SPECTRUM OF LIGHT SCATTERED FROM THERMAL FLUCTUATIONS IN GASES*

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Using a frequency-stabilized single-mode laser, high-resolution Fabry-Perot interferometers, and a detection system with a dark count of three photoelectrons per second, we have measured the spectral distribution of light scattered from thermal fluctuations in five gases (Ar, Xe, N_2, CO_2, CH_4) at a pressure of one atmosphere. This spectrum is the space-time Fourier transform of the particle-distribution function. As the scattering angle is changed from the forward to the backward direction, we observe the change from a hydrodynamic to a kinetic character of the fluctuations giving rise to the spectrum. Nelkin and Yip[1] have recently proposed that experiments of this sort can be used as a test of the Boltzmann equation.

The experimental arrangement has been described elsewhere.[2] The laser delivers 0.6 mW at 6328 Å in a single longitudinal mode locked electronically to the bottom of the Lamb dip.[3] The scattering angles, θ, are determined by conical lenses and the spread in angle accepted, $\Delta\theta$, is of the order of 10^{-3} rad. The scattering toward the forward direction was analyzed with a spherical Fabry-Perot interferometer[4] of 750-Mc/sec free spectral range and an instrumental profile of 28-Mc/sec full width at half-height. For the back scattering we used a flat Fabry-Perot interferometer of 4.96-kMc/sec free spectral range and a width (depending on the reflectivity of the mirrors used) as narrow as 153 Mc/sec. The light was detected with an uncooled ITT model FW130 phototube. Pulse-height discrimination[5] was used to reduce the dark count to about three photoelectrons per second while maintaining an effective quantum efficiency of 2.5%. With this system the primary noise in the experiment was the shot noise due to the signal itself.

The fluctuations in the dielectric constant, ϵ, are responsible for the scattering of light. These fluctuations are caused, in turn, by the fluctuations in the density, in the temperature, and in the orientation of the molecules. In gases near one atmosphere the fluctuations in the number density, ρ, completely predominate, and the cross section, σ, per unit solid angle and unit volume for polarized light can be shown to be[6]

$$\sigma(\vec{K},\Omega)=[(\sin\Phi/4\pi)(\partial\epsilon/\partial\rho)_T]^2 k_0^4 \times\int d^3r dt\langle\Delta\rho(\vec{r},t)\Delta\rho(0,0)\rangle \times\exp[i\vec{K}\cdot\vec{r}-i\Omega t], \quad (1)$$

where $\Omega/2\pi$ is the frequency shift of the scattered light, Φ is the angle between the electric field of the incident light and the wave vector, $\vec{k}$, of the scattered light, $\vec{k}_0$ is the wave vector of the incident light in the medium, and $\Delta\rho$ is the fluctuation of the number density about its average ρ_0. The wave vector of the fluctuation being observed, $\vec{K}$, is the vector difference between $\vec{k}$ and $\vec{k}_0$, and its magnitude is given by $K=2k_0\sin(\theta/2)$, since $k_0\approx k$. The correlation function for the fluctuation in density is related to the classical limit of Van Hove's density-density correlation function,[7] $G(r,t)$, by

$$\langle\Delta\rho(\vec{r},t)\Delta\rho(0,0)\rangle=\rho_0[G(\vec{r},t)-\rho_0]. \quad (2)$$

Van Leeuwen and Yip[8] have shown that for a dilute gas

$$\langle\Delta\rho(\vec{r},t)\Delta\rho(0,0)\rangle=\rho_0\int d^3p\, f(\vec{r},\vec{p},t), \quad (3)$$

where $f(\vec{r},\vec{p},t)$ is the particle distribution function satisfying the linearized Boltzmann equation subject to the initial condition

$$f(\vec{r},\vec{p},0)=(2\pi Mk_BT)^{-3/2}\exp[-p^2/2Mk_BT]\delta(r). \quad (4)$$

Here M is the mass of the molecule, k_B is the Boltzmann constant, and p is the particle momentum. It follows that $\sigma(\vec{K},\Omega)$ is proportional to the double Fourier transform of the space and time distribution function for the gas molecules. The trace we record is the convolution of $\sigma(\vec{K},\Omega)$ with the instrumental profile of the interferometer.

The form of the spectrum of the scattered light is determined by a parameter[9] y, which is a measure of the ratio of the wavelength of the fluctuation observed to the collision mean free path,

$$y\equiv(2\pi/K)/[(2\pi/\alpha)(2k_BT/M)^{1/2}], \quad (5)$$

where α is an effective collision frequency.

Table I. Brillouin shifts and velocities for scattering at an angle 10.6°.

Gas	Pressure (mm Hg)	Temperature (°C)	$\Delta\nu$ (Mc/sec)	Computed v_S (m/sec) (Hypersonic)	Low frequency[a] v_S (m/sec) (Ultrasonic)
Ar	770	28	93.0±2.0	318±6	323[b]
Xe	795	25.2	50.8±2.0	174±7	178[b]
N_2	770	28	100.5±2.0	344±7	354[c]
CO_2	770	24.9	81.5±1.2	279±4	281[d]
CH_4	777	24.7	129 ±4	442±13	454[e]

[a]Measured at frequencies above any vibrational relaxations.

