# Short-Wavelength Sound Modes in Liquid Argon

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Neutron scattering experiments on liquid argon show evidence for the existence of well defined though strongly damped sound waves with wavelengths comparable to the size of the atoms. The dynamic structure factor can be described in terms of Rayleigh and Brillouin lines. The sound oscillation frequency shows an anomaly consistent with the mode-coupling theory. The shape of the dispersion curve resembles that of solid argon except for a wavelength region where the oscillation frequency vanished as predicted by kinetic theory.

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The behavior of fluctuations in a monatomic liquid in equilibrium follows from the linearized hydrodynamic equations as long as the wavelength $\lambda$ of a fluctuation is much larger than the diameter $\sigma$ of the atoms. For light scattering experiments, where $\lambda \gg \sigma$, the measured coherent dynamic structure factor $S(k,\omega)$, with $k=2\pi/\lambda$ the wave number and $\omega$ the frequency, is represented by the Landau-Placzek formula. This relation comprises the effect of hydrodynamic modes in a fluid and describes $S(k,\omega)$ in terms of Rayleigh and Brillouin lines due to the heat and sound modes, respectively. For neutron scattering experiments $\lambda$ is of the order of $\sigma$. In this region the validity of the concept of collective particle motions, which is basic to hydrodynamics, is still an open question. For rubidium[1] and lead[2] one finds distinct side peaks in $S(k,\omega)$ at the positions $\omega \simeq \pm ck$ with $c$ the adiabatic speed of sound. These are therefore identified as Brillouin lines, although the Landau-Placzek formula does not hold for $\lambda \sim \sigma$. Such side peaks are absent in liquid argon at comparable $\lambda$.[3] It has been discussed previously that these observations can be understood in principle if one uses the concept of extended hydrodynamic (collective) modes as introduced by kinetic theory.[4] In particular it was argued that for liquid Rb and Ar the central line in $S(k,\omega)$ is a Rayleigh line due to an extended heat mode, down to $\lambda \simeq \frac{1}{2}\sigma$. Our present neutron scattering experiment on liquid argon shows no distinct side peaks in $S(k,\omega)$. However, using the concept of collective modes, we find the first evidence for the existence of extended sound modes with $\lambda$ down to $\frac{1}{2}\sigma$.

We consider $S(k,\omega)=(1/2\pi)\int dt\, e^{i\omega t}F(k,t)$ and the intermediate scattering function $F(k,t) =\sum_{j,l}^{N} N^{-1}\langle \exp\{i\vec{k}\cdot[\vec{r}_j(t)-\vec{r}_l(0)]\}\rangle$, where the brackets denote an equilibrium ensemble average at temperature $T$ and density $n=N/V$ with $N$ the number of particles and $V$ the volume of the system, and $\vec{r}_j(t)$ is the position of particle $j$ at time $t$. According to kinetic theory[4] $S(k,\omega)$ can be decomposed into an infinite set of Lorentzians,

$$S(k,\omega)=\frac{1}{\pi}\sum_{j=-\infty}^{\infty}\mathrm{Re}\frac{A_j(k)}{i\omega+z_j(k)}. \tag{1}$$

The parameters $A_j$ and $z_j$ either are real or appear in complex-conjugate pairs $(j,-j)$, i.e., $z_{-j}=z_j{}^*$, with $A_{-j}=A_j{}^*$, and obey sum rules which follow from the short-time behavior of $F(k,t)$,

$$\sum_{j=-\infty}^{\infty} A_j(k)[z_j(k)]^n = R_n(k), \tag{2}$$

where $R_0(k)=S(k)=F(k,0)$ is the static structure factor, $R_1(k)=0$, and $R_2(k)=-k_B Tk^2/m$ with $k_B$ Boltzmann's constant and $m$ the mass of a particle. In the hydrodynamic limit $(k\to 0)$ all amplitudes $A_j(k)$ in Eq. (1) vanish except for $j=0$, the heat mode contribution, for which $A_0(k)$ and $z_0(k)$ are real and for $j=\pm1$, the contributions of the two sound modes, for which $z_{-1}(k)=z_1{}^*(k)$ and $A_{-1}(k)=A_1{}^*(k)$. Thus for $k\to 0$,

$$S(k,\omega)=\frac{1}{\pi}\sum_{j=-1}^{1}\mathrm{Re}\frac{A_j(k)}{i\omega+z_j(k)} \tag{3a}$$

$$=\frac{A_0}{\pi}\frac{z_0}{\omega^2+z_0{}^2}+\frac{A_s}{\pi}\frac{z_s+(\omega+\omega_s)\tan\varphi}{(\omega+\omega_s)^2+z_s{}^2} +\frac{A_s}{\pi}\frac{z_s-(\omega-\omega_s)\tan\varphi}{(\omega-\omega_s)^2+z_s{}^2}, \tag{3b}$$

