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Brillouin Scattering in Simple Liquids: Argon and Neon

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Recent theoretical work has suggested that at high frequencies, there should be significant departure from classical hydrodynamic behavior in simple fluids. In particular, the frequency dependence of transport coefficients is no longer negligible and may introduce observable effects into the propagation of high-frequency sound. We have measured the sound velocity of high-frequency phonons (1–3 GHz) in liquid argon and liquid neon along their vapor-pressure equilibrium curves using the Brillouin scattering technique. The Brillouin spectra were excited with a single-mode argon-ion laser operating at 5145 or 4765 Å and were analyzed and detected with a Fabry-Perot interferometer and standard photoelectric techniques. Hypersonic (~3 GHz) velocities observed in argon decrease linearly from 850 m/sec at 85 °K to 742 m/sec at 100 °K and uniformly exhibit a small departure from low-frequency (1 MHz) data obtained under the same thermodynamic conditions. This effect is in qualitative agreement with theoretical-model predictions of a negative velocity dispersion at high frequencies. Our measurements of the sound velocity in liquid neon are the first in this material by any technique, and hence cannot be compared with ultrasonic values. The hypersonic velocity in neon decreases not quite linearly from 620 m/sec at 24.9 °K to 508 m/sec at 32 °K. When compared with results in other noble-gas liquids through corresponding-states arguments, these data suggest the existence of measurable quantum effects in the hypersonic velocity of liquid neon. In addition, an interesting change in slope of the velocity-versus-temperature curve (of 17%) is observed at 28 °K.

I. INTRODUCTION

Although the technique of Brillouin scattering has been widely used to study very-high-frequency sound waves in liquids, scant information of this type is available for simple monatomic liquids.[1] Previous light scattering experiments on noble liquids have been concerned with sound-velocity behavior near temperatures of phase transition,[1] rather than with possible effects due to frequency dependence of the liquid's transport coefficients. Such information is difficult to obtain and yet is very important for further development of theories of the dynamics of the liquid state. Some recent theoretical work has indicated the possibility of nonclassical behavior for very-high-frequency sound waves (i.e., departure from the predictions of the Navier-Stokes equations). Gillis and Puff[2] have shown that for $\omega > \omega^*$ (where ω^* is some critical frequency in the liquid) sound waves propagate at some velocity intermediate between the adiabatic and the isothermal velocities, and that

the sound absorption coefficient becomes frequency-independent in contrast to the quadratic frequency dependence expected classically. Furthermore, Frisch,[3] and Berne, Boon, and Rice[4] have shown that under certain very general assumptions the linear response of a classical fluid becomes wholly nondissipative in the very-high-frequency limit. Thus, all transport coefficients (which, like viscosity, express dissipation at low frequencies) become purely imaginary as $\omega \to \infty$. Consequently, there should exist at very high frequencies certain undamped excitations in the classical fluid such as shear waves, self-diffusion waves, and temperature waves (second-soundlike waves). It is quite well established that it is around frequencies of the order of the reciprocal collision time, i.e., $\omega \sim \tau_C^{-1} \sim 10^{12}$–$10^{13}$ Hz for noble-dense fluids (like liquid argon), that dispersion phenomena should be most important. On the other hand, it is very difficult to predict *a priori* the value of the critical frequency, above which these new effects are expected to be easily observable. Unfortunately, it is presently not possible to perform Brillouin experiments in the characteristic frequency range $\omega_C = \tau_C^{-1}$; it is, however, of great interest to investigate the sound propagation in simple liquids at as high a frequency as possible.

The one critical frequency emerging from classical hydrodynamic theory is the so-called Lucas relaxation frequency[5]

$$\omega_L = \rho \frac{v_S^2}{(\frac{4}{3}\eta_S + \eta_B)} \sim 10^{12}\,\mathrm{sec}^{-1},$$

where ρ is the density, v_S is the sound velocity, and η_S and η_B are the shear and bulk viscosities, respectively. If one assumes such a value for ω^*, then, of course, $\omega^* \simeq \omega_C$, and the above-mentioned, striking effects should not appear in the frequency range accessible to Brillouin scattering. However, even for lower phonon frequencies, one does expect some nonclassical behavior due to the onset of frequency dependence for the transport and thermodynamic coefficients which, at very high frequencies, results in the simple purely nondissipative behavior. If ω^* were in the GHz range, there would be a domain $\omega^* \leq \omega \leq \omega_C$, where this applies. Berne, Boon, and Rice[4] have formally evaluated limiting forms of the frequency dependence of such transport coefficients; but to evaluate explicitly the behavior for low- and intermediate-frequencies one must resort to a model calculation.[6] All these points argue for the desirability of measurements in the 10^9–10^{10} Hz frequency range.

Naturally, the monatomic liquids are most appropriate for studying such effects, since their acoustic properties should be unencumbered by relaxation effects due to internal molecular degrees of freedom. Until now, however, the highest-frequency sound waves studied in simple liquids were in the MHz range. The Brillouin scattering results, reported here, extend this range by some three orders of magnitude. We have measured the temperature dependence of hypersonic velocities along the vapor-pressure equilibrium curve in liquid Ar and liquid Ne. For Ar, our results in the 2–3-GHz range can be compared to earlier 1-MHz ultrasonic experiments performed under the same thermodynamic conditions. For Ne, our Brillouin scattering results constitute the first sound-velocity measurements in this liquid by any technique.

Section II describes the experimental setup and techniques, including the laser source, scattering geometry, sample environment and temperature control, and detection and frequency analysis of the scattered light. Section III provides a summary of our results on the temperature and pressure dependence of hypersonic velocities in liquid Ar and Ne. In Sec. IV, our results are discussed in terms of recent theoretical speculations. The upper limit on velocity dispersion in Ar, provided by these experiments, allows us to set a lower limit for the critical frequency. For Ne, this is not yet possible due to the absence of any ultrasonic data on this liquid. Some speculations on the size of quantum effects in the hypersonic velocity are included, however, in the conclusions of Sec. V.

