# Quasielastic Laser Light Scattering

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## 1 Introduction

A perfectly homogeneous material would allow light to pass through it without deflection. All known materials, however, possess microscopic inhomogeneities giving rise to local fluctuations in dielectric constant (refractive index). Light passing through such systems is scattered in all directions to an extent which is typically $10^{-4}$—$10^{-6}$ of the incident beam intensity. Most investigators in the physical and biological sciences are familiar with the classical use of total-intensity light scattering to determine molecular weights of macromolecules in solution. In addition, information on the size and shape of the macromolecules can be obtained by studying the angular distribution of the scattered intensity.[1]

The dielectric fluctuations of the material which cause light scattering are constantly changing with time owing to thermal (Brownian) motions and consequently the scattered light will have a frequency distribution different from that of the incident radiation. The characteristics of this light-scattering spectrum are determined by the relaxation time decay of the fluctuations. A study of the spectrum can therefore provide information on the dynamics of the fluctuations in addition to the same information derived by total-intensity measurements.

The shifts from the frequency of the incident radiation represented by this light-scattering spectrum are extremely small, ranging from as little as one part in $10^{14}$ ($10^{-11}$ cm$^{-1}$) to perhaps one part in $10^{6}$ (0.01 cm$^{-1}$) of the incident frequency radiation. Such shifts are not to be confused at all with the large shifts observed in Raman spectroscopy.[2] Because of the small frequency changes, the scattering can be assumed elastic within the accuracy of our experimental measurements. For this reason, the studies discussed in this article are often grouped under the heading of quasielastic light scattering.

The theoretical basis of quasielastic light scattering has developed continuously since the early work of Brillouin in 1922.[3] In the simplest case it turns out that

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[1] M. Kerker, 'The Scattering of Light and other Electromagnetic Radiation', Academic Press, New York, 1969.

[2] A. Anderson, 'The Raman Effect', Marcel Dekker, New York, 1971 (two volumes).

[3] L. Brillouin, *Ann. Physik.*, 1922, **17**, 88.

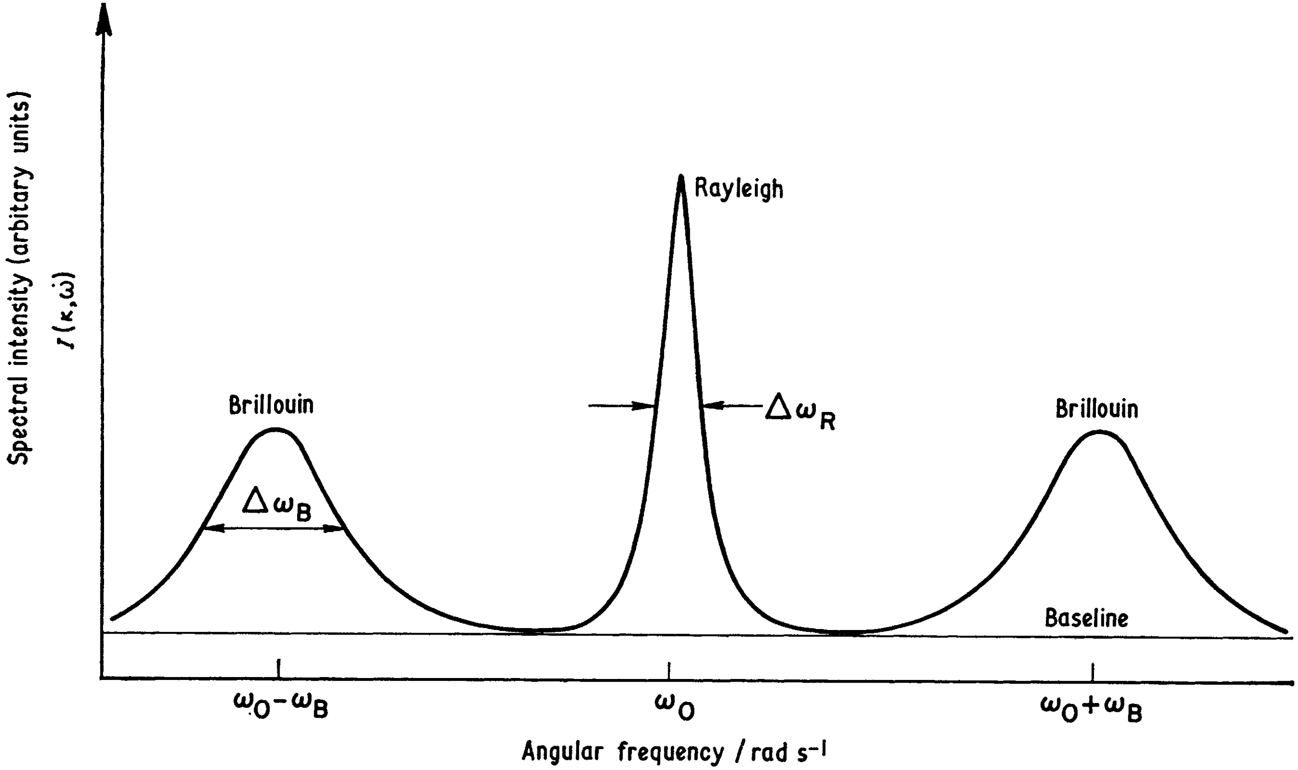

**Figure 1** *Hypothetical quasielastic light scattering spectrum for a pure non-relaxing fluid.* $\omega_0$ *is the incident laser frequency,* $\Delta\omega_R$ *is the halfwidth (full width at half height) of the Rayleigh line,* $\Delta\omega_B$ *is the halfwidth of either Brillouin line, and* $\omega_B$ *is the shift in frequency of the Brillouin lines from* $\omega_0$

the spectrum consists of an extremely narrow central component, the Rayleigh line, with two symmetrically shifted broader lines on either side, the Brillouin doublet. A schematic diagram of the quasielastic spectrum in a simple non-relaxing liquid is shown in Figure 1. Early experimental studies of the Rayleigh–Brillouin spectrum were severely hindered, principally because of the relatively low power and high bandwidths of conventional light sources and filters, coupled with the poor resolving power of classical spectrometers using diffraction gratings or interferometers.[4] For example, classical filters, with bandwidths typically around 0.01 $cm^{-1}$, made it impossible to study the Rayleigh line. The widespread availability of laser light sources which can have bandwidths as narrow as $10^{-5}$ $cm^{-1}$, together with advances in optical and electronic detection devices, have virtually eliminated all of the experimental difficulties. The past seven years have therefore seen a profound resurgence in experimental studies of quasielastic light scattering. This in turn has provided theoreticians with the impetus to develop more detailed theories of light scattering from systems of practical interest.

The review which follows seeks to inform the chemist of the wide variety of information which can be obtained in a rapid, efficient way by a study of the quasielastic spectrum of scattered laser light. This includes molecular weights, particle sizes and shapes, diffusion and activity coefficients, hypersonic velocities, and molecular relaxation times. Before discussing these applications in detail, it will be advantageous to provide the reader with a brief summary of the formalism of quasielastic light scattering. In this way we hope to emphasize the close relation of the light-scattering technique to alternative methods of investigating molecular dynamics such as spin relaxation,[5] dielectric relaxation,[6] and ultrasonics.[7]

## 2 Dielectric Fluctuations and Quasielastic Light Scattering

The origin of the quasielastic frequency broadening of light scattered by a fluid is conceptually most easily envisaged as a simple Doppler frequency shift due to the motions of the molecular scatterers. The collective thermal motions of statistical ensembles of molecules give rise to microscopic fluctuations in the density of the fluid or the relative concentrations of its components, which in turn represent microscopic fluctuations in dielectric constant. Incident light is scattered by these local dielectric fluctuations and the spectral frequency distribution of the scattered light is therefore determined by the time dependence of the spontaneous microscopic density and concentration fluctuations of the fluid.

The time dependence or relaxation of fluctuation phenomena is described by the appropriate correlation functions,[8] which are obtained in turn from the

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[4] I. L. Fabelinskii, 'The Molecular Scattering of Light', English translation, Plenumess Pr, New York, 1968.

[5] A. Abragam, 'The Principles of Nuclear Magnetism', Oxford University Press, Oxford, 1967.

[6] J. Crossley, *R.I.C. Rev.*, 1971, **4**, 69.

[7] E. Wyn-Jones, *R.I.C. Rev.*, 1969, **2**, 59.

[8] R. G. Gordon, *Adv. Magn. Resonance*, 1968, **3**, 1.

equation of motion of the molecular dynamics causing the fluctuation. Most experimental measurements are performed in the frequency domain, however, and in general it transpires that the frequency distribution of the spectral probe is the time-to-frequency Fourier transform of the correlation function.[9]

For the simplest case, a fluctuation decay described by a linear equation of motion, the correlation function is an exponential decay with characteristic time constant $\tau$. The shape of the measured spectrum is then given by equation (1), which is the Fourier transform of this exponential.

$$I_s(\omega) = \frac{\Gamma}{\Gamma^2 + \omega^2} \qquad (1)$$

This equation represents a Lorentzian curve with halfwidth $\Gamma = \tau^{-1}$. The

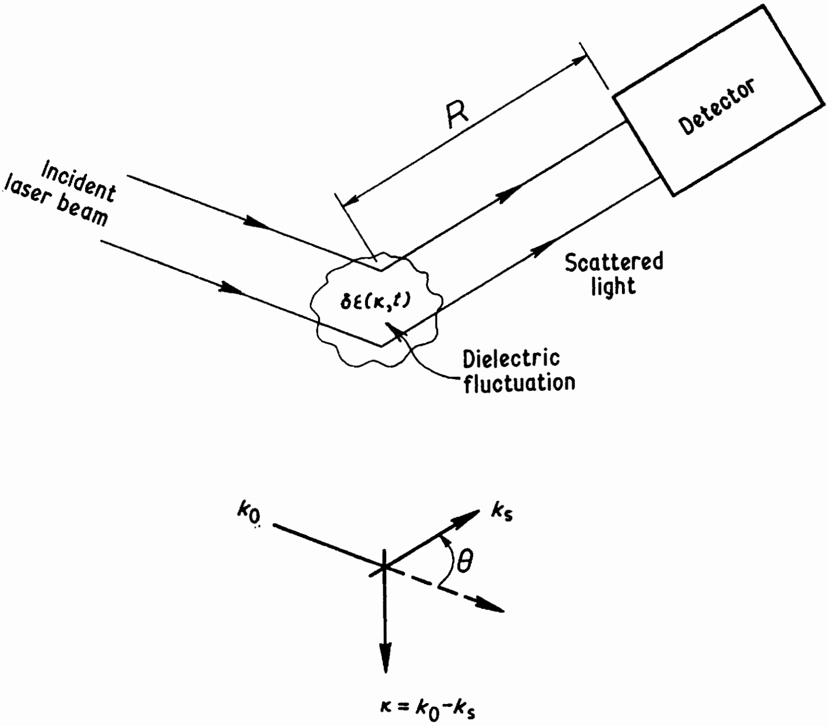

**Figure 2** *Schematic diagram of geometry of light scattering from a single dielectric fluctuation. The absolute magnitudes of* $k_0$ *and* $k_s$ *are* $2\pi/\lambda_0$ *and* $2\pi/\lambda_s$, *where* $\lambda_0$ *and* $\lambda_s$ *are the wavelengths of the incident and scattered light*

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[9] L. Van Hove, *Phys. Rev.*, 1954, **95**, 249.

hypothetical spectrum shown in Figure 1 is a triplet of three such Lorentzian lines.