$$F(k,t)=A_0\exp(-z_0|t|) + 2A_s\exp(-z_s|t|)\frac{\cos(\omega_s|t|-\varphi)}{\cos\varphi}, \tag{4}$$

where $A_s(k)=\mathrm{Re}A_{\pm1}(k)$ and $A_0(k)$ are the areas of one Brillouin and the Rayleigh line, respectively, $z_s(k)=\mathrm{Re}z_{\pm1}(k)$ and $z_0(k)$ are the corresponding linewidths, $\omega_s(k)=\mathrm{Im}\,z_1(k)$ is the sound oscillation frequency, and $\varphi(k)=\tan^{-1}[\mathrm{Im}\,A_1(k)/\mathrm{Re}A_1(k)]$

 

determines the asymmetry of the Brillouin lines.

For small $k$,

$$\begin{aligned} &A_0(k) = [(\gamma-1)/\gamma]\, S(0) + O(k^{3/2}),\\ &A_{\pm 1}(k) = [\,S_0/2\gamma][\,1 \pm i b_s k + O(k^{3/2})],\\ &z_0(k) = \alpha k^2 - a_h k^{5/2} + O(k^{11/4}),\\ &z_{\pm 1}(k) = \pm i c k + \Gamma k^2 + (\pm i - 1) a_s k^{5/2} + O(k^{11/4}). \end{aligned} \tag{5}$$

with $\gamma = c_p/c_v$ the ratio of specific heats, $\alpha$ the thermal diffusivity, $\Gamma$ the sound wave damping factor, and $b_s = [(\gamma-1)\alpha + \Gamma]/c$. The terms containing integer powers of $k$ follow from the hydrodynamic equations.[5] The anomalous terms, containing noninteger powers of $k$, follow from the mode-coupling theory.[6] Explicit expressions for $a_h$ and $a_s$ are given by Ernst and Dorfman.[6] According to kinetic theory[4] $S(k, \omega)$ for $0 \leq k \lesssim \sigma^{-1}$ is described by the Landau-Placzek formula, i.e., by Eq. (3a) with $A_j$ and $z_j$ given by the hydrodynamic terms in Eq. (5). Although for increasing values of $k$ an increasing number of terms on the right-hand side of Eq. (1) is needed to represent $S(k, \omega)$, the collective modes $j = 0, \pm 1$ dominate $S(k, \omega)$ up to $k \approx l^{-1}$, with $l$ the mean free path between collisions. Thus for $\sigma^{-1} \lesssim k \lesssim l^{-1}$ Eq. (3a) approximately applies. However, the parameters $A_j$ and $z_j$ do not follow Eq. (5). In particular, it is possible that, around $k\sigma = 2\pi$, $A_{\pm 1}(k)$ and $z_{\pm 1}(k)$ are real so that Eq. (3a) represents three different central Lorentz lines.[4]

Our experiment was performed with the thermal neutron time-of-flight spectrometer IN-4 at the Institut Laue-Langevin in Grenoble. The incident neutron energy was 12.6 meV corresponding to a wavelength of 2.54 Å. Spectra were measured for 30 h at 59 scattering angles between 9° and 106°. The sample container has been described by Verkerk and Pruisken.[7] The sample consisted of liquid $^{36}$Ar at a temperature of $T = 120 \pm 0.5$ K and a pressure of $p = 20 \pm 1$ bars corresponding to a density[8] $n = 17.6 \pm 0.07$ nm$^{-3}$. Fully corrected values for $S(k, \omega)$ were obtained from the time-of-flight data using the procedures described by Copley, Price, and Rowe[9] and Verkerk[10] with modifications to be described by van Well *et al.*[11] The final results cover the range 0.42 Å$^{-1} \leq k \leq 3.78$ Å$^{-1}$ corresponding to $1.4\sigma^{-1} \leq k \leq 1.25 l^{-1}$ using $\sigma = 3.43$ Å[12] and $l = 0.33$ Å.[4] Thus $k$ is in the region where collective modes are expected to dominate.