[b]M. Greenspan, J. Acoust. Soc. Am. 28, 644 (1956).

[c]M. Greenspan, J. Acoust. Soc. Am. 31, 155 (1959).

[d]M. C. Henderson and L. Peselnick, J. Acoust. Soc. Am. 29, 1074 (1957).

[e]B. T. Kelly, J. Acoust. Soc. Am. 29, 1005 (1957).

When $y > 10$ the hydrodynamic description is very good. The spectrum consists of three distinct, nonoverlapping lines: an unshifted component due to nonpropagating fluctuations (the Rayleigh component) and a symmetrically shifted doublet due to the scattering from thermally excited sound waves (Brillouin scattering). In the region $y \sim 5$, the three lines begin to overlap since their widths increase faster with K than does their splitting; yet, the spectrum can still be described rather accurately by the hydrodynamic equations. However, when $y < 2$ the hydrodynamic equations no longer adequately describe the spectrum. A kinetic theory must be used to take into account the effects of the distribution in molecular velocities. At a pressure of one atmosphere we are able to investigate each of these regions in turn by changing the scattering angle from the forward to the backward direction. We report here the results of our measurements at three scattering angles: 10.6, 22.9, and 169.4°. Previous measurements have been made at 90° in Ar and H_2 by May, Rawson, and Welsh.[10]

The scattering at an angle of 10.6° corresponds to fluctuations with wave vector $K = 1.84 \times 10^4$ cm^{-1}. This corresponds to $y \sim 13$. By measuring the frequency shift, $\Delta\nu$, of the Brillouin components, we are able to determine the velocity, v_S, of sound waves of frequency $\Delta\nu$ ($\Delta\nu$ is ≈100 Mc/sec, at this angle) by means of the relation $v_S = 2\pi\Delta\nu/K$. Table I gives the Brillouin shift, the velocity calculated from it,[11] and the low-frequency velocities for five gases studied at this angle. Figure 1 shows a typical trace of CO_2 gas at 770 mm Hg and 24.9°C. The dashed curve is the result of subtracting the spectrum due to stray elastically scattered light which remains even if the scattering cell is evacuated. At the peak of the Brillouin component, the signal contains about 300 photoelectrons per second. The shape of each of the three peaks is determined almost entirely by the instrumental profile of the spherical Fabry-Perot interferometer, although a slight broadening due to the natural width of the line (of the order of 7 Mc/sec) is detectable. In the two strongest scatterers, Xe and CO_2, the subtraction of the stray light was sufficiently reliable to determine quantitatively the ratio of the power in the Rayleigh line to that in the Brillouin lines. This agrees to within the experimental uncertainty of 3% with the value of $(C_p/C_v)-1$ (0.667 in Xe and 0.304 in CO_2)[14] predicted by Landau and Placzek[12] on the basis of thermodynamic arguments.

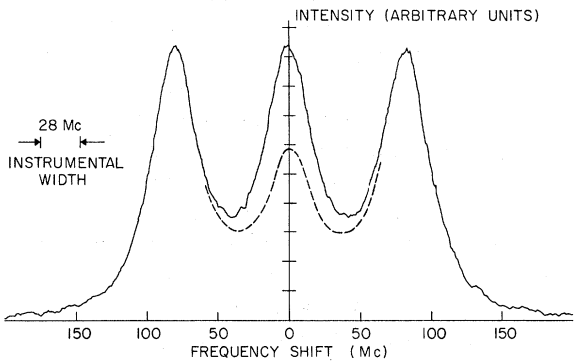

FIG. 1. The spectrum of light scattered from CO_2 at an angle of 10.6° and a pressure of 770 mm of Hg, showing clearly resolved Brillouin components. At the maximum of one of the Brillouin peaks the signal produces about 300 photoelectrons/sec at the photocathode. The dashed curve indicates the subtraction of stray elastically scattered light.

At $\theta = 22.9°$ the wave vector of the observed fluctuations is $K = 3.95 \times 10^4$ cm^{-1}. This corresponds to $y \sim 6$. At this angle the widths of the three lines are comparable with the instrumental width of the interferometer, so a more detailed check can be made with the theoretical spectra. We found, for example, the widths of the Brillouin components in Xe and CO_2 to be, respectively, 28 ± 4 and 36 ± 4 Mc/sec, which would correspond to sound-wave lifetimes of $(1.1 \text{ and } 0.9) \times 10^{-8}$ sec at the frequency of the Brillouin shifts. Because of the overlapping of the three lines at this angle, the "Brillouin shift" is no longer an exact term. We find, however, that the acoustic portion of the spectra has its maximum at 108 ± 3 Mc/sec in Xe and 170 ± 4 Mc/sec in CO_2.

