

Kinetic Theory Analysis of Light Scattering in Gases*

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An analysis of the large-angle laser scattering experiment of Greytak and Benedek is made in terms of initial-value solutions to the linearized Boltzmann equation. Quantitative agreement is obtained between measurements and theoretical results derived for rigid-sphere and repulsive $1/r^4$ interatomic potentials.

THE spectrum of density fluctuations in monatomic gases has recently been measured by Greytak and Benedek by means of scattering of a single-mode laser of 6328 Å.¹ Their data in the forward scattering direction (scattering angle $\theta=10.6^\circ$) showed good agreement with continuum theory predictions, but in the backward direction ($\theta=169.4^\circ$) nonhydrodynamic behavior was clearly discernible. Since the large-angle measurements involve fluctuations in the region where wavelength is comparable to mean free path, the experiment provides a quite precise test of kinetic theory.² The purpose of this paper is to show that the measurements of Greytak and Benedek can be quantitatively interpreted in terms of solutions to the linearized Boltzmann equation.

The scattering of light by gases at atmospheric conditions furnishes information about density fluctuations because the fluctuations in medium susceptibility are mainly density effects.³ The spectrum of scattered light is then determined by the density fluctuation spectrum,⁴

$$S(k, \omega) = \int d^3r \int_{-\infty}^{\infty} dt e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} G(\mathbf{r}, t), \quad (1)$$

where $G(\mathbf{r}, t)$ is the density-density correlation function.⁵ The momentum transfer k is, to a good approximation, $2k_i \sin(\frac{1}{2}\theta)$, where k_i is the wave number of the incident light, and the frequency shift is denoted by $\omega/2\pi$. For a classical gas, $G(\mathbf{r}, t)$ is even in t and depends only on the magnitude of \mathbf{r} ; consequently, $S(k, \omega)$ is even in ω and depends only on the magnitude of \mathbf{k} .

A number of attempts have been made to study

$S(k, \omega)$ as an initial-value problem in kinetic theory.⁶⁻⁹ If one ignores the effects of incomplete collisions, then it can be shown that⁹

$$S(k, \omega) = 2 \operatorname{Re} \left[\int d^3r \int_0^{\infty} dt e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \int d^3v f(\mathbf{r}, \mathbf{v}, t) f_0(v) \right], \quad (2)$$

where $f(\mathbf{r}, \mathbf{v}, t)$ satisfies the linearized Boltzmann equation

$$\left(\frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \right) f(\mathbf{r}, \mathbf{v}, t) = J[f], \quad (3)$$

$$J[f] = n_0 \int d\Omega \int d^3v_1 f_0(v_1) |\mathbf{v} - \mathbf{v}_1| I(\theta, |\mathbf{v} - \mathbf{v}_1|) \times [f(\mathbf{v}') + f(\mathbf{v}_1') - f(\mathbf{v}) - f(\mathbf{v}_1)]. \quad (4)$$

Here n_0 is the equilibrium number density,

$$f_0(v) = (2\pi v_0^2)^{-3/2} \exp(-v^2/2v_0^2),$$

$v_0^2 = k_B T/M$, and $I(\theta, |\mathbf{v} - \mathbf{v}_1|)$ is the binary collision cross section. The initial condition is a density impulse

$$f(\mathbf{r}, \mathbf{v}, t=0) = \delta(\mathbf{r}). \quad (5)$$

Equation (3) has been used directly to obtain $S(k, \omega)$ only in the case of Maxwell molecules (repulsive potential $\sim 1/r^4$).⁷ A polynomial expansion method of calculation was used, and even though this approach is known to fail at short wavelengths, convergent results for the range of wavelengths of interest have been obtained. In comparing their experimental data with this calculation, Greytak and Benedek did not find completely satisfactory agreement.¹ Subsequently, it was realized that an incorrect value of γ , a parameter

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¹ T. J. Greytak and G. B. Benedek, *Phys. Rev. Letters* **17**, 179 (1966).

² M. Nelkin and S. Yip, *Phys. Fluids* **9**, 380 (1966).

³ L. Landau and E. Lifshitz, *Electrodynamics of Continuous Media* (Addison-Wesley Publishing Co., Reading, Mass., 1960), p. 389.

⁴ S. M. Rytov, *Zh. Eksperim. i Teor. Fiz.* **33**, 514 (1957) [English transl.: *Soviet Phys.—JETP* **6**, 401 (1958)]; R. Pecora, *J. Chem. Phys.* **40**, 1604 (1964).