In order to determine how well $S(k, \omega)$ is described by three Lorentz lines and how far these contributions satisfy the sum rules, we applied three fit procedures. (1) For each value of $k$, $A_j$ and $z_j$ in Eq. (3a) are adjusted in a least-squares fitting procedure. We require that $A_0$ and $z_0$ are real and that either $A_{-1} = A_{+1}^*$ and $z_{-1} = z_{+1}^*$ or $A_{\pm 1}$ and $z_{\pm 1}$ are real, whichever fits best. Either case involves six real parameters. (2) The Lorentz lines in Eq. (3a) are fitted with the additional constraint of Eq. (2) for $n = 1$. (3) We require that Eq. (2) is also satisfied for $n = 2$. For each $k$ and each procedure 1, 2, and 3 we determine the mean square relative deviation $\delta(k) = (M-p)^{-1}\sum_{l=1}^{M} \Delta_l^2/s_l^2$, where $M$ is the number of discrete data points at a particular $k$ value, $p$ the number of free parameters, $\Delta_l$ the deviation of $S(k, \omega)$ from the best-fitted Lorentzians, and $s_l$ the estimate of the experimental standard deviation. $\delta(k)$ is a measure for the accuracy of the fit. As a result of the correction procedures applied to the experimental data, the errors in $S(k, \omega)$ are correlated and not distributed normally. Therefore properties of the $\chi^2$ distribution are not applicable in this case. In particular the expectation value of $\delta(k)$ need not be equal to 1. For the present results we consider a fit acceptable when $\delta(k) \leq 1$. We find that $\delta(k) \leq 1$ for all $k$ in case 1, for 95% of the $k$ values in case 2, and for 80% of all $k$ values in case 3. We conclude that $S(k, \omega)$ is well described by three Lorentz lines. There was no indication for the need to use more than three lines. We consider the results for the six parameters of the three lines in the cases 1, 2, and 3 as equally likely and attribute differences to experimental errors.

We display the results in the following way (cf. Fig. 1). For each parameter we draw error bars large enough to include the values obtained in all three cases. The data points in the figure represent the center of each line. The results reveal the following features. (1) We find for all $k$ that, within the experimental error, $\sum_j A_j(k) = S(k)$, where $S(k)$ is determined directly from $S(k, \omega)$.[12] The values for $S(k)$ are consistent with data from computer simulations[13] and from x-ray scattering experiments[14] as will be discussed in Ref. 12. (2) In Fig. 1 we also display the hydrodynamic predictions, using[8] $\gamma = 2.82$, $S(0) = 0.208$, $c = 6.13$ Å/ps, $\alpha = 5.8$ Å$^2$/ps, and $\Gamma = 19$ Å$^2$/ps. All parameters show a tendency towards their corresponding hydrodynamic values. This and the fact that at least three sum rules are satisfied lead us to an interpretation of the three Lorentz lines in terms of collective modes. (3) The shape of $\omega_s(k)$ is remarkably similar to that found in solid argon.[15] (4) We find a region 1.7 Å$^{-1} \lesssim k \lesssim 2.1$ Å$^{-1}$

where three central Lorentz lines fit the experiments best, implying $\omega_s(k)=0$ and $\varphi(k)$ is a multiple of $\pi$ (cf. Fig. 1). Thus our experiments confirm the existence of a gap around $k\sigma=2\pi$ in the dispersion curve.[4] (5) $\omega_s(k)$ is close to its hydrodynamic value $ck$ up to about $k\sigma\simeq\pi$, similar to the case of liquid Rb.[1] There is, however, a significant tendency of $\omega_s(k)$ to be larger than $ck$. This effect has also been observed in liquid helium and is known as anomalous dispersion.[16] In Fig. 1 we show the nonanalytic dispersion relation $\omega_s(k)=ck+a_s k^{5/2}$ [cf. Eq. (5)] with $a_s=6.32$ $\mathrm{\AA}^{5/2}/\mathrm{ps}$ determined from Refs. 6 and 8. The global agreement for $k\leqslant 0.8$ $\mathrm{\AA}^{-1}$ might indicate that anomalous dispersion is caused by the coupling of hydrodynamic modes. (6) The area of one Brillouin line, $A_s(k)$, is negative for $k\gtrsim 1$ $\mathrm{\AA}^{-1}$. This peculiar phenomenon agrees with a result in Ref. 4 namely that just beyond the hydrodynamic regime the area of the Rayleigh line is larger than the total area. (7) We find that our values for $S(k,\omega)$ are fitted badly by a relation similar to Eq. (3b) with $\varphi=0$, corresponding to *symmetric* Brillouin lines. For example, for $k\leqslant 1.3$ $\mathrm{\AA}^{-1}$ we find that $\delta(k)\geqslant 5$ if $\varphi=0$. Thus in the neutron scattering regime *asymmetric* Brillouin lines are essential for the description of $S(k,\omega)$.

We are led to two conclusions which disagree with assessments by Copley and Lovesey (cf. p. 507 of Ref. 17). The absence of distinct peaks in $S(k,\omega)$ does not imply the absence of sound modes. We find that the positions of the two maxima in $\omega^2 S(k,\omega)$ are close to $\pm\omega_s(k)$ and thus are related to the propagation of sound. This is a direct consequence of Eq. (3a) and the results shown in Fig. 1.