Mountain[13] has recently obtained an expression for the spectra from an exact solution of the linearized hydrodynamic equations. We have compared our results in Xe and CO_2 with his expression using the low-frequency values[14] of the specific heats, thermal conductivity, viscosity, and sound speed. The spectrum is the real part of his Eq. (13) with $s = i\omega$. The convolution of this spectrum with the instrumental profile matched the acoustic region of the spectrum to within the noise; a similar comparison could not be made near zero frequency shift because of the stray elastically scattered light.

Figure 2 shows the spectra of Xe and CO_2 measured at $\theta = 169.4°$ for which $K = 1.98 \times 10^5$ cm^{-1}. The spectrum of a small amount of stray elastically scattered light, about $\frac{1}{8}$ of the height of the Xe spectrum at the origin, has been subtracted. The superimposed broken curves are the numerical convolution of various theoretical spectra with the instrumental profile of the system. They are normalized to the height of the experimental trace at zero frequency shift.

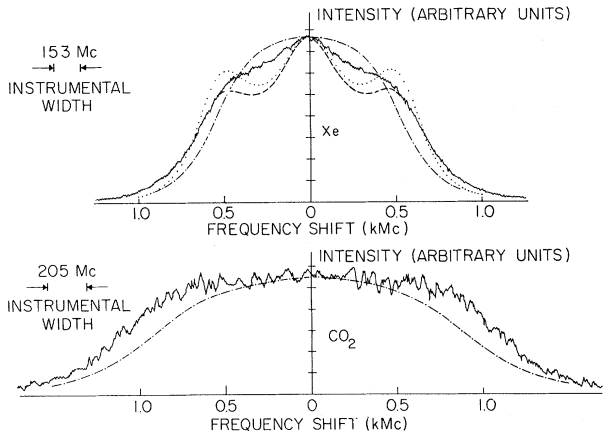

FIG. 2. The spectrum of light scattered from Xe and CO_2 at an angle of 169.4° and pressures near one atmosphere. The curves are experiment (solid), Maxwell molecule theory (dotted), Krook model theory (dashed), and the hydrodynamic approximation (dash-dotted).

The upper curves refer to Matheson research-grade Xe at 780 mm Hg and 24.8°C. The solid curve showing noise is a typical experimental trace. The dotted curve represents an exact solution of the linearized Boltzmann equation obtained by Ranganathan and Yip[15] for the special case of point molecules interacting by means of a repulsive $1/r^4$ potential (Maxwell molecules). The dashed curve represents an exact solution[9] of the linearized Krook equation,[16] which is the Boltzmann equation with the collision integral replaced by a phenomenological term that maintains conservation of particle number, momentum, and energy. This curve is drawn only to 0.6 kMc/sec after which the Krook solution is nearly the same as the one for the Maxwell molecules. The parameter y was 1.26, based on a value of α computed[17] from the viscosity of Xe. The dash-and-dot curve represents the hydrodynamic spectrum.[13] Comparison of this hydrodynamic spectrum with the kinetic ones shows that the peaks associated with the sound waves, or acoustic modes, maintain their identity to higher values of K in the kinetic theories than in the hydrodynamic approximation. The experimental trace shows that the acoustic modes do persist to a much greater degree than predicted by the hydrodynamic equations. However, they appear to be less marked than is expected from the present kinetic theories.

The lower trace in Fig. 2 is the spectrum of Matheson Coleman instrument-grade CO_2 at 750 mm Hg and 25.1°C. Only the hydrodynamic spectrum is shown for comparison, since present kinetic theories are applicable only to monatomic gases. The presence of broader shoulders on the experimental trace than on the hydrodynamic curve indicates again the tendency toward persistent acoustic modes.

These experiments show that the spectrum of light scattered from low-density gases can provide detailed information on the molecular distribution function and can serve as a delicate test of the validity of various theoretical solutions of the Boltzmann equation.

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BOSE-EINSTEIN PHASE TRANSITION IN AN INTERACTING SYSTEM*

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It is shown that for both the Hartree-Fock and Bogoliubov models of interacting bosons associated with the disappearance of the Bose-Einstein condensation at a temperature T_c, the specific heat C_V has a square root singularity, $C_V \sim A(T_c - T)^{-1/2}$, and the superfluid density ρ_S is discontinuous, with $\rho_S(T) - \rho_S(T_c - 0) \sim B(T_c - T)^{1/2}$ for temperatures $T \to T_c - 0$. Except near $T_c = T_\lambda$ the theoretical and experimental results for ρ_S are in good agreement.

It is well known that in an ideal (Bose-Einstein) gas of He^4 atoms, the specific heat C_V is continuous but $\partial C_V/\partial T$ is discontinuous at $T_I = 3.13°K$.[1] By contrast, the measured specific heat of liquid He^4 is logarithmically singular at $T_\lambda = 2.18°K$.[2] Because of calculational difficulties inherent in studies of phase transitions, little progress has been made in showing that the introduction of interactions between atoms leads to agreement between the predicted and observed values of C_V.[3-5] We report here that for both the Hartree-Fock and Bogoliubov models of a system of bosons interacting via repulsive two-body potentials, C_V has