II. EXPERIMENTAL TECHNIQUE

To appreciate the tolerances on various experimental parameters required for Brillouin scattering in simple cryogenic fluids, a brief review of the basic equations for scattering of light by acoustic phonons is in order. The Brillouin scattering process is most simply viewed as an inelastic collision between an incident photon (of frequency ν_1 and wave vector $\vec{k}_1$) and a thermally excited acoustic phonon (ν_S, $\vec{k}_S$), in which the phonon is destroyed or excited (for anti-Stokes or Stokes scattering, respectively) and a scattered photon (ν_2, $\vec{k}_2$) is emitted. Over-all momentum and energy conservation in the process requires that

$$\nu_2 = \nu_1 \pm \nu_S, \qquad \text{and} \qquad \vec{k}_2 = \vec{k}_1 \pm \vec{k}_S, \tag{1}$$

where the + and − signs correspond to the creation or the destruction of a phonon, respectively. If, as is the case here, $\nu_S \ll \nu_1, \nu_2$, then $|k_1| \approx |k_2|$, and the wave-vector triangle becomes an isosceles triangle. One is then led directly to the basic equation for the frequency shift $\Delta\nu$ observed in Brillouin scattering,

$$\pm\Delta\nu = |\nu_1 - \nu_2| = \nu_S = 2\nu_1 v_S(\nu_S)(\eta_1/c)\sin\tfrac{1}{2}\theta, \quad (2)$$

where c is the velocity of light in vacuum, θ is the scattering angle (between the incident and scattered wave vectors), v_S is the phase velocity of the phonon with frequency ν_S, and η_1 is the medium's refractive index at the incident frequency ν_1. The experiment measures $\Delta\nu$ and θ; and, of course, ν_1 and η_1 must also be known. From these, we infer v_S. Since v_S/c for a liquid is typically of order 10^{-5}, $\Delta\nu/\nu_1$ is also of order 10^{-5} for $\theta = \frac{1}{2}\pi$. With ν_1 in the visible part of the spectrum, one has

$$\Delta\nu \sim 10^{-5} \times 10^{15}\,\text{Hz} = 10^{10}\,\text{Hz}.$$

Equation (2) implies the need for a very stable and monochromatic light source and for a spectrometer of quite high resolution. The source for the experiments described below was an argon-ion laser, forced to oscillate in a single longitudinal mode by replacing the rear mirror with a triangular prism which forms a second optical cavity. The device is similar in principle to that employed by Smith,[7] although this particular scheme was developed by Rigrod and Johnson.[8] The prism is coated so as to optimize the cavity couplings. Its over-all dimensions are such that the prism cavity modes are separated by 7.5 GHz. Thus, only one prism mode at a time lies under the gain curve of the argon laser. The laser mode which oscillates is that mode of the long cavity whose frequency corresponds to the prism cavity mode. The prism cavity is tuned and stabilized by enclosing it in an oven whose temperature is maintained to within ~0.01 °K. Using this simple scheme and with no stabilization on the long laser cavity, the laser was made to operate on a single longitudinal mode whose frequency excursions (due to fluctuations in the long cavity) were less than 100 MHz. This was deemed tolerable for these experiments, because the instrumental width of our Fabry-Perot interferometer was of order 250 MHz (for a 7.5-GHz free-spectral range).

The single-frequency laser power we obtained was typically 100 mW at 5145 Å and 50 mW at 4765 Å. The performance was essentially as obtained by Rigrod and Johnson.[8] One advantage of this single-mode prism in the argon laser is that one may change laser wavelengths by the order of 10% by simply rotating the prism. Our particular prism worked stably at either 5145 or 4765 Å, at the experimental oven temperature (34 °C). The obvious convenience of this feature for Brillouin scattering is that one can examine different frequency phonons without having to change the scattering angle.

The rest of the apparatus (depicted in Fig. 1) consists of a sample cell, described below, a flat

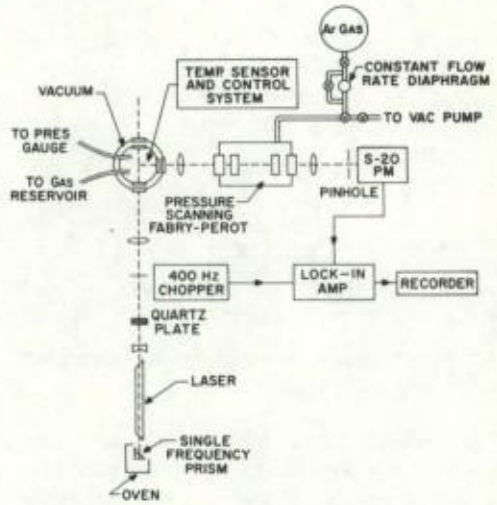

FIG. 1. Experimental arrangement for Brillouin scattering in simple liquids.

pressure-swept Fabry-Perot (FP) interferometer, and a lock-in photoelectric scheme for detecting the scattered light. The diameter of the FP plates was 2 in., flat to better than $\frac{1}{50}\lambda$, and dielectrically coated for 96% reflectivity at 5000 Å. With a 2.0-cm Invar spacer corresponding to a free spectral range of 7.5 GHz, the total observed instrumental width (laser plus FP) was ~340 MHz. Pressure sweeping of the FP was achieved by leaking Ar gas into the FP chamber through a needle valve preceded by a constant pressure-differential diaphragm to linearize the flow rate. An S-20 photomultiplier was used as a detector.