**A. Light-scattering Formalism.**—The intensity of light scattered from a fluid of $N$ molecules of polarizability $\alpha$ can be written[10]

$$I_s(\varkappa,\omega) = I_0\frac{Nk_0{}^4\alpha^2}{2R^2}(\sin^2\phi)\,S(\varkappa,\omega) \tag{2}$$

where $S(\varkappa,\omega)$ is a function representing the shape of the spectrum, $\boldsymbol{\varkappa}$ is the scattering vector (Figure 2), and $\omega$ is the displacement in angular frequency of the scattered light from the frequency of the incident radiation. $I_0$ and $k_0 = 2\pi/\lambda_0$ are the intensity and wave vector of the incident radiation; $\lambda_0$ is the wavelength of incident light. $R$ is the distance from the scattering volume to the point of observation and $\phi$ is the angle between the electric vector of the incident radiation and $R$. The magnitude of the scattering vector $|\kappa|$ is given by the difference in magnitude of the wave vectors of the incident radiation $k_0$ and the scattered radiation $k_s$

$$|\boldsymbol{\varkappa}| = |\boldsymbol{k}_0 - \boldsymbol{k}_s| \tag{3}$$

Since the absolute frequency shifts of the scattered light are very small compared with the incident frequency we can assume to a very high degree of approximation that no change in wavelength occurs (elastic scattering). We can thus write the so-called quasielastic relation, *cf.* the Bragg condition for $X$-ray scattering:

$$|\boldsymbol{\varkappa}| = 2nk_0\sin(\theta/2) = \frac{4\pi n}{\lambda_0}\sin(\theta/2) \tag{4}$$

Equation (4) enables one to fix accurately the scattering geometry in terms of the known parameters refractive index $n$, wavelength of incident light $\lambda_0$, and scattering angle $\theta$.

The shape function of $S(\varkappa,\omega)$ is the space-time Fourier transform of the function $G(\boldsymbol{r},t)$:

$$S(\varkappa,\omega) = \int_{-\infty}^{+\infty}\int_{-\infty}^{+\infty} G(\boldsymbol{r},t)\exp[-\mathrm{i}(\omega t - \boldsymbol{\varkappa}.\boldsymbol{r})]\,\mathrm{d}t\mathrm{d}\boldsymbol{r} \tag{5}$$

where

$$G(\boldsymbol{r},t) = \langle E(\boldsymbol{r}_0,t_0)\,E^*(\boldsymbol{r},t)\rangle \tag{6}$$

is the autocorrelation function of the electric field of the scattered light $E(\boldsymbol{r}.t)$ and the angular brackets refer to an average over the ensemble of scattered photons. In simple terms $G(\boldsymbol{r},t)$ is a function which is a statistically averaged measure of the magnitude of the scattered field at position $\boldsymbol{r}$ and time $t$ relative to its

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[10] I. L. Komarov and I. Z. Fisher, *Soviet Phys. JETP*, 1963, **16**, 1358.

value at some arbitrary space–time origin and thus characterizes the relaxation or decay dynamics of the scattered field.

Since the fluctuating field $E(\boldsymbol{r},t)$ is proportional to the fluctuations in dielectric constant $\delta\epsilon(\boldsymbol{r},t)$ which cause scattering of the incident light, equation (5) can be written

$$S(\varkappa,\omega) = A\int_{0}^{\infty}\langle\delta\epsilon(\varkappa,0)\,\delta\epsilon(\varkappa,t)\rangle\exp(-i\omega t) \tag{7}$$

where $\delta\epsilon(\varkappa,t)$ represents the Fourier transform in space of $\delta\epsilon(\boldsymbol{r},t)$ and $A$ is a constant. This relation now expresses the shape of the quasielastically scattered spectrum as a Fourier transform of the correlation function which describes the relaxation dynamics of the dielectric fluctuations of the material. To complete the analysis we must therefore compute this correlation function using an appropriate model of molecular dynamics.

The above analysis assumes for simplification that the dielectric constant is a scalar quantity. This holds only for a liquid composed of isotropic scattering units. In a liquid with anisotropic scatterers, $\epsilon$ will be a tensor and orientational molecular motions will cause depolarized light scattering. Details of the theoretical treatment of scattering from orientational fluctuations can be found in the literature[11] and we will content ourselves in a later section of this review with merely discussing applications of the method.

**B. Fluctuation Dynamics in Fluids.**—For a multicomponent fluid system, the dielectric fluctuations can be related in a very simple way to fluctuations in the independent thermodynamic variables entropy, pressure, and concentration of the component species

$$\begin{aligned}\delta\epsilon(\varkappa,t) = {} & \left(\frac{\partial\epsilon}{\partial p}\right)c_{i,S}\,\delta p(\varkappa,t) + \left(\frac{\partial\epsilon}{\partial S}\right)c_{i,p}\,\delta S(\varkappa,t) \\ & + \sum_i\left(\frac{\partial\epsilon}{\partial c_i}\right)_{p,S,c_{j\neq i}}\partial c_i(\varkappa,t)\end{aligned} \tag{8}$$

where $c_i$ is the concentration of species $i$, $p$ is pressure, and $S$ is entropy. For small fluctuations, which is usually a good approximation for a system at thermal equilibrium far from a phase transition, the relaxation dynamics can be described by the linearized laws of hydrodynamics.[12]

Relaxation of the concentration fluctuations is found from Fick's Law of Diffusion[12] to be the exponential relation

$$\delta c_i(\varkappa,t) = \delta c(\varkappa,0)\exp(-D_i\kappa^2 t) \tag{9}$$

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[11] D. A. Pinnow, S. J. Candau, and T. A. Litovitz, *J. Chem. Phys.*, 1968, **49**, 347; R. Pecora and W. A. Steele, *ibid.*, 1965, **42**, 1872; R. Pecora, *ibid.*, 1968, **49**, 1036.

[12] L. D. Landau and E. M. Lifshitz, 'Fluid Mechanics', Addison Wesley, Reading, Mass., 1959.

$D_i$ being the translational diffusion coefficient of species $i$. The decay of isobaric entropy fluctuations is also found, from the law of heat conduction,[12] to be exponential:

$$\delta S(\varkappa,t) = \delta S(\varkappa,0) \exp[-(\kappa^2\lambda_t/\rho C_p)] \tag{10}$$

where $\lambda_t$ is the thermal conductivity, $\rho$ is density, and $C_p$ is the specific heat at constant pressure. Finally, from the hydrodynamic equations, it is found that the isentropic pressure fluctuations correspond to two oppositely propagating sound waves:

$$\delta p(\varkappa,t) = \pm\delta p(\varkappa,0) \cos(v.\kappa t) \exp[-(B\kappa^2 t)] \tag{11}$$

In equation (11) $v$ is the velocity of sound in the fluid and the quantity $B$ is related to the sound absorption coefficient $a$ by the equation

$$B = \frac{1}{2}\,\rho\left[(4/3)\eta_s + \eta_v + \lambda_t\left(\frac{1}{C_V} - \frac{1}{C_p}\right)\right] \tag{12}$$

The RHS of equation (12) contains the parameters shear viscosity $\eta_s$, volume viscosity $\eta_v$, and specific heats $C_p$ and $C_V$ which contribute to the sound absorption $a$ according to the relation

$$a = B\kappa^2/v \tag{13}$$

To obtain the shape of the scattered-light spectrum we simply insert the relations (9), (10), and (11) into (5), using (7) and (8), and carry out the Fourier transform in time. We find that the spectrum is indeed composed of the three lines centred on the frequency of the incident radiation as observed by early workers:

$$I(\varkappa,\omega_0) = \text{const.}[I_R(\varkappa,\omega) + I_B^{(1)}(\varkappa,\omega - \omega_B) + I_B^{(2)}(\varkappa,\omega + \omega_B)] \tag{14}$$

The central Rayleigh line, $I_R(\varkappa,\omega)$, is a superposition of a number of Lorentzian frequency distributions: a broad component as a result of scattering from entropy fluctuations and having a halfwidth $\kappa^2\lambda_t/\rho C_p$, and a number of narrow lines which arise from the concentration fluctuations, one corresponding to each species, with a halfwidth $D_i\kappa^2$. The oppositely propagating sound-wave modes are the source of the satellite Brillouin lines $I_B(\varkappa,\omega \pm \omega_B)$ on either side of the Rayleigh line. The frequency shift of these Brillouin peaks is $\omega_B = \pm iv\kappa$ and each is a Lorentzian distribution with halfwidth $B\kappa^2$. The ratio of the intensity in the Rayleigh line to the intensity in the two Brillouin lines is commonly called the Landau–Placzek ratio $I_R/2I_B$.

For a pure liquid the Rayleigh line is the result of scattering only from entropy fluctuations and in these systems the Rayleigh and Brillouin lines will usually have comparable intensities. In multicomponent systems scattering from concentration fluctuations is very intense, perhaps 200 times greater than that from entropy fluctuations, and it may be that the Brillouin lines are much smaller in comparison. In macromecular solutions and suspensions, of course, the Rayleigh line is so intense relative to the Brillouin peaks that it is usually difficult to observe the latter.

