# *Theory of Light Scattering in Fluids*

This review of light scattering theory [1] brought together a range of concepts which had been developed over more than half a century. Light scattering has been used to measure thermal properties of liquids and solids ever since Einstein showed that the intensity of light scattered by density fluctuations is proportional to the isothermal compressibility of the fluid. Density fluctuations, in turn, can be considered to be a sum of pressure fluctuations and entropy fluctuations. Independently, Brillouin and Mandel'shtam realized that the pressure fluctuations are associated with acoustic modes and would shift the frequency of the scattered light by an amount proportional to the speed of sound. In 1935, Landau and Placzek published a short note in which the contribution of the entropy fluctuation component of density fluctuations to the scattering of light was identified and shown to be unshifted in frequency. The intensity ratio of the two components of the scattered light (entropy fluctuation component divided by the pressure fluctuation component) is equal to the ratio of $(C_p–C_v)/C_v$, the specific heat difference divided by the constant volume specific heat. (This has come to be known as the Landau-Placzek ratio.) They also noted that the spectral width of the light scattered by the non-propagating density fluctuations would be proportional to the thermal diffusivity of the fluid.

Prior to the advent of the He-Ne gas laser, it was not possible to exploit these ideas fully because the spectral width of available light sources was larger than the frequency broadening due to the non-propagating fluctuations. It was only possible to estimate sound speed and heat capacity ratios if a great deal of care was taken. This changed when He-Ne lasers became available as light sources that were nearly monochromatic and coherent. Heterodyne and homodyne detection schemes now made it possible examine the structure of scattered light in detail. In short order, light scattering became an active research topic and tool with particular attention paid to scattering near critical points, where the scattering intensity is large. It would not be an understatement to say that the prospect of using a new technique to study dynamics near critical points was exciting.

The theoretical ideas mentioned above were not organized in a form that would be readily accessible to the students entering the field. The necessary theory can be extracted from three of the volumes of the Landau and Lifshitz series, *Statistical Physics, Fluid Mechanics, and Electrodynamics of Continuous Media,* but only if one knows where to look. Thus, a review article putting the pieces together was timely. At the urging of M. S. Green, Chief of the Statistical Physics Section, Raymond Mountain prepared the review article *Spectral Distribution of Scattered Light in a Simple Fluid* [1] that brought these theoretical ideas together. The emphasis of the article was on how the spectra are related to fluid properties. The review also showed how light scattering theory was related to the theory of sound propagation in a liquid. It was an opportunity to put statistical mechanics in contact with experiments. In structuring the article, use was made of the work of I. L. Fabelinskii, S. M. Rytov, and R. Pecora.

The underlying idea in the theory of scattering by fluctuations is that scattering provides an average over the fluctuations in both space and in time. Statistical mechanics provides the theoretical framework needed to relate the observed scattered light to fluid properties, and that is the approach followed in the paper. The result is an explicit formula connecting the intensity and frequency distribution of the scattered light to the thermodynamic and transport properties of the fluid.

This theory of light scattering is phenomenological. It provides the connection between the spectrum of the scattered light and various thermodynamic and transport properties of the fluid. The use of the inherently macroscopic equations of hydrodynamics to describe events on the scale probed by light scattering may seem to be an unjustified extrapolation. It is not for two reasons. First, the fluctuations that lead to light scattering have a size on the order of the wavelength of light, that is micrometers. The distance between near neighbor molecules in a liquid is on the order of tenths of a nanometer, over a thousand times smaller. Second, the time scale of these fluctuations is much longer than the time intervals associated with molecular scattering processes. With these considerations in mind, the use of hydrodynamic fluctuation theory is quite reasonable. This approach would break down for the case of scattering from a gas, where the mean-free-path of a molecule is on the order of the wavelength of light. (Although not part of the review, this has been demonstrated experimentally. Agreement between theory and experiment is recovered when kinetic theory of gases is used in place of hydrodynamics to describe the time evolution of the fluctuations [2].)