The sample gas was liquified directly into the scattering cell, which consists of a metal block with three $\frac{1}{4}$-in.-thick quartz windows in contact with the liquid. As shown in Fig. 2, the sample temperature was controlled by cold gas flowing from the reservoir Dewar through coils in the block and by cartridge heaters imbedded in the block. The vicinity of the desired temperature was reached by adjusting the gas-flow rate. For the argon experiments, the reservoir was filled with liquid nitrogen. A continuous flow of cold helium gas was used for the measurements in liquid neon. Fine-temperature control was provided by the heaters which were automatically activated by a Pt resistance sensor and a feedback bridge circuit. The sample temperature remained stable to within ±0.02 °K for periods of hours. While the cell was provided with an additional sensing resistor, the temperatures reported here were obtained from the vapor-pressure readings of the liquid vapor pressure in the cell. Calibration tests of the pressure gauge were done on each filling of the cell by a triple-point measurement.

The sample gases were obtained from Baker Chemical and were guaranteed to have <0.002%

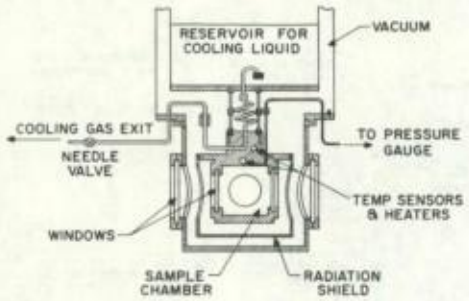

FIG. 2. Sample chamber and cryogenic equipment.

impurity concentration. The gas was admitted to a glass reservoir system in which it could be stored, and to which it could be returned at the end of each data run. This arrangement minimized chances of contamination between runs.

In placing the various components of the experiment, care was taken to ensure that the laser beam was normally incident to the cell entrance window and that the direction of observation was normal to the exit window. The scattering angle was measured by triangulation over distances of the order of 5 m. The accuracy in determining the scattering angle is ±2′; corresponding to a possible error of ±0.07% in sound-velocity determination [see Eq. (2)].

III. EXPERIMENTAL RESULTS

A. Hypersonic Velocities in Argon

A typical Brillouin spectrum for 5145 Å laser light scattered from liquid Ar is shown in Fig. 3, taken for $\theta = 90°14'$ and $T = 84.97\,°\mathrm{K}$, with $f/30$ collecting optics. The Brillouin peaks are shifted up and down by 2.8828 GHz for anti-Stokes and Stokes scattering, respectively. The central peak is due to the quasielastic or Rayleigh scattering from entropy fluctuations.[9] In a simple nonrelaxing fluid like Ar, the expected ratio of the Rayleigh to the Brillouin scattering intensity is given in first approximation by the Landau-Placzek ratio $I_R/2I_B = \gamma - 1$, where γ is the ratio of the specific heats. For liquid argon[10] at 85 °K, $\gamma = C_P/C_v = 2.19$. The ratio observed in Fig. 3 is ~1.2, indicating that stray light reflected in the cell makes a negligible contribution to the central component.

Scattering measurements were made in liquid Ar at its vapor pressure ranging between 592.5 and 2470.5 mm Hg, corresponding to temperatures between 84.97 and 100.15 °K. Because the sound velocity varies with temperature, the phonon frequencies observed for fixed scattering angle and fixed laser frequency are different for different temperatures. We were also able to observe slightly different phonon frequencies at the same temperature by changing the laser frequency. By switching from 5145 to 4765 Å excitation, phonons differing in frequency by ~8% could be observed without changing the geometry or the liquid conditions. This procedure provided a check on the reproducibility and absolute accuracy. The velocities measured with the different laser frequencies at the same temperatures should be the same when corrected for possible frequency dependence of the liquid's refractive index. In fact, within experimental error, the present data agree with our preliminary results obtained with a 6328 Å He-Ne laser.[11] While no refractive index measurements at 4765 or 5145 Å have been reported for Ar, we believe the values obtained by Abbiss *et al.*[12] at 5893 Å are quite adequately accurate for our purposes. An estimate of the dispersion in η is provided by a comparison of the 5893 Å values with the infinite wavelength value, taken as the square root of the static dielectric constant.[13] Figure 4 illustrates the comparison. Since these results differ by only about 0.1%, we expect the variation of η between 5893 Å and the laser wavelengths we employed to be entirely negligible (~10^{-4}%).

The experimental results for liquid argon are summarized in Table I.

The velocity data are uncorrected for line pulling by the larger Rayleigh line. A theoretical investigation of this effect has recently been carried out by Leidecker and LaMacchia for the case of

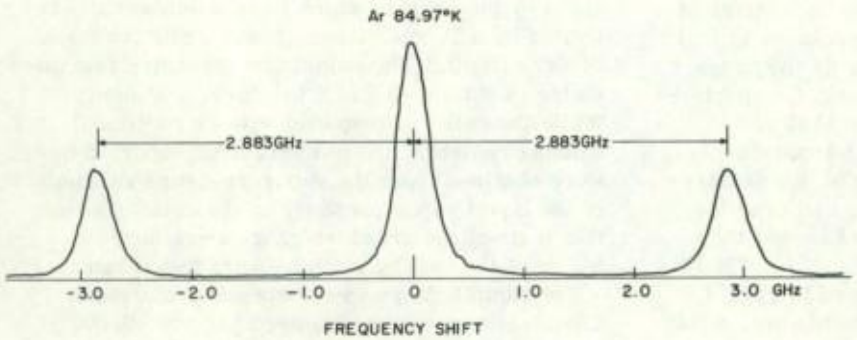

FIG. 3. Brillouin spectrum of liquid argon, $T = 84.97\,°\mathrm{K}$, $\theta = 90°14'$, laser wavelength is 5145 Å.