**C. Coupling of Fluctuations with Internal Relaxations.**—The preceding discussion is oversimplified, applicable only to an idealized system, and designed merely to outline the general formalism used to predict theoretically the quasielastic spectrum of light scattered from fluids. The description specifically assumed that the concentration fluctuations do not couple with each other (*i.e.* no chemical reaction occurs between the components) and ignored internal relaxations of the scatterers, such as vibrational and rotational excitations or exchange between two structural states of the fluid, which can also cause local changes in the dielectric constant. To a good approximation, the net result of these internal relaxation processes may be regarded as twofold. First, they will introduce additional non-propagating fluctuation modes representing coupling between the internal relaxation and the concentration and entropy fluctuations. These will also scatter light in a characteristic manner, giving rise to additional unshifted Lorentzian components with halfwidths proportional to the relaxation time $\tau$ characterizing decay of the fluctuation. Coupling to orientational fluctuations is characterized by a $\tau$ which is inversely proportional to the rotational diffusion coefficient $D_r$ of the molecules[11] and usually will only cause a depolarized spectral line to appear when the molecules are optically anisotropic (one exception discussed later is rotational diffusion of an anisometric macromolecule); coupling to structural states of a fluid is described by the structural relaxation time $\tau_s$ representing, for example, the time constant characterizing exchange between molecules of the fluid clustered in transient solid-like configurations and those in disordered ensembles;[13] coupling to intramolecular vibrational excitations is characterized by $\tau_{vib}$, a measure of the rate of decay of the vibrational state[14] (in Kneser liquids $\tau_{vib}^{-1}$ could be the rate of exchange of isomerizable states of a molecule); finally, coupling of diffusion fluctuations to chemical reactions decays with a relaxation time proportional to $\tau_r$ which reflects the rate of the reaction.[15] As an example, for the simplest reaction:

$$\mathrm{A} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{B} \tag{15}$$

$$\tau_r^{-1} = (k_f + k_b) \tag{16}$$

These relaxation times are the same parameters measured by perturbation–relaxation techniques such as ultrasonic dispersion, dielectric relaxation, or temperature-jump methods. In general, it may be a difficult task to observe scattering from the coupled modes, for two reasons. First, the integrated intensity of the scattering is much smaller than that from the first-order fluctuations and,

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[13] K. F. Herzfeld and T. A. Litovitz, 'Absorption and Dispersion of Ultrasonic Waves', Academic Press, New York, 1959.

[14] R. D. Mountain, *J. Res. Nat. Bur. Stand. Sect. A*, 1966, **70**, 207.

[15] D. L. Knirk and Z. W. Salsburg, *J. Chem. Phys.*, 1971, **54**, 1251, and references therein.

secondly, it is spread over a much wider spectral range since the internal relaxation processes are much faster than the hydrodynamic modes. An exception to this case is that of solutions of macromolecules which can have relatively slow intramolecular relaxations.[16]

The presence of internal relaxation processes has a second tangible effect on the quasielastic spectrum which is often more easily observed. At high $\kappa$-vectors, when the frequency of the Brillouin peak approaches that of the internal relaxations, the thermodynamic constants of the hydrodynamic equations which determine the phonon frequency and damping constant are no longer constant with frequency. Two effects can be distinguished. Structural relaxation or chemical transformation involves a volume change and causes a time-dependent viscosity, for example:

$$\eta(t) = \int_{-\infty}^{\infty} \mathrm{d}t'\eta(t - t') = \eta_0 \exp(-t/\tau_s) \tag{17}$$

where $\tau_s$ is the structural relaxation time. Kneser relaxation on the other hand represents a time- or frequency-dependent specific heat due to vibrational coupling to translational modes. These effects cause a dispersion or shift of hypersonic velocity and absorption analogous to the dispersion at ultrasonic frequencies in relaxing media. Since the hypersonic velocity once again depends on the relaxation times of the internal fluctuations it can also be used to probe the dynamics of these processes.

**D. Relaxation Time-scales.**—Figure 3 shows the relaxation time domains of the various fluctuation phenomena which we have discussed above, and the time-scales accessible by the various techniques currently available. It is immediately evident that laser light scattering in principle provides a probe for molecular dynamics over a very wide range of frequencies. In particular, one can simultaneously extract information on the equilibrium and kinetic properties of a system. Another feature evident from Figure 3 is that quasielastic light scattering bridges the frequency gap between ultrasonic absorption and neutron scattering, where many important relaxation phenomena occur. In general any internal relaxation process will usually be characterized by some distribution of relaxation times and the measured value $\tau$ will be a mean of this distribution. Often the form of the distribution of relaxation times can be deduced by careful analysis of spectral profiles.[17]

We note that one can distinguish between fluctuations involving internal and external degrees of freedom simply by studying the quasielastic spectrum at different scattering vectors $\kappa$, *i.e.* by changing the scattering angle or changing the laser wavelength. Scattering from external fluctuations such as diffusion or sound-wave propagation exhibits a $\kappa^2$-dependence whereas the spectral contribu-

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[16] A. M. North, *Chem. Soc. Rev.*, 1972, **1**, 49.

[17] C. J. Montrose and T. A. Litovitz, *J. Acoust. Soc. Amer.*, 1968, **43**, 117.

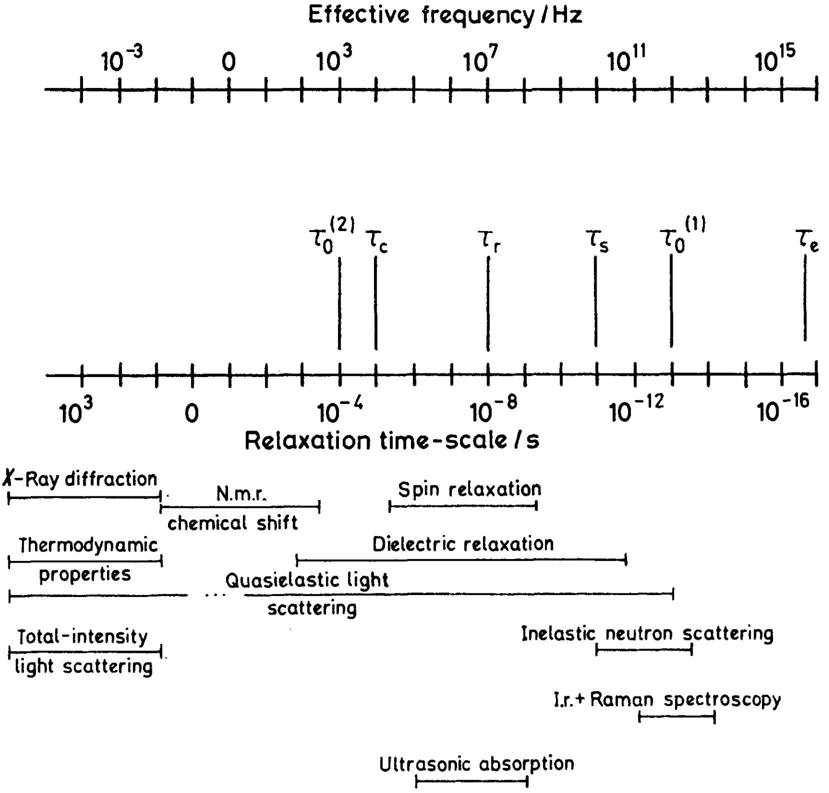

**Figure 3** *Time-scales of molecular dynamics accessible by some of the more commonly used relaxation techniques:* $\tau_e$ *is the time required for an electron to complete one circuit in the innermost Bohr orbit,* $\tau_0^{(1)}$ *and* $\tau_0^{(2)}$ *are representative orientational relaxation times for small molecules and macromolecules respectively,* $\tau_s$ *is a typical structural relaxation time,* $\tau_r$ *is a typical relaxation time for chemical reaction in aqueous solution, and* $\tau_c$ *is a representative time for conformational transition of macromolecules. Depending on the type of system many of these relaxation times may vary by as much as one decade of frequency on either side*

tion from internal relaxations is angle-independent. Under favourable conditions the two types of scattering can be distinguished in this way.

## 3 Experimental Techniques

The high-resolution analysis of the quasielastic spectrum requires, as we mentioned in the introduction, the use of a laser light source. Details of the characteristics of laser radiation and types of laser available can be found in previous reviews.[18] The Brillouin doublet can be adequately resolved by inter-

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[18] See, for example, W. J. Jones, *Quart. Rev.*, 1969, **23**, 73.

ferometry but one cannot usually achieve with interferometric methods the extremely high resolving power necessary to examine in detail the narrow spectral distribution of the central Rayleigh line. This is accomplished by a different technique which utilizes the optical mixing property of photomultiplier tubes (PMT), and we will find it advantageous to describe the two detection methods separately.

Descriptions of experimental schemes used by various investigators can be found in the references quoted in the section on applications. The equipment assembled by the authors at Case Western Reserve University and successfully applied to a wide range of fluid systems is a combined optical mixing–interferometric spectrometer incorporating the same argon ion laser. A schematic diagram of the equipment is shown in Figure 4.

**A. Optical Mixing Spectroscopy.**—The optical mixing methods take advantage of the fact that photomultiplier tubes act as square-law detectors. The photocurrent generated is proportional to the square of the field and the oscillating components of the field therefore effectively mix or beat with each other at the surface of the phototube. The difference 'beats' which correspond to the molecular Doppler frequency shifts in the scattered light can be measured in the photocurrent with a conventional audiofrequency spectrum analyser.

Details of the basic theory and instrumentation of the technique have been reviewed elsewhere.[19] There are two ways of observing the spectrum of scattered radiation by beat-frequency detection. These are commonly labelled the homodyne and heterodyne methods. In the former, only the radiation scattered by the fluid medium is allowed to mix on the photocathode surface; in the latter the quasielastically scattered radiation is purposely mixed with some unbroadened laser light, either by beam-splitting some reference light to the phototube[19] or by elastic scattering from a stationary surface near the scattering volume in the fluid.[19] The advantages of the heterodyne method are that, by regulating the amount of unbroadened light, one can analyse very low light-scattering levels and also that it is easier, for the same reason, to obtain pure spectra than in the homodyne system, which will have a heterodyne component if any stray elastic scattering reaches the phototube (*e.g.* from the scattering cell walls, lens surface, *etc.*). One disadvantage is that any uncorrelated motions of the fluid and elastic scatterers will produce a false spectrum (*e.g.* convection in the fluid or microphonic vibrations of the elastic scattering source). Also, if the beam-splitting method is used, it may be difficult to phase-match the scattered and reference beams at the phototube surface, which is necessary to optimize the efficiency of the light-beating process. Fortunately these effects can all be minimized by appropriate instrumental design.[19]

The optical mixing spectrometer shown in Figure 4 incorporates a swept-filter audiofrequency spectrum analyser and a digital averager which smooths out the random noise of the photocurrent. The characteristics of our spectrometer,

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[19] H. Z. Cummins and H. L. Swinney, in 'Progress in Optics', ed. E. Wolf, North Holland, Amsterdam, 1970, vol. 8.