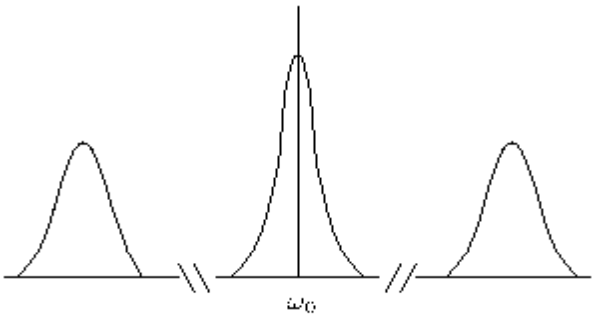

**Fig. 1.** The spectrum of light scattered by density fluctuations is sketched here. The central component, centered at $\omega_0$ the frequency of the incident light, has a width on the order of MHz. The other components are shifted from the incident frequency by an amount on the order of GHz. Hence, the break indicated on the horizontal axis. The Landau-Placzek ratio is the ratio of the area under the central component to the area under the other two components.

The spectrum of the scattered light consists of a central, unshifted component with a width proportional to the thermal diffusivity and two Brillouin-Mandel'shtam components that are shifted in frequency by an amount proportional to the adiabatic sound speed. The width of the shifted components is proportional to the acoustic attenuation coefficient. If a He-Ne source is used and the scattered light is observed at an angle of 90° from the direction of propagation of the incident light, the widths of these spectral features are on the order of megahertz and the shifts are on the order of gigahertz.

When the fluid is close to the liquid-vapor critical point, the density fluctuations are large enough to make the scattering visible to the naked eye. The fluid takes on a milky color, called critical opalescence. Since critical opalescence was a "hot topic," the review utilized the theory to predict how the scattered light would appear for states close to the critical point of carbon dioxide, a substance for which the relevant thermodynamic and transport property data were available. There followed some speculations on how these predictions would be modified very close to the critical point. (These speculations were later shown to be only crude approximations to the observations since renormalization ideas were not included [3].) Finally, a cautionary note was sounded about carefully characterizing the state of the system being studied. "It is important to keep in mind that *light-scattering experiments are only as good as the PVT data used to specify the thermodynamic state of the scattering system.*"

Since hydrodynamic fluctuation theory is also pertinent to acoustic wave propagation and attenuation, a section discussing the connections between light scattering and sound propagation was included. In both situations, the same dispersion relation is used. The difference is that in light scattering the wavelength is fixed and the frequency varies, while in acoustic wave propagation the frequency is held fixed and the wavelength is allowed to vary. The lesson is that the interpretations of the two types of measurements are different, a point that had not been widely appreciated.

The article provides an introduction to the theory that can be readily understood by most physical scientists. The review was well received and was widely referenced. It has been reprinted in collections. In 1980 it was highlighted in Science Citation Index as a "Citation Classic," meaning that it had been cited more than 250 times since the article was published. Many of the features of the review had been incorporated into books by then [2,4].

Some of the theory expounded in the review did not conform to the experimental results on the scattering of light in molecular liquids. In many cases, the ratio of the intensity of the central component to the Brillouin components (the Landau-Placzek ratio) exceeded the specific heat ratio for the liquid. This experimental finding indicated that the spectrum of the scattered light contained additional features. This led Mountain to develop a hydrodynamic fluctuation theory for the spectrum of the scattered light that included internal molecular degrees of freedom, such as vibrational states. This theory predicts that some of the intensity associated with the sound modes is transferred to an unshifted, but quite broad, spectral feature which is separate from the entropy fluctuation component, which has a spectral width proportional to the thermal diffusion coefficient. The existence of this component was demonstrated experimentally at the same time the short note describing the feature appeared [5-7]. This feature is sometimes called the "Mountain peak" although it is a fairly weak, broad feature in the spectrum of many liquids. The story is different for polymers and for strongly supercooled liquids, where there are many internal degrees of freedom that have a major influence on the density fluctuations, so that the additional feature is large.

The same sort of theory developed for one-component liquids has been developed for mixtures. In that case, the dominant fluctuations that lead to scattering are composition fluctuations. The spectrum of these fluctuations are more complex due to the additional variable (composition) in the problem [8-10].

Raymond D. Mountain came to NBS as a Postdoctoral Research Fellow in 1963 and became a regular staff member of the Heat Division in 1965. The review article was prepared while he was a postdoc. He became chief of the Statistical Physics Section in 1968 when M. S. Green left NBS for Temple University, and served

in this position until 1982. In 1986 he was named a NIST Fellow. He received the Department of Commerce Gold Medal in 1983 for his research on the liquid state. In 1974 he was named a Guggenheim Fellow and spent a year at the Institute for Theoretical Physics in Utrecht, The Netherlands.

*Prepared by Raymond D. Mountain.*

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