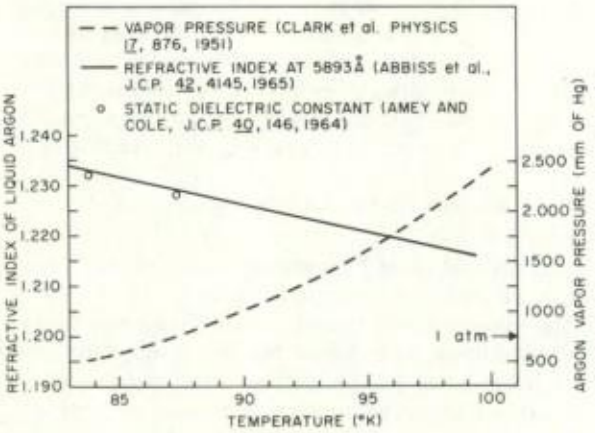

FIG. 4. Temperature dependence of the refractive index and of the vapor pressure of liquid argon along the liquid-vapor equilibrium curve. Dashed curve: $P=f(T)$, from X. Clark *et al.*, Physica 17, 876 (1951). Solid line: $\eta=f(T)$, at 5893 Å, from C. P. Abbiss *et al.*, J. Chem. Phys. 42, 4145 (1965). Circles: refractive index at infinite wavelength as calculated from the static dielectric constant, R. L. Amey and R. H. Cole, J. Chem. Phys. 40, 146 (1964).

Lorentzian lines.[14] Were the total line shapes (phonon plus laser plus FP) Lorentzian in our case, the correction would be of the order of 1% according to the evaluation by Leidecker and LaMacchia. However, as is evident from Fig. 3, the total line shapes fall off much faster than Lorentzians as one departs from the center frequency, although the falloff is not so rapid as that for a Gaussian function. An estimate of the line pulling can be made roughly as follows: Consider a Lorentzian line sitting atop a linear tail which we take to represent the tail of the central component in the vicinity of the Brillouin line. The intensity profile for this combination is

$$I(\nu) = \frac{I_B(\Delta\nu_B)^2}{(\Delta\nu_B)^2 + (\nu-\nu_B)^2} + \tfrac{1}{2}a\left(1 - \frac{(\nu-\nu_B)}{n\Delta\nu_B}\right). \tag{3}$$

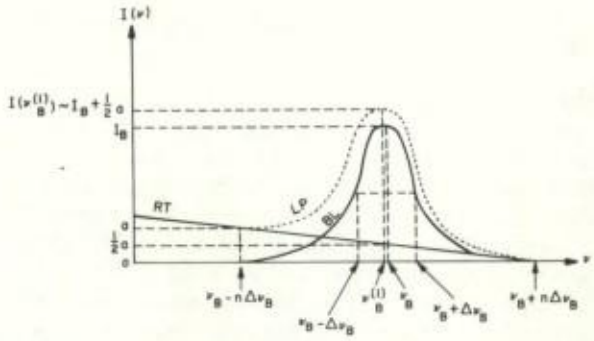

FIG. 5. Illustration of the line-pulling effect. RT is the Rayleigh component linear tail, BL is the Lorentzian-Brillouin peak, and LP is the line pulling, sum of RT and BL.

The meaning of the symbols in Eq. (3) should appear clearly from the representation of Eq. (3), as depicted in Fig. 5. $\Delta\nu_B$ is the half-width at half-maximum of the Brillouin peak; a is the difference between the intensities on the high- and low-frequency sides of ν_B at a distance $\pm n\Delta\nu_B$ away, i.e., for $\nu-\nu_B=\pm n\Delta\nu_B$. Were there no tail to the Rayleigh component, i.e., $a=0$ in Eq. (3), the maximum intensity would occur at $\nu=\nu_B$, with a peak value

$$I(\nu_B) = I_B. \tag{4}$$

In the presence of a linear Rayleigh tail ($a\neq 0$), the frequency displacement of the peak intensity is easily evaluated from Eq. (3) by a standard maximum calculation. To first order, one finds the corrected value

$$\nu_B^{(1)} = \nu_B - (a/I_B)\Delta\nu_B/4n. \tag{5}$$

A glance at Fig. 3 reveals that a/I_B is less than 10^{-2} for $n=4$, and that $2\Delta\nu_B \simeq 350$ MHz. Thus, the line pulling effect as evaluated above would yield

TABLE I. Frequency shift ($\Delta\nu$) and hypersonic velocity (v_s) in liquid argon along the vapor-pressure equilibirum curve; scattering angle: $\theta=90°14'$.

Laser λ(Å)	P(mm Hg)	T(°K)	$\eta(T)$	$\Delta\nu$(GHz)	v_s(m/sec)
5145	592.5	84.97	1.2319	2.8822	849.6
5145	1012.5	90.12	1.2264	2.7561	815.9
5145	1590.5	94.95	1.2212	2.6305	782.1
5145	2470.5	100.15	1.2154	2.4824	741.6
4765	609.5	85.22	1.2317	3.1054	847.8
4765	1007.5	90.07	1.2265	2.9763	816.0
4765	1600.5	95.00	1.2211	2.8334	780.2
4765	2467.5	100.13	1.2153	2.6824	742.2

$$\nu_B^{(1)} - \nu_B \lesssim -\frac{175}{16} \times 10^{-2}\ \text{MHz} \simeq -0.1\ \text{MHz}. \quad (6)$$

Now for the case of the present work, the above estimation, Eq. (5), certainly overestimates the pulling effect as the observed peaks decay faster than Lorentzians. One may therefore ascertain that the correction to the frequency shifts displayed in Table I is smaller than $5 \times 10^{-3}\%$, which is negligible with respect to the total experimental error. In view of the experimental conditions (pressure, temperature) and of the errors made in the measurements (scattering angle, frequency shift, ...), the absolute velocity data are considered to be accurate to ~0.5%. Although the reproducibility accuracy (indicated by comparison of 4765 with 5145 Å data) is clearly much better; it approaches 0.2%.