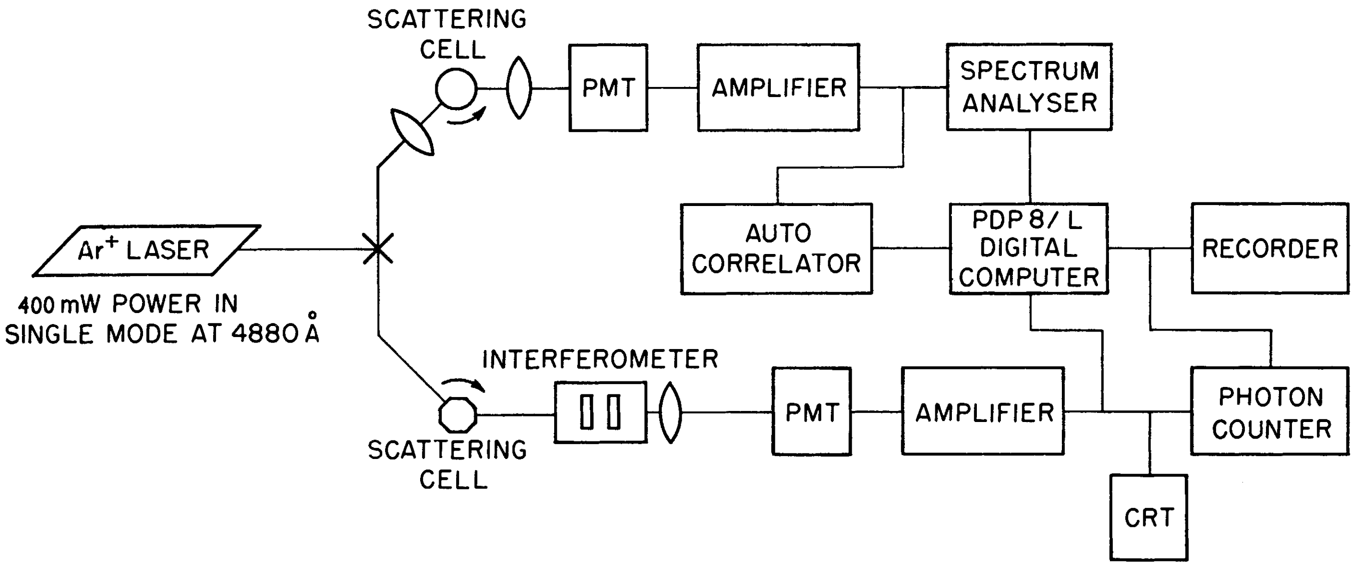

**Figure 4** *Schematic diagram of combined optical mixing spectrometer and Brillouin spectrometer assembled by the authors*

which is flat to 1 MHz, have been described previously.[20] Recently a new generation of multichannel, real-time spectrum analysers and correlators have become commercially available.[21] These instruments have enormously decreased the time required to generate the spectral density function of equation (5) or the equivalent autocorrelation function of equation (6). Finally, it is also possible to measure the autocorrelation characteristics of the scattered light by a photon-counting method which determines the photon statistics of the light incident on the phototube.[22] The advantages of this detection scheme are the ability to work with extremely low light levels and to study very fast relaxation processes (nanosecond relaxation times) at high resolution.

For experimental purposes, it is mandatory that the laser output be free of amplitude fluctuations since these will produce a false low-frequency spectrum.[19,20] Phase fluctuations, however, do not cause false spectra to appear.[19] Also, because the Rayleigh linewidth is usually much narrower than the spacings of the longitudinal laser modes, beats between these modes will not usually interfere with spectral observations and experiments can be performed with multimode lasers. In addition, since the signal to noise ratio is inversely proportional to the number of coherence areas within the solid angle subtended by the collection optics, and since the number of coherence areas in a given solid angle decreases as the scattering volume decreases, it is important to make the scattering volume as small as possible. For this reason, the laser beam should have a small angular divergence and is usually focused into the scattering medium with a short focal length lens. To ensure a well-defined scattering angle, the collecting aperture should be small. As a cautionary note, however, we note that at small scattering angles a significant spread in angular definition of the focused beam can lead to distortion of the observed spectra, an effect which is equivalent to a spread in scattering angles due to a collecting aperture that is too large.[23] The aperture has to be wide enough, however, so that at least one coherence area is irradiated on the photocathode surface.[19] The frequency limit to which spectra can be accurately measured is also determined by the limit of flat frequency response of the PMT and operational amplifier electronics.

**B. Interferometric Spectroscopy.**—The modern Fabry–Perot interferometer consists essentially of two very flat pieces of glass, the inner surfaces of which are coated with a dielectric coating to give reflectivities of 90—99%. The spectral content of light passing through the interferometer is analysed by changing the optical path length between the two mirrors. This is achieved by changing the air pressure between the mirrors or by moving one of the mirrors. The quality of the information obtained from a Brillouin scattering experiment is largely dependent on the stability characteristics of the interferometer.[24] For example,

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[20] A. M. Jamieson and A. G. Walton, *J. Chem. Phys.*, 1973, **58**, 1054.

[21] Y. Yeh, *J. Chem. Phys.*, 1970, **52**, 6218.

[22] C. J. Oliver and E. R. Pike, *Brit. J. Appl. Phys.* [*J. Phys.* (*D*)], 1968, **1**, 690.

[23] R. V. Edwards, J. C. Angus, M. J. French, and J. W. Dunning, jun., *J. Appl. Phys.*, 1971, **42**, 837.

[24] A. R. Maret, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1971.

high-resolution work demands that the two mirrors be kept parallel to angular resolutions of 0.05 arc sec. Commercial instruments are available with piezoelectric adjustment devices which permit an angular resolution of 0.01 arc sec.

In the spectrometer[24] diagrammed in Figure 4, light from an argon ion laser passes through a thermostatted octagonal scattering cell located at the centre of a rotary table. The frequency content of the scattered light collected at an angle $\theta$ to the incident beam is analysed with a piezoelectrically driven Fabry–Perot interferometer. The light then passes to a photomultiplier detector. Three methods are used for processing the signal from the PMT. These are (i) d.c. detection: the output voltage across the PMT load resistor is fed directly in a strip chart or $x$–$y$ recorder with a time constant of ~0.5 s; (ii) photon counting: the PMT output passes to a photon-counting system consisting of a variable-shaping preamplifier, pulse-height discriminator, and linear counter; the resulting signal is then displayed on a strip chart or $x$–$y$ recorder; and (iii) signal averaging: the output of the PMT is signal-averaged by the PDP8/L computer, whose memory is swept in synchronization with the interferometer scan; at the end of a predetermined number of sweeps the signal-averaged spectrum is displayed on an $x$–$y$ recorder.

Interferometric spectroscopy places more stringent demands on the laser source than optical mixing spectroscopy. To reduce the linewidth of the incident radiation as far as possible the laser is operated in a single longitudinal mode using an intracavity etalon. The frequency drift and linewidth jitter of the single mode must be minimal if the Brillouin shifts and linewidths are to be obtained to better than 5%. Good single-mode stability is therefore a very necessary criterion for the laser source which should, in addition, ideally have as short a wavelength exciting line as possible to allow study of maximum Brillouin frequency shifts.

For both the optical mixing and interferometric methods, the laser should have high power to allow a good signal from fluids of low scattering power and also a short-wavelength exciting line since PMT's are usually more efficient at shorter wavelengths. Early studies were conducted with He–Ne lasers, which have high stability but relatively low power. More recently stable commercial argon ion lasers have become available and are being widely used because of their higher power and shorter-wavelength lines.

Finally, it is worth pointing out that interferometric spectroscopy, like classical light scattering, is very sensitive to stray dust particles, which are highly efficient scatterers and cause an erroneously intense Rayleigh line. To obtain accurate Landau–Placzek ratios, it is therefore necessary to achieve a high degree of optical purity for the solutions, either by repeated filtration procedures or by multiple distillation. In the instrument at Case, this was achieved by incorporating the cell in a closed recycling filtration loop consisting of a centrifugal pump and a 0.45 $\mu$m Millipore filter. Since the scattering cell is permanently connected in the filtration loop it was possible to verify Landau–Placzek ratios by refiltering the sample *in situ*. Optical mixing spectroscopy is not nearly so sensitive to parasitic scattering from dust, which merely causes an abnormally intense signal around zero frequency. The main part of the spectral distribution is, however, not at all affected by the dust and can be accurately studied by computer curve fits. This feature is indeed one of the attractive advantages of the technique for measuring molecular weights over alternative methods such as angular dissymmetry of light-scattering intensity.

## 4 Applications

**A. Pure Liquids, Solutions, and Suspensions.**—By far the largest area of applications of quasielastic light scattering has been to the study of molecular properties in the liquid state. We feel it is convenient to separate our review of these investigations into the categories of equilibrium (steady state) and non-equilibrium (relaxation) states.

(i) *Equilibrium Properties. Molecular weights and particle sizes and shapes.* The technique of optical mixing spectroscopy provides a powerful new method for determining particle sizes and molecular weights of macromolecular species in dilute solution which has certain striking advantages over traditional methods, *i.e.* the rapidity of data acquisition, the ability to work with extremely small amounts of macromolecular material, and the decreased importance of solution contamination by large particles (*e.g.* dust, biological debris, *etc.*). The first consideration allows one to follow by repeated measurements quite rapid molecular-weight changes, as in aggregation processes,[25] or rapid size changes, as in denaturation of a protein (*i.e.* one can monitor the kinetics of an irreversible change from the equilibrium state); the last two considerations are very important for many biological applications when only small amounts of pure material may be available or when substantial contamination by cellular debris or other macromolecular contaminants arises.

The parameter measured from the Rayleigh spectrum of concentration fluctuations in a solution of macromolecules is the translational diffusion coefficient $D_t$ of the macromolecules as described in the discussion following equation (14). To obtain a measure of the size of the macromolecules, the Stokes–Einstein relationship can be used in the limit of very dilute solutions:

$$D_t = \frac{kT}{8\pi\eta r_h} \tag{18}$$

where $k$ is the Boltzmann constant, $T$ the absolute temperature, $\eta$ the solvent viscosity and $r_h$ the hydrodynamic radius of the particle. Note that quasielastic light scattering measures the hydrodynamic size, which is the same as that measured by a sedimentation equilibrium experiment but may be slightly different from the size measured by small-angle $X$-ray scattering or electron microscopy. The molecular weight $M$ can be derived by rewriting expression (18) as

$$D_t = \xi M^{-\gamma} \tag{19}$$

[25] A. M. Jamieson, C. E. Downs, and A. G. Walton, *Biochim. Biophys. Acta*, 1972, **271**, 34.

where $\xi$ and $\gamma$ are positive constants.[26] The constant $\gamma$ depends on the conformation of the polymer in solution and has a value which varies from *ca.* 0.5 for a free-draining random-coil molecule to a value of *ca.* 1.0 for a rigid rod conformation. A measurement of molecular weight can be made in one of three ways: it is necessary to know the constants $\xi$ and $\gamma$ either from standards or from having established the conformation of the macromolecule or to combine the diffusion-coefficient data with knowledge of the sedimentation coefficient $S$, for example using the equation[26]

$$S_0/D_0 = M(1 - \bar{V}_2\rho_0)/RT \qquad (20)$$

where $S_0$ and $D_0$ are the sedimentation and diffusion coefficients extrapolated to infinite dilution, $R$ is the gas constant, $\bar{V}_2$ is the partial specific volume of the solute, and $\rho_0$ is the density of the solvent.