⁵ L. van Hove, *Phys. Rev.* **95**, 249 (1954).

⁶ S. Yip and M. Nelkin, *Phys. Rev.* **135**, A1241 (1964); S. Yip and S. Ranganathan, *Phys. Fluids* **8**, 1956 (1965); E. P. Gross, *Phys. Rev.* **158**, 146 (1967).

⁷ S. Ranganathan and S. Yip, *Phys. Fluids* **9**, 372 (1966).

⁸ E. P. Gross, in *Boulder Summer School Lectures on Kinetic Theory, 1966* (Gordon and Breach Science Publishers, Inc., New York, to be published).

⁹ J. M. J. van Leeuwen and S. Yip, *Phys. Rev.* **139**, A1138 (1965).

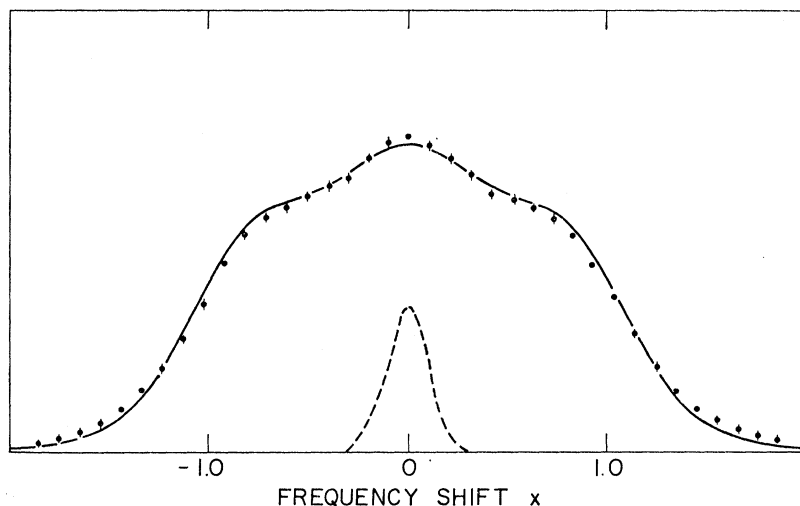


FIG. 1. Spectrum of 6328 Å light scattered at an angle of 169.4° by xenon gas at 24.8°C and 780 mm Hg. Experimental points are taken from Greytak and Benedek (see Ref. 1) and have been converted to dimensionless frequency variable $x = \omega / \sqrt{2}kv_0$, with $k = 1.98 \times 10^5 \text{ cm}^{-1}$, and $v_0\sqrt{2} = 1.943 \times 10^4 \text{ cm/sec}$. The Boltzmann-equation solution (solid curve) for rigid-sphere molecules has been convoluted with the experimental resolution function (dashed curve). The computed spectrum is obtained for $y = 1.17$.

which is a measure of the wavelength to mean-free-path ratio, had been used.^{10,11}

We have recently computed $S(k, \omega)$ from Eq. (3) using the method of generalized kinetic models.¹² This approach has the advantage of an interpolation procedure in that the solutions are always constrained to have the correct limiting behavior at long and short wavelengths. Our Maxwell molecule results are in agreement with those found using polynomial expansion¹² whenever the earlier method converged, and in addition we have obtained similar results for rigid-sphere molecules. As in previous calculations $S(k, \omega)$ is most conveniently expressed in terms of the dimensionless variables $x = \omega / \sqrt{2}kv_0$ and y , the definition of which depends on the interaction potential. For Maxwell molecules we define y as $|\lambda_{11}| / \sqrt{2}kv_0$, where λ_{r1} is the eigenvalue of $J[f]$. For rigid-sphere molecules we take y to be $|J_{02,02}| / \sqrt{2}kv_0$, where

$$J_{r1, r1} = \int d^3v f_0(v) \psi_{r1} J[\psi_{r1}], \quad (6)$$

and ψ_{r1} denote the Maxwell molecule eigenfunctions. Both the force constant χ in the Maxwell interaction potential and the rigid-sphere diameter d are determined in terms of the shear-viscosity coefficient η . By requiring both molecules to have the same value of η we obtain a value of 1.524 for the ratio of Maxwell to rigid sphere y .