Of primary interest in these experiments is a comparison of the hypersonic (~2–3 GHz) velocities measured here with those at much lower frequencies [15] (~ 1 MHz), obtained by conventional ultrasonic techniques to determine the presence or absence of velocity dispersion. The comparison is illustrated in Fig. 6. One observes that the hypersonic velocities are uniformly lower by ~0.4% than the ultrasonic velocities. This difference, however, is just barely, if at all, outside the limits of experimental error and could be due, despite the precautions taken in the experiments, to some systematic effect (possibly in absolute temperature of the liquid) in either the low- or the high-frequency measurements. In addition, ultrasonic data obtained by different authors [16–18] exhibits a spread of ±0.2% about the velocity values quoted in Ref. 15. At some temperatures, our Brillouin data are only about 0.2% lower than some of the ultrasonic data. [17] However, at no temperature in the 85–100 °K range do the ultrasonic and Brillouin velocities overlap. With these experimental reservations in mind, we note that theoretically one predicts the existence of a negative velocity dispersion for liquid argon at high frequencies. A fuller discussion appears in Sec. IV.

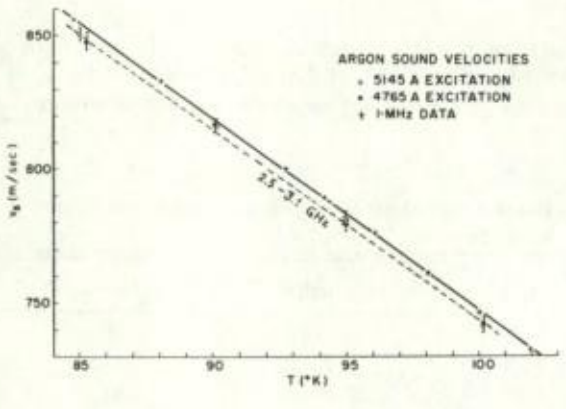

FIG. 6. Sound velocities in liquid argon, as a function of the temperature, along the vapor-pressure equilibrium curve. Comparison of the ultrasonic data at 1.2 MHz (solid line) and the hypersonic values at 2.5–3.1 GHz (dashed line).

B. Brillouin Linewidths in Argon

The absorption of hypersonic waves in Ar is less sensitive by an order of magnitude than velocity to the expected effects of the high-frequency transport coefficients discussed below. Also, our measurement of Brillouin linewidths in Ar is considerably less accurate than our measurement of the Brillouin frequencies. Nevertheless, we were able to observe broadening of the Brillouin components. An average of all the runs at 5145 Å and 85 °K indicates a total width at half-maximum of the central component of 340 MHz, while the average total width of the Brillouin peaks is 357 MHz. However, because the line shapes involved are not Lorentzian as mentioned above, the correct subtraction procedure is only approximated by the direct subtraction appropriate to Lorentzian functions. Departure from the Lorentzian shape toward the Gaussian shape results in a value of phonon broadening of the order of, but larger than, 17 MHz. Just how much larger depends on the precise line shapes involved. Because of the fluctuations in instrumental width arising from the wandering of the single-mode laser frequency, it was not deemed worthwhile to compute the phonon linewidths by a numerical analysis of line shapes. Thus, we can only say on this point that the Brillouin line broadening we observe in liquid argon is consistent with the expected absorption of 3-GHz phonons obtained by extrapolating from ultrasonic measurements [19] according to the classically predicted quadratic dependence of sound absorption upon sound frequency. The measured ultrasonic absorption [19] coefficient $\alpha/\nu^2 = 15 \times 10^{-17}\ \text{cm}^{-1}\,\text{sec}^{-2}$ predicts a Brillouin linewidth of $\Delta\nu_B = \alpha v_s/\pi$ of ~35 MHz for 3-GHz phonons at 85 °K. Because these ultrasonic measurements imply the existence of a bulk viscosity in Ar of the same order as the shear viscosity, one would expect precise measurements of hypersonic phonon lifetimes by Brillouin scattering to be of interest. [20,21]

C. Hypersonic Velocities in Neon

Our experimental results on liquid neon constitute the first measurement of sound velocity in this system by any technique. Neon was selected for study rather than xenon or krypton because our results in argon indicated that nonclassical behavior is at most on the threshold of detectability in the heavier noble liquids. Neon, however, might appear as a better candidate for anomalous high-

frequency behavior because it can be considered a semiquantum fluid. Indeed, considering the de Broglie wavelength Λ, to be unity in arbitrary units for helium and ~0 for xenon, one has $\Lambda = 0.13$ for neon.[22] (For instance, the ratio of quantum to classical contribution to the self-diffusion coefficient goes as the square of the ratio of the de Broglie wavelength to the length parameter characteristic of the intermolecular potential energy; this ratio, for liquid neon, is found to be ~10%).[22] In addition, some recent measurements in liquid neon indicated a possible anomaly in the vicinity of the normal boiling point (27.2 °K) for the shear viscosity.[23]

Primarily for this reason, our temperature measurements in Ne were made on a much finer scale than for Ar. Table II summarizes our results from just above the triple point ($T_t = 24.6$ °K, $P_t = 324$ mm Hg) to a few degrees above the normal boiling point, taken with 5145 Å excitation. Absolute values of the velocities are dependent upon our use of the square root of the dielectric constant as an approximation to the optical refractive index. The dielectric constant values are taken from Ref. 24 and are plotted in Fig. 7. As with argon discussed above, we expect this approximation to introduce an error of $\lesssim 0.1\%$. To check the reproducibility of our measurements, some runs were also taken with 4765 Å excitation. These results are summarized in Table III.

