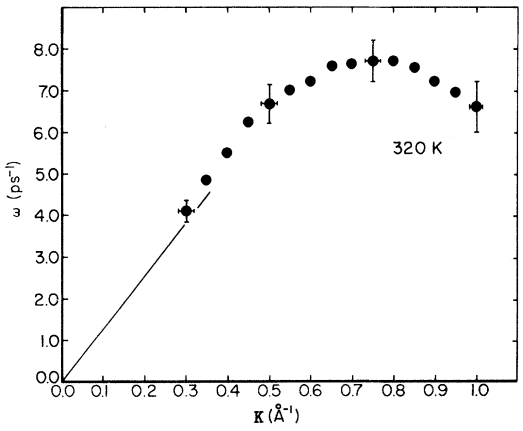

FIG. 2. "Dispersion curve" for liquid rubidium derived from the measured $\tilde{S}(\kappa, \omega)$. Error estimates reflect the width of the observed peaks and the resolution in κ. Solid line, derived from the measured sound velocity (Ref. 16).

The earlier results on liquid[1] H_2 and liquid[2] Pb contained more than one peak in $S(\kappa, \omega)$ at finite ω. The high-frequency peak was interpreted as a longitudinal mode, while the low-frequency peak was interpreted as a transverse mode by analogy with the known solid dispersion relations. In the case of H_2, these low-frequency peaks were seen only for $\kappa > \kappa_0/2$, in accord with polycrystalline results where transverse modes are observed only for κ larger than the boundaries of the first Brillouin zone. However, in Pb the low-energy peak was seen for values of $\kappa < \kappa_0/2$. In the present study, and in the molecular-dynamics results presented in the Letter following this one,[7] *no* evidence was found for two peaks at finite frequency for any κ. In fact, even the single longitudinal peak was observable only for $\kappa < 0.7\kappa_0$, so that direct comparison with the observations for H_2 is impossible.

Carneiro, Nielson, and McTague[1] suggested that their observation of propagating modes in H_2 might be explained either by the quantum nature of the liquid or by the fact that the modes in hydrogen were not thermally populated at the temperature of measurement. The present results, and the earlier results for Pb,[2] show that neither of these effects is necessary for the existence of short-wavelength propagating collective modes. It is clear that further work will be required to establish those factors that determine the existence of such modes in simple liquids. Since both neutron-scattering and molecular-dynamics studies of these excitations are expensive and time consuming, we feel that continued close interaction between the two techniques is essential to progress in this area.

We thank R. Kleb, R. Stefiuk, and G. Ostrowski for valuable technical assistance. Stimulating discussions with A. Rahman, D. L. Price, and J. P. McTague are gratefully acknowledged.

*Work supported in part by the U. S. Atomic Energy Commission.

†Present address: Institut Laue-Langevin, B.P. 156, 38042 Grenoble Cedex, France.

[1]K. Carneiro, M. Nielsen, and J. P. McTague, Phys. Rev. Lett. 30, 481 (1973).

[2]B. Dorner, T. Plesser, and H. Stiller, Discuss.