Jamieson *et al.*[27] obtained the empirical relation $D_t = 1.33 \times 10^{-4}\, M^{-0.59}$ from the plot of log $D_t$ *versus* log $M$ for three sulphated mucopolysaccharides shown in Figure 5. This relation was then used to determine molecular weights

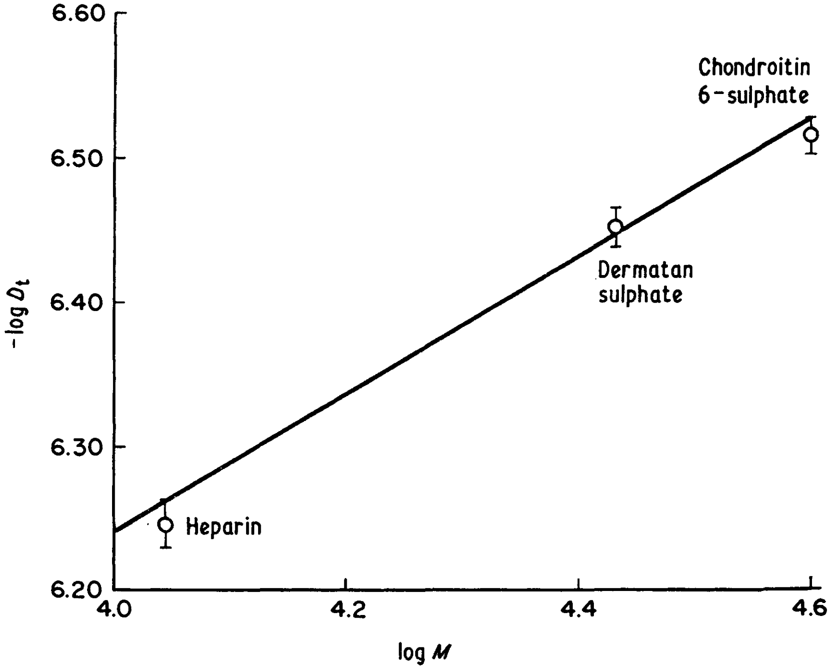

**Figure 5** *Plot showing relationship between weight-average molecular weight and diffusion coefficient for three mucopolysaccharides at* 25 °C

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[26] C. Tanford, 'Physical Chemistry of Macromolecules', John Wiley & Sons, New York, 1965.

[27] A. M. Jamieson, T.-Y. Lee, and I. A. Schafer, *Biophys. J.* 1973, **13**, A154; submitted for publication in *Biochemistry*.

of small quantities of the mucopolysaccharide dermatan sulphate extracted from the human placenta at two stages of foetal development.[27] The susceptibility of the two species of dermatan to molecular-weight degradation by the enzyme hyaluronidase was then studied to investigate the effect of development on the hybrid structure of the material. Frederick *et al.* have studied the relation between $D_t$ and $M$ for the synthetic polymer polystyrene.[28] Various workers have reported studies in which, using equation (18), hydrodynamic sizes have been deduced for a wide range of macromolecular species including viruses,[29] bacteriophages,[30] enzymes,[29,31] and proteins,[25,32] as well as synthetic polymers[33] and latexes.[34]

It is important to note that the diffusion coefficient must be measured in the limit of very dilute solutions where intermolecular interactions are not effective, since otherwise it will not reflect molecular size or weight in a simple way. Also, in many macromolecular systems, especially synthetic polymers, there will often be a distribution of molecular weights and the measured molecular weight will be a statistical average. The nature of the average has been discussed by several authors, notably Pecora[35] and Ford.[36] It turns out that the average measured by quasielastic light scattering is closely related to the weight-average quantity just as in classical light scattering.[36] Information about the shape of the molecular-weight distribution can be obtained, but this requires careful analysis of the spectral profiles.[35,36]

The latest instrumentation allows measurements of diffusion coefficients in as little as 30 seconds. This means that molecular weight (size) changes as in aggregation or flocculation processes or the conformational change of a macromolecule can be monitored by the technique. Biologically significant examples of such phenomena which have been studied are the thermally driven coacervation of the structural protein elastin[25] and the aggregation of the fibrous protein collagen.[23]

It is also possible, in principle, to deduce molecular weights by interferometric spectroscopy from the Landau–Placzek ratio of light scattered from macromolecular solutions.[37] We do not feel this approach is as generally useful as the optical mixing method, however, since contamination of the solutions by macroscopic debris can have a potentially disastrous affect on Landau–Placzek ratios so that a high degree of optical purity is required of the solutions. In addition. data acquisition is much slower. The interested reader is referred to the literature.[37] Two features of Brillouin measurements of molecular weights are that an empirical relation between molecular size and weight does not have to be

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[28] J. E. Frederick, T. F. Reed, and O. Kramer, *Macromolecules*, 1971, **4,** 242.

[29] S. B. Dubin, J. H. Lunacek, and G. B. Benedek, *Proc. Nat. Acad. Sci. U.S.A.*, 1967, **57,** 1164.

[30] M. J. French, J. C. Angus, and A. G. Walton, *Science*, 1969, **163,** 345.

[31] L. Rimai, J. T. Hickmott, T. Cole, and E. B. Carew, *Biophys. J.*, 1969, **9,** 518.

[32] M. J. French, J. C. Angus, and A. G. Walton, *Biochim. Biophys. Acta*, 1971, **251,** 320.

[33] N. C. Ford, W. Lee, and F. E. Karasz, *J. Chem. Phys.*, 1969, **50,** 3098.

[34] J. W. Dunning and J. C. Angus, *J. Appl. Phys.*, 1968, **39,** 2479.

[35] R. Pecora and Y. Tagami, *J. Chem. Phys.*, 1969, **51,** 3298.

[36] N. C. Ford, R. Gabler, and F. E. Karasz, *Adv. Chem.*, in the press.

[37] G. A. Miller, *J. Phys. Chem.*, 1967, **71,** 2305; G. A. Miller and C. S. Lee, *ibid.*, 1968, **72,** 4644.

established beforehand and that it is possible to measure the molecular weights of even very small molecules such as oligomers.

An anisometric molecule will have an orientational degree of freedom and a rotational diffusion mode characterized by the whole-molecule rotational diffusion coefficient. If the molecule is optically anisotropic, the quasielastic light-scattering spectrum will have a broad, unshifted *depolarized* component whose halfwidth is proportional to the rotational diffusion coefficient.[11] A large (polymer) molecule, even if it is optically isotropic, will also have an additional, unshifted polarized component which will begin to contribute substantially to the spectrum at large scattering angles when the concentration fluctuation wavelength $\Lambda = 2\pi/\kappa$ is of comparable size to the length of the molecule.[38] Since the spectral component arising from rotational diffusion does not vary with scattering angle, it is possible to measure the rotational diffusion coefficient of both optically isotropic and anisotropic macromolecules by studying either the polarized Rayleigh spectrum at large scattering angles[38] or the depolarized spectrum at small angles, respectively.[11] Optical mixing studies of rotational diffusion by both experimental approaches have been reported.[39,40] Comparison of translational and rotational diffusion coefficients of macromolecular species can provide accurate information on the molecular geometry.[41] Interferometric analysis of the depolarized spectrum of optically anisotropic small molecules can be used to study the mechanism of rotational diffusion of these species[11] and also to deduce the molecular geometry of macromolecules of intermediate size whose rotational diffusion is too fast to observe by optical mixing methods.[41]

*Activity coefficients.* Interferometric and also optical mixing studies of solutions can provide thermodynamic data in the form of the derivative $(\partial\mu/\partial c)_{p,T}$ describing the concentration dependence of the chemical potential $\mu$. This can then be used to evaluate activity coefficients or 'excess' thermodynamic functions which describe departures from ideal-solution behaviour. This information can be obtained by interferometric measurement of the Rayleigh–Brillouin intensity ratio $J$.[42–44] The complete equation determining $J$ for a binary solution contains many terms.[24,43] Some of the terms are small compared with the concentration-fluctuation term $(\partial n/\partial c)^2/(\partial\mu/\partial c)$ and thus may be neglected within the experimental accuracy of most measurements, leading to the simple equation

$$J = J_0 + J_0K(\partial c/\partial\mu)_{p,T} \tag{21}$$

where $J_0$ is the intensity ratio of the pure solvent (Landau–Placzek ratio) and $K$ is a composite constant which can usually be evaluated from literature data.[24] Maret and Yeager[44] have determined values of $J$ in aqueous electrolyte solutions

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[38] R. Pecora, *J. Chem. Phys.*, 1964, **40**, 1604; *ibid.*, 1968, **48**, 4126.

[39] A. Wada, N. Suda, T. Tsuda, and K. Soda, *J. Chem. Phys.*, 1969, **50**, 3098.

[40] H. Z. Cummins, F. D. Carlson, T. J. Herbert, and G. Woods, *Biophys, J.*, 1969, **9**, 518; D. W. Schaefer, G. B. Benedek, P. Schofield, and E. Bradford, *J. Chem. Phys.*, 1971, **55**, 3884.

[41] S. B. Dubin, N. A. Clark, and G. B. Benedek, *J. Chem. Phys.*, 1971, **54**, 5158.

[42] R. D. Mountain and J. M. Deutch, *J. Chem. Phys.*, 1969, **50**, 1103.

[43] R. D. Mountain and L. Fishman, *J. Phys. Chem.*, 1970, **74**, 10.