A typical spectrum obtained for liquid neon at $T = 25$ °K is shown in Fig. 8. The velocity as a function of temperature is plotted in Fig. 9. Again, these velocities are uncorrected for line pulling due to the central component. For the data shown in Fig. 8, similar arguments to those given above for the case of liquid argon indicate that the displacement of the Brillouin peaks toward the central peak due to the tail of the central peak

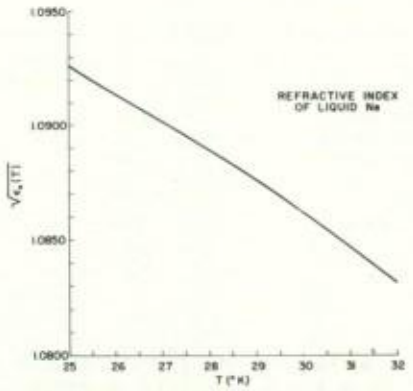

FIG. 7. Temperature dependence of the refractive index for liquid neon at infinite wavelength.

is at most a few MHz $\lesssim 0.2\%$ to the Brillouin shift. The central peak shown in Fig. 8 is stronger relative to the corresponding Brillouin peaks than that one for liquid argon, as illustrated in Fig. 3. On an absolute scale, however, it is weaker by a factor of ~5. The stray light contribution to Fig. 8 is probably larger than that due to scattering from entropy fluctuations in the liquid. For liquid neon[25] at 25.2 °K, $C_p/C_v = 2$. Thus, $I_R/2I_B = 1$; and ~25% of the central component in Fig. 8 is due to entropy fluctuations scattering.

The relative efficiencies of the Brillouin scattering for Ar and Ne are found experimentally to be $\sigma_{Ar}/\sigma_{Ne} \sim 25$. This agrees well with the ratio evaluated from thermodynamic calculation of scattering efficiencies, $\sim(\eta^2 - 1)^2 kT\rho/\beta_S$, with β_S the adiabatic compressibility.

The absence of sound velocity measurements in the MHz range for neon precludes our discussing anomalous velocity dispersion in this liquid from the experimental viewpoint. However, the same

TABLE II. Frequency shift ($\Delta\nu$) and hypersonic velocity (v_s) in liquid neon along the vapor-pressure equilibrium curve; 5145 Å excitation; scattering angle: $\theta = 91°43'$, except for the data marked *, where $\theta = 90°14'$.

P(mm Hg)	T(° K)	η (est)	$\Delta\nu$(GHz)	v_s(m/sec)
360	24.90	1.09270	1.8921	620.7
400	25.17	1.09236	1.8799	616.9
450	25.50	1.09195	1.8650	612.3
490	25.75	1.09163	1.8490	607.2
540	26.02	1.09133	1.8304	601.2
547*	26.07	1.09123	1.8158	604.2
575	26.23	1.09105	1.8321	602.0
620	26.45	1.09080	1.8207	598.3
670	26.73	1.09041	1.8078	594.3
730	27.00	1.09030	1.7897	588.4
737*	27.05	1.09002	1.7854	594.7
952*	28.05	1.08875	1.7300	576.9
1672*	30.03	1.08607	1.6096	538.1
2522*	31.97	1.08315	1.5165	508.3

TABLE III. Frequency shift ($\Delta\nu$) and hypersonic velocity (v_s) in liquid neon along the vapor-pressure equilibrium curve; 4765 Å excitation, scattering angle: $\theta = 90°14'$.

P(mm Hg)	T(°K)	η (est)	$\Delta\nu$(GHz)	v_s(m/sec)
547	26.07	1.09123	1.9660	605.8
942	28.02	1.08880	1.8550	572.9
1672	30.03	1.08607	1.7536	542.9
2552	32.02	1.08308	1.6297	506.0

arguments, as for the case of liquid argon, hold and predict a negative velocity dispersion of the same order, i.e., $\sim 10^{-2}\%$, for liquid neon. Perhaps the most striking feature of Fig. 9 is the change in slope of the sound velocity-versus-temperature curve near 28 °K. Below 28°K, the data show $\Delta v/\Delta T = -14.6$ m/sec °K; while above 28°K, the slope is -17.1 m/sec °K. At present, we have no theoretical explanation for this effect, although we note that similar temperature effects seem to exist for various transport coefficients in liquid neon. In particular, the temperature dependence of both the thermal conductivity[26] and the shear viscosity[23] changes at 28 °K in neon. On the other hand, neither the dielectric constant nor the density exhibits unusual behavior in this temperature range.[24] The intimate relation between the transport properties and the sound velocity and absorption suggest the existence of an interesting physical effect in neon in the vicinity of its normal boiling point. To elucidate this further, we plan more accurate hypersonic velocity measurements as well as attenuation (Brillouin linewidth) measurements in neon using improved apparatus.

IV. DISCUSSION

From classical hydrodynamics, the semiphenomenological theory of light scattering from thermal fluctuations in classical fluids predicts the analytic form of the spectrum of the scattered light to be a succession of three Lorentzians, respectively centered around the incident light frequenty ω_1 (Rayleigh component), and around $\omega_1 \pm \omega_S$ (Stokes and anti-Stokes lines).[9] In the procedure of this calculation, an important point is the solution of the dispersion equation, which, to first order and with very good approximation, exhibits the roots[9]

$$\pm i v_0 k_s - \Gamma_s k_s^2, \qquad -\Gamma_R k_s^2, \tag{7}$$

$$\text{with } \Gamma_s = (2\rho)^{-1}\left[\tfrac{4}{3}\eta_s + \eta_B + \kappa\left(C_v^{-1} - C_p^{-1}\right)\right], \tag{8}$$

$$\text{and } \Gamma_R = \frac{\kappa}{\rho C_p}, \tag{9}$$

where v_0 is the low-frequency sound velocity, and κ is the thermal conductivity (the other symbols have been defined in the preceding sections). Thus, the phonon frequency is given by

$$\omega_s = \pm v_0 k_s; \tag{10}$$

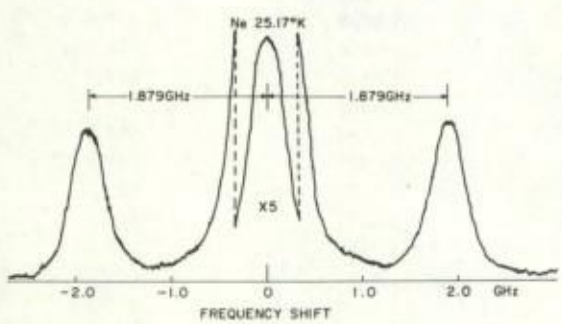

FIG. 8. Brillouin spectrum of liquid neon; $T = 25.17$ °K; $\theta = 91°43'$; laser wavelength is 5145 Å.