Faraday Soc. 43, 160 (1967).
[3]D. Levesque, L. Verlet, and J. Kürkijarvi, Phys. Rev. A 7, 1690 (1973).
[4]K. Sköld, J. M. Rowe, P. D. Randolph, and G. E. Ostrowski, Phys. Rev. A 6, 1107 (1972). A limited experiment for $Q \approx 0.4$ Å^{-1} showed no evidence of well-defined excitations (K. Sköld and J. M. Rowe, unpublished).
[5]J. R. D. Copley and B. N. Brockhouse, Can. J. Phys. 51, 657 (1973).
[6]W. M. Shyu, K. S. Singwi, and M. P. Tosi, Argonne National Laboratory Report No. ANL-7761, 1970 (unpublished).
[7]A. Rahman, following Letter [Phys. Rev. Lett. 32, 52 (1974)].
[8]J. R. D. Copley and J. M. Rowe, to be published.
[9]A. Rahman, to be published.
[10]J. R. D. Copley, Acta Crystallogr., Sect. A 26, 376 (1970); F. F. Y. Wang and D. E. Cox, Acta Crystallogr., Sect. A 26, 377 (1970); P. Meriel, C. R. Acad. Sci., Ser. B 270, 560 (1970).
[11]S. J. Cocking, Advan. Phys. 16, 189 (1967).
[12]R. Kleb, G. E. Owstrowski, D. L. Price, and J. M. Rowe, Nucl. Instrum. Methods 107, 501 (1973).
[13]J. R. D. Copley, Comput. Phys. Commun., to be published. Note that the modification to slab geometry is described in a separate paper in this journal.
[14]L. van Hove, Phys. Rev. 95, 249 (1954).
[15]J. R. D. Copley, D. L. Price, and J. M. Rowe, Nucl. Instrum. Methods 107, 501 (1973).
[16]J. Jarzynski, J. R. Smirnow, and C. M. Davis, Jr., Phys. Rev. 178, 288 (1969).
[17]P. A. Egelstaff, *An Introduction to the Liquid State* (Academic, New York, 1967).

Propagation of Density Fluctuations in Liquid Rubidium: A Molecular-Dynamics Study*

Aneesur Rahman
Argonne National Laboratory, Argonne, Illinois 60439
(Received 12 November 1973)

Liquid rubidium has been simulated on a computer. Density fluctuations in the computer liquid are essentially identical with those in the real liquid as measured by neutron inelastic-scattering experiments. Hence the interaction potential used for the simulation should be considered reliable for the study of liquid rubidium. Density waves are found to propagate even at wavelengths as small as the nearest neighbor distance in the liquid, a property not found in liquid argon.

In a liquid-argon-like system, molecular-dynamics (MD) calculations indicate that Brillouin side peaks in the spectrum of density fluctuations disappear already at a wavelength λ of about 8 times the first-neighbor distance in the liquid.[1] For shorter λ the fluctuations are over-damped oscillations with a single, λ-dependent decay time.[2]

MD calculations in a liquid-rubidium-like system are reported here. They show clear Brillouin peaks for λ almost as short as the first-neighbor distance; the λ dependence of the width and intensity of these peaks shows features of interest to the theory of density fluctuations in monatomic liquids.

The interparticle potential for liquid rubidium, obtained by Price and co-workers,[3] has an oscillatory decay to zero and, in this respect, is very different from a Lennard-Jones (6-12) potential which has been found suitable for the study of liquid-argon-like systems. Since the spatial and temporal behavior of density fluctuations, apart from its dependence on temperature and density, is determined by the nature of the interparticle interaction, a MD calculation with a potential qualitatively different from the Lennard-Jones

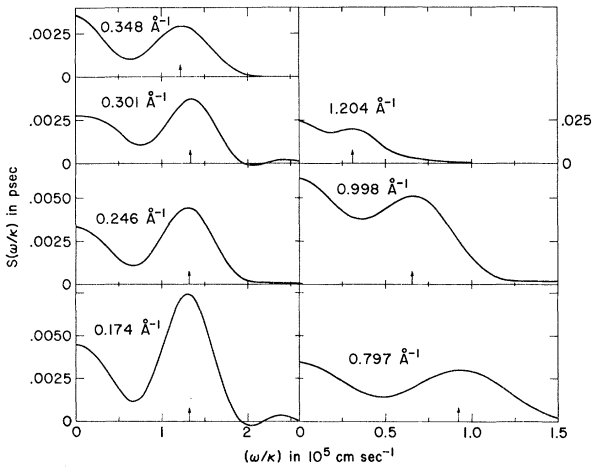

FIG. 1. $S(\kappa,\omega)$ for a few selected values of κ. Note that the abscissa is a velocity. The velocity of sound is seen to be 1.32×10^5 cm sec^{-1}. Note also that the vertical scale for $\kappa = 1.204$ Å^{-1} is different.