[44] A. R. Maret and E. Yeager, *J. Chem. Phys.*, 1972, **57**, 2225; *ibid.*, 1973, **59**, 206.

of chlorides, nitrates, and sulphates at concentrations up to 3M. A typical Brillouin spectrum is shown in Figure 6. They obtained agreement to within

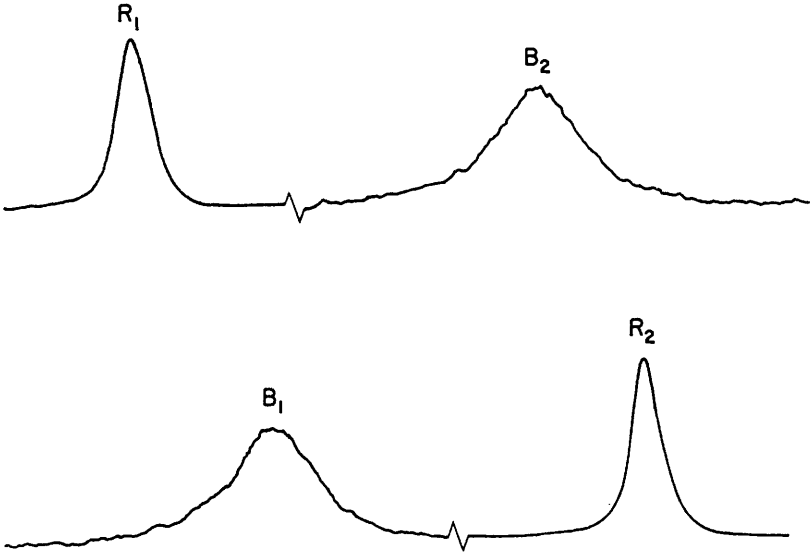

**Figure 6** *Brillouin spectrum of* 0.31M-$NiSO_4$ *at* 25 °C. *The diagram represents one complete interferometer scan from Rayleigh peak* $R_1$ *to Rayleigh peak* $R_2$. *The strong scattering from concentration fluctuations makes it necessary to attenuate the Rayleigh peak by a factor of ten*

5% between the experimentally determined activity coefficients using equation (21) and literature data with the exception of the sulphate solutions. This discrepancy can be plausibly accounted for by the ion-association reactions of the 2:2 sulphates (discussed in a later section) which produce additional terms in equation (21).

Berge *et al.* have examined the Rayleigh line from binary mixtures or organic solvents using the heterodyne technique.[45] By computer-fitting Lorentzians, they were able to separate the two principle components of the Rayleigh line, *i.e.* one due to concentration fluctuations and a broader component due to entropy fluctuations, and thus obtain values of $(\partial\mu/\partial c)$. This method, however, requires a complete and accurate knowledge of the Rayleigh spectral distribution whereas the interferometric method employs a simple measurement of intensities.

*Activation energies.* By monitoring the temperature dependence of the relaxation time for a fluctuation process, it is possible to compute the activation energy for the process from the Arrhenius equation. Figure 7, for example, displays the

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[45] P. Berge, P. Calmettes, M. Dubois, and C. Laj, *Phys. Rev. Letters*, 1970, **24**, 89; M. Dubois and P. Berge, *ibid.*, 1971, **26**, 121.

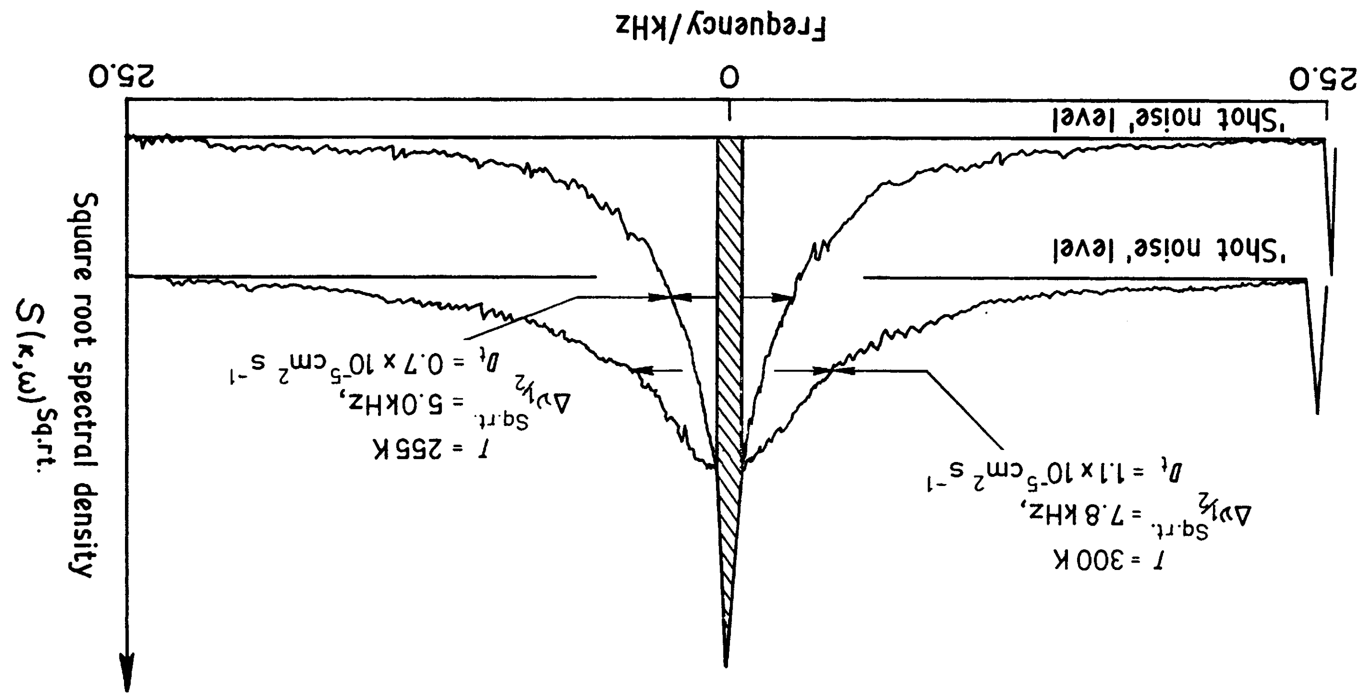

**Figure 7** *Temperature dependence of the high-resolution Rayleigh spectrum of an equimolar mixture of n-hexane and carbon disulphide. The shaded region defines the zero-frequency spike of the spectrum analyser. The output of the spectrum analyser is the square root of the light-scattering spectrum*

optical mixing spectra of a 0.5 mole fraction mixture of n-hexane in carbon disulphide at temperatures of 300 K and 255 K respectively. Knowing the refractive index of the solution at the two temperatures the mutual diffusion coefficients can be calculated and the activation energy for mutual diffusion in this system derived. The value for this system turns out[46] to be 1.4 ± 0.2 kcal mol$^{-1}$, which is somewhat lower than typical values measured in mixtures of liquid hydrocarbons using diffusion-cell techniques.[47] One reason for this is certainly the fact that the molar volume of carbon disulphide is much smaller than that of any of the hydrocarbons studied. Within the experimental error, a similar value, 1.2 kcal mol$^{-1}$, was obtained for a 0.5 molar mixture of n-pentanol in carbon disulphide.[46] This value is much lower than typical self-diffusion coefficients in alcohols measured by n.m.r. techniques,[48] which is understandable since self-diffusion reflects the relative transport of the alcohol and requires breaking of hydrogen bonds. In order to compare these two measurements it would be necessary to study the concentration dependence of the two values and extrapolate to infinite dilution, where they should coincide. Recently these questions have been discussed in an elegant paper by Ahn *et al.*[49] The similarity of the values of the mutual diffusion coefficient in the n-hexane and n-pentanol systems reflects the fact that there is no substantial difference between the interactions of the two species with the carbon disulphide.

(ii) *Non-equilibrium Properties. Diffusion coefficients and electrophoretic mobilities.* The diffusion coefficient of a macromolecule in a solution characterizes its rate of transport through the solvent and of course is an important parameter in its own right. For example, many important chemical and physiological reactions, such as certain free-radical reactions of polymers or the antigen–antibody reaction of the bodyare diffusion controlled. The diffusion coefficient is of course determined by other factors besides its molecular size or geometry, such as degree of ionization, ion atmosphere, and interactions with other molecules. Thus Stephen[50] has proposed using optical mixing spectroscopy to measure the partial charge of macromolecular species and in an interacting system of polymers, one of us has demonstrated the feasibility of studying collision-induced anisotropic translational diffusion phenomena.[51]

At some smaller limiting size, the Stokes–Einstein relation (18) is no longer accurate and the diffusion coefficient does not reflect hydrodynamic diameter in a simple way but is a mutual property of solvent and solute. Berge *et al.* have made some small-angle measurements of mutual diffusion in binary liquid mixtures.[45] Jamieson and Walton[20] (taking advantage of the higher power of their argon laser source) have studied the effect of concentration, chain length, and hydrogen-bonding on mutual diffusion of mixtures of primary alcohols in carbon disulphide and nitrobenzene at somewhat larger scattering angles where

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[46] A. M. Jamieson and A. G. Walton, unpublished results.

[47] A. L. Van Geet and A. W. Adamson, *J. Phys. Chem.*, 1964, **68**, 238.

[48] D. E. O'Reilly and E. M. Peterson, *J. Chem. Phys.*, 1971, **55**, 2155.

[49] M.-K. Ahn, S. J. K. Jensen, and D. Kivelson, *J. Chem. Phys.*, 1972, **57**, 2940.

[50] M. J. Stephen, *J. Chem. Phys.*, 1971, **55**, 3878.

[51] A. M. Jamieson and C. T. Presley, *Macromolecules*, 1973, **6**, 358.

instrumental errors are easier to control. By extrapolating the concentration dependence to infinite dilution it is possible to determine the self-diffusion coefficient of one species for comparison with measurements by other techniques.

An interesting recent development has involved a study of the Rayleigh spectrum of charged particles in solution or suspension when perturbed by an electric field. This combination of electrophoresis with laser light scattering permits the simultaneous measurements of electrophoretic mobilities and diffusion coefficients[52] in a rapid fashion without the complications of concentration gradients and boundary effects. Electrophoretic resolutions are greater than those obtained by moving-boundary experiments.[52] This method appears to have great potential in industrial work involving charged suspensions, *e.g.* electrocoat paint suspensions and liquid developer suspensions for copying machines. In addition, electrophoretic light scattering may provide an important probe for studying the kinetics of interacting systems[52] of macromolecules.

*Vibrational and structural relaxation.* Studies of the relaxation dynamics of molecular processes in pure fluids offer a powerful method of gaining insight into the mechanisms of such processes, which serves as a critical test of theories of the liquid state. As explained in Section 2C, relaxation phenomena manifest themselves as a dispersion or change in magnitude of both the sound velocity $v$ and the absorption coefficient $\alpha$ at frequencies near the relaxation frequency, $\omega = 1/\tau$. For many systems, the change in velocity due to relaxation is of the same magnitude as the experimental precision and usually absorption measurements are more applicable. Relaxation times are obtained from a relation of the form[13]

$$\frac{\alpha}{\omega^2} = \frac{A}{1 + \omega^2\tau^2} + B \tag{22}$$

where $A$ and $B$ are constants. By studying the frequency dependence of $\alpha$, we can deduce the relaxation time $\tau$.