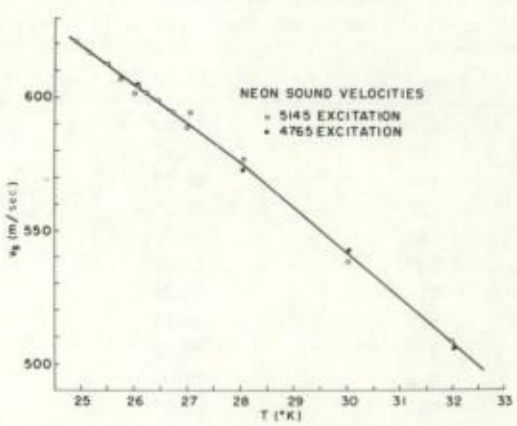

FIG. 9. Hypersonic velocities in liquid neon as a function of temperature, along the vapor-pressure equilibrium curve.

in other words one obtains the classical result that the sound velocity at frequency ω_S is equal to the low-frequency value v_O, provided the hydrodynamic conditions are satisfied. Similarly, the sound attenuation is found to be measured by the Brillouin linewidth

$$\Delta\omega_S = 2\Gamma_S k_S^2. \tag{11}$$

Now, the phonon frequencies measured in the present work, $\omega_S \sim 10^{10}$ Hz, are considerably higher than those encountered in usual hydrodynamic (or acoustic) experiments, although they are still in the low-frequency range when compared to the characteristic frequency ω_C in simple fluids: $\omega_S/\omega_C \sim 10^{-2}$. In other words, the hydrodynamic limit is still valid here and the semiphenomenological approach mentioned above can be used. However, Γ_S and Γ_R, Eqs.(8) and (9), are essentially linear functions of the transport coefficients, and it is now established that at high frequencies, these coefficients should be replaced by general transport functions [3,4] leading to new Γ functions of the form

$$\Gamma(\omega_S) = \Gamma'(\omega_S) + i\Gamma''(\omega_S), \tag{12}$$

where the real and imaginary parts refer, respectively, to the dissipative and nondissipative parts of the corresponding frequency-dependent transport coefficients, as e.g., for the shear viscosity

$$\eta_S(\omega_S) = \eta'_S(\omega_S) + i\eta''_S(\omega_S). \tag{13}$$

Once this is recognized, the dispersion equation and its solution are modified accordingly. The details of the theory are reported elsewhere [6]; here we merely quote the general form of the results. The hypersound velocity reads

$$v_S = v_O\left[1 - \frac{\Gamma''_S}{\Gamma^O_S}\left(\frac{\Gamma_S{}^O k_S}{v_O}\right) - O\left(\frac{\Gamma_S{}^O k_S}{v_O}\right)^2\right], \tag{14}$$

where $\Gamma_S{}^O$ is the zero-frequency quantity as given by Eq. (8), and $\Gamma''_S/\Gamma_S{}^O$ is the lowest-order correction (to which the calculation is restricted here) arising from the frequency dependence of the transport coefficients. The theory thus predicts the existence of a negative dispersion, which is primarily due to the nondissipative (imaginary) part of the transport coefficients at finite frequency. Similarly, a dispersion relation for the high-frequency attenuation follows from the dissipative part of the transport coefficients; one obtains

$$\Delta\omega_S = 2\Gamma_S{}^O k_S{}^2\left[1 + \frac{\Gamma'_S}{\Gamma_S{}^O} + O\left(\frac{\Gamma_S{}^O k_S}{v_O}\right)^2\right], \tag{15}$$

and similarly for Γ_R (i.e., for $\Delta\omega_R$, the linewidth of the Rayleigh peak). An estimation of the dispersion given by Eq. (14) for simple dense fluids like argon and neon in the normal liquid range, and for phonon frequencies $\sim 10^{10}$ Hz, predicts that

$$(v_S - v_O)/v_O \lesssim -10^{-4}. \tag{16}$$

A nonclassical increase in the attenuation of the same order of magnitude ($\Delta\alpha/\alpha_{\text{class}} \sim 10^{-4}$) follows from Eq. (15). This behavior is due to the fact that the nondissipative part of the transport coefficients is an odd function of the frequency, i.e., in the low-frequency range and to the lowest order, $\Gamma''/\Gamma^O \sim O(\omega/\omega_C)$, which is multiplied by $(\Gamma^O k_S/v_0)$ to give the first dispersive term to the hypersonic velocity – while the lowest-order correction to the attenuation is just the second significant term of the expansion of the real part of the transport function, which is even in the frequency, i.e.,

$$\Gamma'/\Gamma_0 = 1 + O((\omega/\omega_C)^2). \tag{17}$$

Both corrections are of the order of $(\Gamma^O k_S/v_0)^2$, which implies that the dispersion equation must be solved to the second order, [27] as seen from the results displayed in Eqs. (15) and (16). As mentioned above, the experimental error precludes our drawing quantitative conclusions from the comparison of ultrasonic data and hypersound velocities in liquid argon. However, there is reasonably good evidence that a negative dispersion has been observed, which is in qualitative agreement with the theoretical prediction.

V. CONCLUSION

At present, the existence of negative dispersion in liquid argon should be regarded as tentative, but appears nevertheless quite plausible. While this observation might indeed be the first experimental indication for nonclassical hydrodynamic behavior in a simple fluid, the desirability of further theoretical investigation and complementary experimental work on this problem is clear. So far as the theoretical approach is concerned, more accurate evaluations of the frequency-dependent effects are in progress, and will lead to numerical results which should be tested against experimental data.