In Figs. 1 and 2 the results of our analysis are compared with the measurements of Greytak and Benedek for xenon gas at 24.8°C and 780 mm Hg. The value of η under these conditions is $234.5 \times 10^{-6} \text{ g/cm sec}$,¹³ and

¹⁰ T. J. Greytak, thesis, MIT, 1967 (unpublished).

¹¹ S. Ranganathan, thesis, Cornell University, 1967 (unpublished).

¹² A. Sugawara, S. Yip, and L. Sirovich, *Phys. Fluids* (to be published).

¹³ *American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill Book Co., New York, 1963), 2nd ed., pp. 2-228.

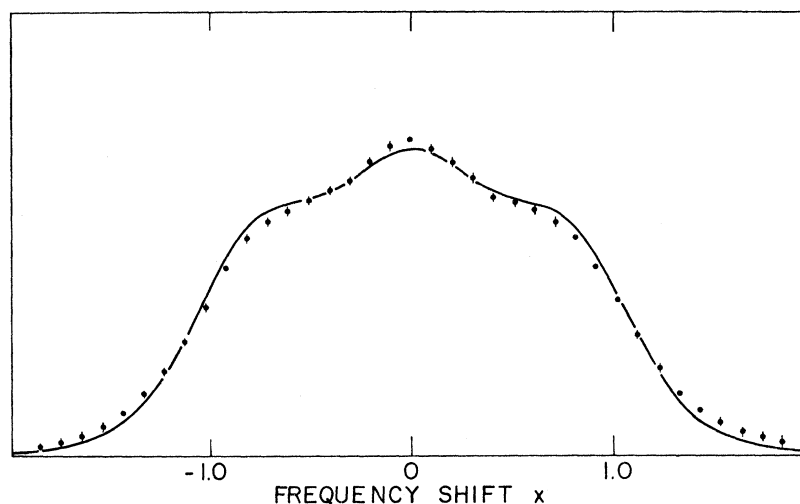
with $\theta = 169.4^\circ$ this leads to y values of 0.767 and 1.17 for Maxwell and rigid-sphere molecules, respectively. The computed spectra have been convoluted with a measured resolution spectrum, and the results are then area normalized (between $x = -1.5$ and 1.5) with respect to the experimental points. It can be observed that both Maxwell-molecule and rigid-sphere calculations are in good agreement with the data, but in the vicinity of the shoulder in $S(k, \omega)$ the rigid-sphere results are slightly superior.

Our analysis strongly suggests that in gases the spectrum of density fluctuations observed with light scattering is not particularly sensitive to the details of the repulsive part of the interaction. It still remains to determine explicitly the effects of attractive forces. This is a difficult computational problem. For xenon gas (attractive well depth about 220°K ¹⁴) at room temperature, Figs. 1 and 2 indicate that the effects should be no more than 3-4% if the discrepancy is due to attractive forces. At higher temperatures, the attraction should play an even less significant role and we can expect the rigid-sphere calculations to be even more appropriate.

It would be very interesting to measure $S(k, \omega)$ at a series of temperatures. Because the spectrum depends only on the parameter y , measurements carried out at different temperatures should yield the same result if the scattering angle is also varied to keep y constant. This scaling property of the Boltzmann equation was first pointed out by Nelkin in connection with the variation of $S(k, \omega)$ with density. One can show quite generally that y can be expressed as $n_0 A / k$, where A is a quantity determined solely by the binary-collision cross section. Once the interaction potential [including force constant(s)] is specified, the temperature and density dependence of $S(k, \omega)$ are determined by the

¹⁴ J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *The Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 1110.

FIG. 2. Same as Fig. 1 except that the theoretical curve is for Maxwell molecules and the corresponding value of $\gamma=0.767$.



Boltzmann equation. Thus far we have used the measured value of shear viscosity to specify χ and d . However, this procedure leads to a slight ambiguity unless the temperature dependence of η is precisely that predicted with either the Maxwell molecule or the rigid-sphere interaction. In the case of xenon, the viscosity data imply that the repulsive force is slightly harder¹⁵ than $1/r^5$; consequently values of χ and d derived at different temperatures will not be the same.

¹⁵ G. Sandri, A. Kritz, and F. Schatzman, *Ann. Phys. (N. Y.)* **43**, 452 (1967).

The extent of their variation is an indication of the inadequacy of the Boltzmann description with a purely repulsive, temperature-independent potential, and one way to correct this is to use measured values of η at every temperature.

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