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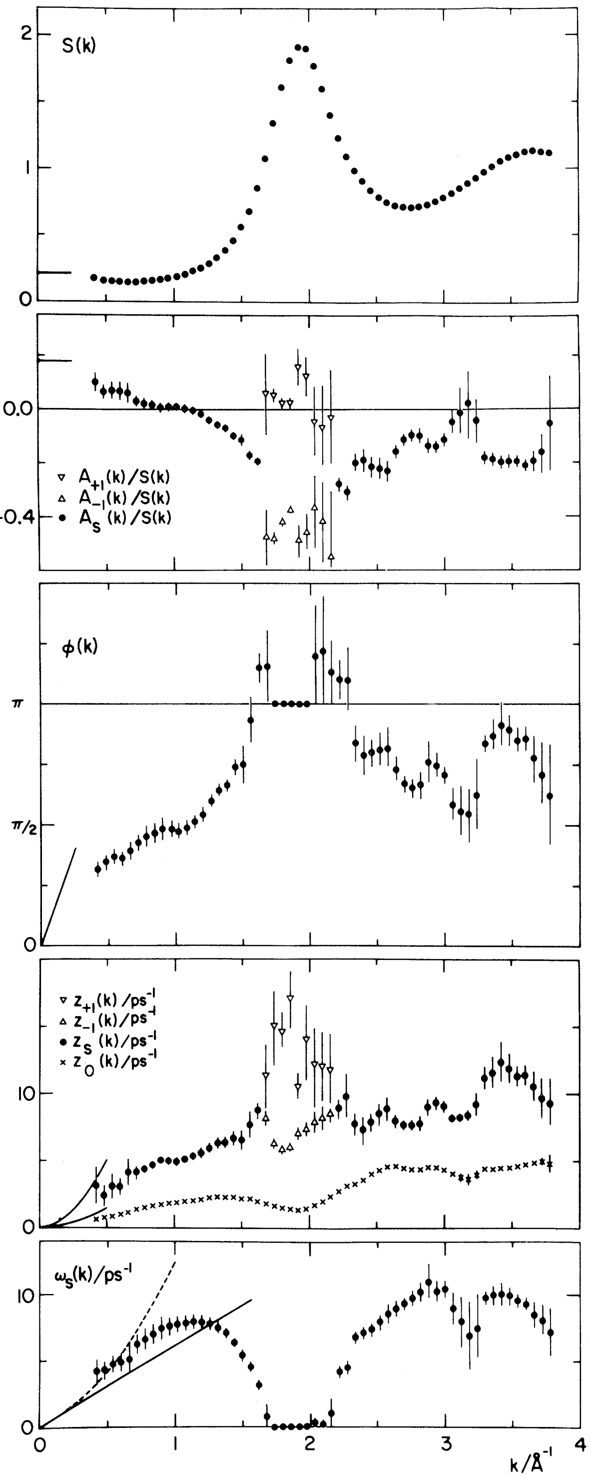


FIG. 1. The six parameters of the three Lorentz lines which describe the experimentally obtained dynamic structure factor $S(k,\omega)$ for liquid argon at $T=120$ K and $p=20$ bars, as functions of wave number $k$ [cf. Eqs. (3)]. $A_{\pm1}(k)$ and $z_{\pm1}(k)$ are the parameters of the two Brillouin lines. For $k\lesssim 1.7$ $\mathrm{\AA}^{-1}$ and $k\gtrsim 2.1$ $\mathrm{\AA}^{-1}$, $A_s(k)=\mathrm{Re}A_{\pm1}(k)$ is the area and $z_s(k)=\mathrm{Re}z_{\pm1}(k)$ the half-width of each line, $\pm\omega_s(k)=\mathrm{Im}z_{\pm1}(k)$ are the two positions with $\omega_s(k)$ the sound oscillation frequency, and $\pm\tan\varphi(k)=\mathrm{Im}A_{\pm1}(k)/A_s(k)$ where $\varphi(k)$ determines the asymmetry of the lines. For 1.7 $\mathrm{\AA}^{-1}\lesssim k\lesssim 2.1$ $\mathrm{\AA}^{-1}$, $A_{\pm1}(k)$ and $z_{\pm1}(k)$ are real and the Brillouin lines are two central lines with different areas $A_{\pm1}(k)$ and different half-widths $z_{\pm1}(k)$. For all $k$, $A_0(k)$ is the area and $z_0(k)$ the half-width of the (central) Rayleigh line, and the static structure factor is $S(k)=A_0(k)+A_{+1}(k)+A_{-1}(k)$. Note that, although the area of two of the three lines might be negative, $S(k)>0$ for all $k$. The full lines and the dashed curve represent the predictions from hydrodynamics and the mode-coupling theory, respectively.

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