Experimentally, it seems worthwhile to improve the accuracy of Brillouin velocity measurements by at least a factor of 3. With the present apparatus, this could be achieved by stabilizing the long laser cavity to reduce the ~100 MHz of wander in the light frequency. Also, a thorough study of the Brillouin spectra at very large and very small

scattering angles might be of interest. With better laser stability and an improved FP, accurate Brillouin linewidth measurements could also be made.

Of course, sound velocity measurements in the MHz range in liquid neon would certainly be desirable, especially because one might expect quantum effects to play some role in eventual dispersion. Presently, it is, however, extremely difficult to forecast the importance of such effects. About all one can do is to estimate their magnitude from corresponding states principles. Along the saturated vapor-pressure curve the reduced velocity v_s^* is a function only of the reduced temperature T^*,

$$v_s(T) = \chi v_s^*(T^*), \tag{18}$$

with the reduction parameter

$$\chi = (\epsilon/m)^{1/2}, \tag{19}$$

where ϵ is the characteristic minimum of the interaction potential curve, and m is the mass. For two different molecular species obeying the theorem of corresponding states and taken at the same reduced temperature, Eq. (18) yields (e.g., for argon and neon)

$$v_{\mathrm{Ne}}(T) = (\epsilon_{\mathrm{Ne}} m_{\mathrm{Ar}}/\epsilon_{\mathrm{Ar}} m_{\mathrm{Ne}})^{1/2} v_{\mathrm{Ar}}(T_{\mathrm{corr}}), \tag{20}$$

the sound velocity of liquid argon being taken at a corrected temperature: $T_{\mathrm{corr}} = T\epsilon_{\mathrm{Ar}}/\epsilon_{\mathrm{Ne}}$. Now, as already mentioned in Sec. III, neon exhibits a weak, but non-negligible quantum behavior as compared to a classical fluid like argon. Indeed, their respective, reduced de Broglie wavelengths are[22]

$$\Lambda_{\mathrm{Ar}}^{*2} = 0.035; \quad \Lambda_{\mathrm{Ne}}^{*2} = 0.352. \tag{21}$$

Here, considering the square of the Λ^* parameter follows from the fact that the expansion of the scattering cross section for small and moderate wavelengths is even in $\hbar$. Therefore, to account for the quantum effects, Eq. (20) should be modified accordingly,[22]

$$v_{\mathrm{Ne}}(T) = (\epsilon_{\mathrm{Ne}} m_{\mathrm{Ar}}/\epsilon_{\mathrm{Ar}} m_{\mathrm{Ne}})^{1/2} [\, v_s^*(\Lambda_{\mathrm{Ne}}^{*2})/ v_s^*(\Lambda_{\mathrm{Ar}}^{*2})\,]\, v_{\mathrm{Ar}}(T_{\mathrm{corr}}), \tag{22}$$

where $v_s^*(\Lambda_{\mathrm{Ne}}^{*2})/v_s^*(\Lambda_{\mathrm{Ar}}^{*2})$

$$= [\,1 + (\Delta\Lambda^{*2})(\partial \ln v_s^*/\partial(\Lambda^*)^2)\Lambda_{\mathrm{Ne}}^*\,]^{-1}, \tag{23}$$

and $$\Delta\Lambda^{*2} = \Lambda_{\mathrm{Ar}}^{*2} - \Lambda_{\mathrm{Ne}}^{*2}. \tag{24}$$

The evaluation of the right-hand side of Eq. (23) is quite involved, since the explicit dependence of the sound velocity with respect to the de Broglie wavelength is not known. An estimate is nevertheless possible from a graphical representation of the available data for simple liquids. This leads to a quantum correction of ~2% for the velocity in liquid neon as compared to liquid argon. We have reported in Table IV the results of the corresponding-states calculation. One should not attribute too much importance to the quantitative agreement between the experimental data and the corresponding-states results for sound velocity. Some indirect evidence for the importance of quantum corrections in neon is given by the fact that the simple corresponding-states argument gives much better agreement for xenon, which has no quantum effect ($\Lambda_{\mathrm{Xe}}^{*2} = 0.004$), than for neon which does. In particular, based on our measured velocities for argon and the value of 236.6 °K for ϵ_{Xe} one predicts

$$v_{\mathrm{Xe}}^{\mathrm{cs}}(164\ ^\circ\mathrm{K}) = (\epsilon_{\mathrm{Xe}} m_{\mathrm{Ar}}/\epsilon_{\mathrm{Ar}} m_{\mathrm{Xe}})^{1/2}$$

$$v_{\mathrm{Ar}}(85.5^\circ\mathrm{K}) = 646\ \mathrm{m/sec}.$$

This is in excellent agreement with the recently measured value $v_{\mathrm{Xe}}^{\mathrm{obs}}(164\ ^\circ\mathrm{K}) = 635 \pm 7\ \mathrm{m/sec}$ reported by Gornall and Stoicheff.[28] As seen from Table IV, on the other hand, the corresponding-states velocity without quantum corrections for liquid neon is 3% higher than the measured velocity. The quantum correction reduces the difference from experiment to less than 1%. Thus, it seems that the quantum effect in liquid neon is observable. How large a role such effects play in velocity dispersion remains an open question, however.

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TABLE IV. Evaluation of the sound velocity in liquid neon from the principle of corresponding states. The numerical values of the parameters appearing in Eqs. (20) and (22) and used to calculate v_s are those given in Ref. 22.

T(°K)	v_s^{calc}(m/sec) [Eq. (20)]	v_s^{calc}(m/sec) [Eq. (22)]	v_s^{exp}(m/sec)[a]
25	636.4	623.9	618.0[b]
26	619.0	606.9	605.8[c] 601.2[b]
27	600.0	588.2	588.4[b]
28	580.3	568.9	572.9[c] 577.0[b]
29	560.6	549.6	557[b]

[a] From Tables II and III.
[b] 5145 Å excitation.
[c] 4765 Å excitation.

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