Brillouin scattering techniques have been employed in the determination of acoustical parameters at gigahertz ($10^9$) frequencies, more or less as an extension of existing ultrasonic methods at megahertz ($10^6$) frequencies. The majority of liquids exhibit their important vibrational and structural relaxation phenomena within this frequency domain, which is not in general accessible by other techniques as pointed out earlier in Figure 3.

Brillouin scattering techniques permit sound velocities to be determined to within $\pm 0.2\%$ and sound absorption coefficients to $\pm 3\%$, *i.e.* with precisions approaching those obtainable with ultrasonic techniques.[24] Some examples of the use of Brillouin scattering as a probe for molecular dynamics will now be described.

Several groups have investigated the relaxation of the vibrational specific heat of benzene using ultrasonics and Brillouin scattering. There is disagreement on whether the system exhibits a single or multiple relaxation. O'Connor *et al.*[53]

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[52] B. R. Ware and W. H. Flygare, *Chem. Phys. Letters*, 1971, **12**, 81; B. R. Ware and W. H. Flygare, *J. Colloid Interface Sci.*, 1972, **39**, 670.

[53] C. L. O'Connor and J. P. Schlupf, *J. Acoust. Soc. Amer.*, 1966, **40**, 663.

have proposed a single relaxation time of $5.2 \times 10^{-11}$ s. In more recent work, Nichols *et al.*[54] contend that no single total relaxation of all the vibration modes can make the Brillouin scattering data (> 2 GHz) consistent with ultrasonic data (100 MHz). They proposed two relaxation times $\tau_1 = 3.0 \times 10^{-10}$ s and $\tau_2 = 3.6 \times 10^{-11}$ s.

A number of hypersonic investigations of vibrational relaxation in CCl have been reported in the literature, the most extensive being the work of Stoicheff *et al.*[55] (experimental) and Nichols and Carome[56] (theoretical). These studies used computer techniques to obtain the relaxation time by fitting theoretical expressions to the observed spectra. The results have shown that $CCl_4$ undergoes a thermal relaxation with $\tau = 6.5 \times 10^{-11}$ s, and that the total vibrational contribution to the specific heat is 11.6 cal $mol^{-1}$ $°C^{-1}$, in good agreement with the value of 11.9 cal $mol^{-1}$ $°C^{-1}$ calculated from the known vibrational frequencies of the $CCl_4$ molecule.

Structural relaxation is a general phenomena applicable to all liquids. The time-scales, however, vary considerably from, for example, values of $10^{-9}$ s in highly associated liquids like glycerol at room temperature to $10^{-12}$ s for water at room temperature or the liquefied noble gases at cryogenic temperatures.

The noble-gas liquids have received considerable attention[57,58] because of the possibility of correlating experimental data with machine calculations as well as theories of the liquid state which can be expected to be more rigorous in these simple systems.

Toluene exhibits a structural relaxation spectrum which can be entirely covered by the Brillouin scattering method. The most extensive evaluation of the relaxation curve for toluene has been carried out by Chiao and Fleury,[59] who measured the hypersonic velocity at 14 different frequencies (*i.e.* scattering angles) and found a velocity dispersion of 70 m $s^{-1}$ between the ultrasonic value and their highest frequency. These data correspond to a relaxation time of $2 \times 10^{-11}$ s.

Brillouin scattering in the ultraviolet offers the possibility of measuring even shorter structural relaxations. For example, one could observe in water and aqueous solutions the departure from a constant value of $\alpha/\omega^2$ associated with the structural relaxation curve of structured forms of water ($\tau_S = 10^{-12}$ s at 25 °C). Maret[24] has used an argon laser–harmonic generator system operating at 257.3 nm in an attempt to observe such deviations, but difficulties connected with poor resolving power of the u.v. interferometer prevented the acquisition of accurate data.

As we mentioned earlier, an alternative way of investigating vibrational and structural relaxation is through observation of the additional non-propagating spectral line often called the Mountain line. This fourth component has been

[54] W. H. Nichols, C. R. Kunsitis-Swyt, and S. P. Singal, *J. Chem. Phys.*, 1969, **51**, 5659.

[55] B. P. Stoicheff, G. I. A. Stegemann, W. Gornall, and V. Volterra, *J. Acoust. Soc. Amer.*, 1971, **49**, 979.

[56] W. H. Nichols and E. F. Carome, *J. Chem. Phys.*, 1968, **49**, 1000.

[57] L. Y. Wong and A. Anderson, *J. Opt. Soc. Amer.*, 1972, **62**, 1112.

[58] P. A. Fleury and J. P. Boon, *Phys. Rev.*, 1969, **186**, 244.

[59] R. Y. Chiao and P. A. Fleury, 'Physics of Quantum Electronics', McGraw Hill, New York, 1966.

observed in carbon tetrachloride[55] where there is strong coupling between vibrational and translational modes and also in glycerol,[60] where structural relaxation dominates. The relaxation time can be obtained from the relationship

$$\Gamma_M + 2\Gamma_B = 1/\tau \qquad (23)$$

where $\Gamma$ represents the width of the corresponding spectral component. The advantage of this procedure is that it is possible, in principle, to obtain $\tau$ from a single measurement, in contrast to the use of equation (22), which requires data at many different frequencies.

Macromolecules have relatively slow vibrational relaxation times which can be observed by optical mixing spectroscopy. Fujime and co-workers[61] have studied the relaxation times of these backbone flexing motions in the muscle protein actin and observed the effect of $Ca^{2+}$ ion concentrations on the dynamics of the motions.

*Chemical kinetics.* Kinetic constants of solution reactions can be obtained from a study of the width of the Rayleigh component. Relaxation times as high as $10^{-5}$ s can be measured using the optical mixing technique; faster time regimes require the use of a high-resolution Fabry–Perot interferometer. However, even 'fast' chemical reactions usually have time-scales which cause dispersion at ultrasonic frequencies rather than hypersonic frequencies. The preferred method is therefore the study of the additional non-propagating reactive component of the spectrum. The halfwidth of this fourth component is proportional to the relaxation time $\tau_R$ and, for a simple reaction process with only two distinct species, the kinetic rate constants are related to $\tau_R$ by equation (16).

Yeh has used interferometry to study the relaxation time $\tau$ for the following fast step in 2:2 sulphate association[62]

$$[M^{2+}(H_2O)SO_4^{2-}]aq \rightleftharpoons [MSO_4]aq + H_2O \qquad (24)$$

where M = Zn or Mn. The relaxation times were in good agreement with those measured by ultrasonic relaxation methods. Hypersonic absorption measurements of 2:2 sulphate solutions have been obtained in an attempt to complete the ultrasonic characterization of ionic association in such systems.[63] It has been shown that the high-frequency absorption coefficient must be determined with an accuracy of a few tenths of a percent to distinguish adequately between various proposed mechanisms for the ion association.[64] Unfortunately, measurement of sound-absorption coefficients at hypersonic frequencies have not yet been of sufficient accuracy to be a useful tool for distinguishing various proposed mechanisms of ion association in the 2:2 sulphates.

Optical mixing studies have been reported of the relatively low reaction rates involved in conformational transitions of macromolecules. In one study Yeh measured the rate constant for the helix–coil transition of the copolymer deoxy-

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[60] B. P. Stoicheff, H. F. D. Knaap, and W. S. Gornall, *Phys. Rev. (A)*, 1968, **166**, 13.

[61] S. Ishiwata and S. Fujime, *J. Mol. Biol.*, 1972, **68**, 511, and references therein.

[62] Y. Yeh and R. N. Keeler, *J. Chem. Phys.*, 1969, **51**, 1120.

[63] A. R. Maret and E. Yeager, *J. Acoust. Soc. Amer.*, 1973, **54**, 666.

[64] L. Jacobin and E. Yeager, *J. Phys. Chem.*, 1970, **74**, 3766.

adenylate–deoxythymidylate.[21] Once again, the value of $2.33 \times 10^{-3}$ $s^{-1}$ was in good agreement with temperature-jump relaxation measurements. Simultaneously Yeh found the linear diffusion coefficient within the transition region to have a value of $2.9 \times 10^{-8}$ $cm^2$ $s^{-1}$. Jamieson *et al.*[65] have studied the helix to charged coil transition of poly-L-lysine hydrobromide and identified a broad spectral component in the transition region as due to relaxation *via* the conformation change. Since the relaxation time derived is an order of magnitude smaller than that measured by ultrasonics, they have proposed that it represents an intramolecular diffusion contribution to the conformational kinetics based on the earlier theoretical work of Simon.[66]

**B. Gases, Solids, and Liquid Crystals.**—In this section we will give a brief description of recent developments in applying quasielastic light scattering to the study of gases, solids, and liquid crystals. Brillouin scattering studies have given insight into the nature of molecular dynamics in gaseous systems.[67,68] The hydrodynamic equations are valid in gases only for small scattering vectors.[67] As $\kappa$ increases, the 'size' of the fluctuation becomes small relative to the mean free collision diameter. Under such circumstances a kinetic theory must be invoked to take into account the effects of a distribution of molecular velocities.[69] Thus Brillouin scattering studies of gases can effectively be used as a test of the Boltzmann equation.[67]

Brillouin scattering is also a very useful tool for the measurement of the elastic and photoelastic constants of crystals.[70–72] For example, Gewurtz *et al.*[70] have calculated the adiabatic elastic constants of single crystals of the noble gases from the experimentally determined sound velocity. Studies in these systems provide sensitive tests of recent theories of lattice dynamics. Other measurements have been successfully performed on the theoretically less well characterized crystal systems of calcite[71] and lithium acetate.[72] Berge *et al.* have recently made the first optical mixing experiment on a solid.[73] They found that the spectrum of Rayleigh scattering from entropy fluctuations in single-crystal succinonitrile was exactly that predicted for Rayleigh scattering in a liquid; see equation (10). Brillouin measurements of hypersonic velocities[74] and Landau–Placzek ($J$) ratios[74,75] at the glass transitions in amorphous polymeric solids have been

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[65] A. M. Jamieson, L. Mack, and A. G. Walton, *Biopolymers*, 1972, **11**, 2267.

[66] E. M. Simon, *J. Chem. Phys.*, 1971, **54**, 4738.

[67] T. J. Greytak and G. B. Benedek, *Phys. Rev. Letters*, 1966, **17**, 179.

[68] D. P. Eastman, T. A. Wiggins, and D. H. Rank, *Appl. Optics*, 1966, **5**, 879.

[69] A. Sugawara and S. Yip, *Phys. Fluids*, 9167, **10**, 1911.

[70] S. Gewurtz, H. Kiefte, D. Landheer, R. A. McLaren, and B. P. Stoicheff, *Phys. Rev. Letters*, 1972, **29**, 1768.

[71] D. F. Nelson, P. D. Lazay, and M. Lax, *Phys. Rev.* (*B*), 1972, **6**, 3109.

[72] R. Vacher and L. Boyer, *Phys. Rev.* (*B*), 1972, **6**, 639; R. Vacher, L. Boyer, and M. Boissier, *ibid.*, p. 674.

[73] M. Adam, G. Searby, and P. Berge, *Phys. Rev. Letters*, 1972, **28**, 228.

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reported. Friedman *et al.*[74] discovered a sharp discontinuity in hypersonic velocity at the transition, indicating a discontinuity in the temperature coefficient of the specific volume, but no measurable change in $J$ values, indicating no major discontinuity in the adiabatic compressibility. These results were taken to indicate that the glass transition is not a classical second-order transition, conflicting with the earlier work of Peticolas *et al.*[74] With improved instrumentation Brillouin scattering experiments should provide insight into the relaxation effects associated with the glass transition.

A rapidly developing area for applications of the laser light-scattering techique is that of liquid-crystalline materials which have a highly anisotropic molecular polarizability. Such systems are extremely important both in the biological area, *e.g.* in the physical chemistry of the lipids of the cell membranes, and in commercial applications, *e.g.* as potential electro-optic storage materials. Thermal fluctuations in the orientation of the ordered regions (equivalently, angular fluctuations of the molecular axis or director) cause large fluctuations in the optical anisotropy of these systems and intense depolarized Rayleigh scattering. The initial theoretical work of de Gennes *et al.*[75] and subsequent experimental optical mixing studies by the Orsay Liquid Crystal Group[76] have established a relationship between this depolarized quasielastic spectrum and the various elastic and viscosity coefficients which describe the anisotropic dynamic properties of the ordered matrix of nematic liquid crystals. Recently Galerne *et al.*[77] have observed similar effects in certain smectic liquid-crystal systems.

Much interest has focused on the order–disorder transition behaviour at the temperature where the liquid crystal changes to the normal isotropic liquid state. In the nematic–isotropic transition Stimson and Litster have shown,[78] by high-resolution interferometric studies of the laser light scattering from the fluctuations of ordered regions in the isotropic phase, that as the transition temperature is approached the spectrum exhibits the characteristics (discussed in the next section) of a second-order phase transition, even though the transition itself is known to be first-order.[78] Early Brillouin scattering studies[79] near a cholesteric–isotropic transition temperature showed a dramatic discontinuity in hypersonic velocity and damping coefficient at the transition, which would indicate a well-defined, first-order phase transition. The more recent work of Rosen and Shen,[80] however, found no measurable discontinuity and indicates that the earlier results were due to crystal domain boundary effects.

**C. Second-order Phase Transitions.**—Optical mixing spectroscopy has found particularly valuable application in studies of the critical opalescence which occurs at either the liquid–gas or liquid–liquid phase-separation temperatures.

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As a binary liquid mixture approaches the temperature at which its two components separate, long-range concentration fluctuations develop, causing a striking increase in the intensity of light scattered by the fluid (*i.e.* opalescence). The spectral halfwidth $\Gamma_c$; of this scattered light has a more complicated dependence on scattering vector and temperature than that indicated by equation (7):

$$\Gamma_c = D_0\kappa^2(T - T_c)^\nu[1 + \tfrac{1}{6}l^2\kappa^2 T_c\gamma/(T - T_c)] \qquad (25)$$

where $D_0$ is the mutual diffusion coefficient far from the phase transition, $T_c$ is the critical point temperature, $l$ is a characteristic length defining the range of intermolecular forces which are driving the phase separation, and $\nu$ and $\gamma$ are critical 'scaling' parameters whose determination serves as a crucial test of the theories of the critical point.[81] As the temperature $T_c$ is approached, equation (25) indicates that the halfwidth of the spectrum becomes increasingly narrow. Analysis of the temperature dependence and angle dependence of the spectrum enables one to deduce the parameters $l$, $\nu$, and $\gamma$. A similar relation to (25) holds for the spectrum of light scattered by entropy fluctuations of a pure liquid near its critical point[82] and for the diffusion coefficient of a polymer in solution[83] as the critical temperature of its separation from the solvent phase approaches. Studies of the Rayleigh spectrum in the critical region have been successfully carried out in all of these cases,[81-83] and have proved to be extremely useful in developing a molecular understanding of these important phase-separation processes. Bak *et al.*[84] have also carried out a spectral analysis of the laser scattering from concentration fluctuations at the critical point of a ternary liquid mixture to study the effect on the 'scaling' parameters of the third component.

Brillouin spectroscopy has been successfully used to probe the behaviour of thermodynamic parameters, such as the isothermal compressibility of a fluid, and the relaxation times of internal degrees of freedom at the critical point. Mountain[85] has successfully explained the experimental Brillouin linewidth data of Ford *et al.*[86] and the Rayleigh linewidth data of Swinney and Cummins[87] for scattering from $CO_2$ at temperatures just above the critical point. The model used was a modification of the linearized hydrodynamic equations to include a non-local relationship between density and pressure fluctuations, and a frequency-dependent volume viscosity of the type shown in equation (17).

**D. Miscellaneous.**—A number of novel applications of optical mixing spectroscopy have recently appeared in the literature. The early work of Bouchiat and co-workers[88] demonstrated the usefulness of the method for studying the

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[82] N. C. Ford and G. B. Benedek, *Phys. Rev. Letters*, 1965, **15**, 649.

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[87] H. L. Swinney and H. Z. Gammon, *Phys. Rev.*, 1968, **21**, 9.

[88] M. A. Bouchiat, J. Meunier, and J. Brossel, *Compt. rend.*, 1968, **266**, *B*, 255; M. A. Bouchiat, *ibid.*, 1966, **266**, *B*, 301; M. A. Bouchiat and J. Meunier, *Phys. Rev. Letters*, 1969, **23**, 752.

viscoelastic properties of liquid surfaces by analysing the light scattered from surface tension waves ('ripplons'). This work has been extended recently by Mann *et al.*[89] and Fan[89] to studies of the mechanical deformation behaviour of model biomembrane systems. Maeda and Fujime[90] have successfully constructed a mixing spectrometer incorporating an optical microscope which will allow one to monitor the dynamics of localized cellular events *in situ*. Some workers, notably Berge *et al.*, experimentally,[91] and Nossal, in a later theoretical treatment,[92] have demonstrated the feasibility of using optical mixing spectroscopy to measure the mean lateral swimming rates of motile micro-organisms, such as spermatozoa.[91] The method seems to offer a useful probe for observing the effects of chemotactic agents on the mobility of these species.[92] Finally, Carlson *et al.*[93] in an important paper have recently shown that, in an associating system of macromolecules (specifically the dimerization of the muscle protein myosin), information on the association constants and geometry molecular complex can be deduced by quasielastic light scattering.

**E. Stimulated Brillouin Scattering.**—We conclude the applications section with a brief discussion of stimulated Brillouin scattering.[94,95] In this technique, the continuous-wave laser light source is replaced with a high-power *Q*-switched solid-state laser. The back-scattered Brillouin light mixes with the incident-light pulse producing extremely strong pressure waves owing to electrostrictive effects. The frequency of this pressure wave is equal to that of the thermal fluctuations which are the source of the back-scattering. Further scattering of the incident pulse from these induced sound waves occurs, and the scattered light waves increase in amplitude until the energy of the incident wave is depleted. Clearly the magnitude of the stimulated Brillouin-scattered light depends on the amplitudes of the incident and scattered light waves, *i.e.* the maximum interaction will occur at 180° scattering angle. The principal advantage of this technique over conventional Brillouin scattering is that the sound velocity is obtained in a more direct way because the relatively high intensity of the scattered radiation permits the concentric ring output of the Fabry–Perot interferometer to be photographed. For further details the reader is referred to the literature.[94,95]

## 5 Prognosis

The past five years have seen a remarkable proliferation of literature in the field of quasielastic laser light scattering analogous to the surge of applications of laser Raman spectroscopy following the pioneering measurements of that

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[89] J. A. Mann, J. F. Baret, F. J. Dechow, and R. S. Hansen, *J. Colloid Interface Sci.*, 1971, **37**, 14; C. Fan, *ibid.*, 1973, **44**, 369.

[90] T. Maeda and S. Fujime, *Rev. Sci. Inst.*, 1972, **43**, 566.

[91] P. Berge, B. Volochine, R. Billard, and A. Hamelin, *Compt. rend.*, 1967, **265**, *D*, 889.

[92] R. Nossal, *Biophys. J.*, 1971, **11**, 341.

[93] T. J. Herbert and F. D. Carlson, *Biopolymers*, 1971, **10**, 2231.

[94] N. R. Goldblatt and T. A. Litovitz, *J. Acoust. Soc. Amer.*, 1967, **41**, 1301.

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technique: there is every reason to expect this expansion to continue in the years ahead.

**Optical Mixing Spectroscopy.**—The optical mixing technique has obvious dramatic advantages over the traditional methods for size, shape, and molecular weight determinations of macromolecules because of the ease, rapidity, accuracy, and relative freedom of the measurements from errors due to particulate contamination. Similarly, optical mixing spectroscopy now offers the best method for measuring diffusion coefficients, particularly since the laser beam is a light probe which does not perturb the medium. The dynamics of relatively slow solution processes (relaxation times down to $10^{-6}$ s) can also be usefully studied by this technique. Again, most macromolecular systems fall into this category and consequently a single mixing spectrometer enables essentially a complete physical characterization of such systems.

The major experimental difficulties have now been resolved and we expect commercial instruments to become available in the near future.

**Brillouin Spectroscopy.**—Brillouin scattering using interferometric techniques is capable of providing acoustical information in the form of sound velocities and absorption coefficients with precision and convenience equal to that obtainable with ultrasonic techniques. In addition, the technique has won acceptance as an important tool to the investigator in chemical physics for the study of the dynamics of processes with relaxation times in the range $10^{-6}$—$10^{-11}$ s. The measurement of Rayleigh–Brillouin intensity ratios can provide accurate values for thermodynamic parameters such as activity coefficients, specific heats, and compressibilities.

The stability characteristics of commercial interferometers and lasers are less than optimum for many Brillouin measurements. However, there is every reason to expect that these difficulties will be surmounted.

We have reviewed many diverse chemical problems to which quasielastic light scattering has been successfully applied in an increasing number of laboratories. In this context we point out, in conclusion, that a single laser source in its optimum experimental configuration, allowing both the Rayleigh and Brillouin spectrum to be accurately studied, enables the investigation of a complete range of molecular dynamics from the steady-state (thermodynamic) parameters to relaxation times as small as $10^{-13}$ s.