Light scattering from condensed matter—Contributions of the Raman school

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Abstract

An attempt has been made to highlight some of the contributions of Raman and his coworkers to the field of light scattering from condensed matter. The topics reviewed cover Rayleigh, Brillouin and Raman scattering from a variety of systems—pure liquids, liquid mixtures, colloids, crystals and glasses.

Key words: Light scattering, condensed matter, Raman.

1. Introduction

Light scattering which encompasses Rayleigh, Brillouin and Raman scattering has played a key role in the understanding of static and dynamic properties of condensed matter—be it liquids, crystals, glasses, colloidal suspensions, emulsions or polymers. Professor C. V. Raman published more than 70 papers and his students, collaborators and those who were inspired by him published about 400 papers on various aspects of light scattering from a wide variety of systems[1]. The remarkable and pioneering results are too many to be reviewed in this paper, and hence we attempt to highlight only a few of them. All the results presented here are from the pre-laser era. It will be seen that even without lasers which have completely revolutionized and rejuvenated the field of light scattering, Professor Raman and his school made notable contributions—the foremost one, of course, being the discovery of the effect which bears his name.

The scattering of light, in general, occurs due to optical inhomogeneities in the scattering medium. These inhomogeneities can arise due to different reasons, the most obvious case being of gross inclusions of one substance in the other as in colloidal suspensions. The thermodynamic fluctuations of density and temperature (or pressure and entropy), orientations of anisotropic molecules, the fluctuations of concentrations in mixtures or the vibrations of atoms about their equilibrium positions produce fluctuations of dielectric constant of the medium and hence scatter light. The temporal behaviour of different fluctuations is different with time and therefore they modulate the scattered light in different ways.

The entropy fluctuations at constant pressure or the concentration fluctuations do not propagate in the medium and hence result in the Rayleigh scattering unshifted in frequency. The Rayleigh line is, of course, broadened due to the dissipation of the fluctuations. The temperature fluctuations will damp out due to thermal dissipative processes which depend on thermal conductivity and the concentration fluctuations are governed by translational diffusion of the molecules. The orientational fluctuations of the anisotropic molecules dissipate due to rotational relaxation processes.

The fluctuations of density or pressure at constant entropy (adiabatic) represent local compressions or rarefactions which can travel in the medium with velocity of elastic waves. The incident light is scattered due to the grating formed by the periodic stratifications of a particular wavelength governed by the well-known Bragg condition. The propagation of the 'grating' produces Doppler shift of the incident frequency. This view was first put forward by Brillouin[2] and hence the Doppler-shifted components on either side of the Rayleigh line due to waves travelling in opposite directions but with the same speed are called Brillouin lines. These lines are broadened due to thermal dissipative processes which damp out the elastic waves (sound waves or acoustic phonons).

The fluctuations in the dielectric function can also arise due to the time dependence of some excitations of the medium. These excitations which can be the vibrational modes of a molecule or optical phonons in solids, electronic excitations or magnons in magnetic systems cause inelastic scattering of light called Raman scattering. This was first discovered by Professor C. V. Raman on February 28, 1928 when he pointed a direct-vision spectroscope on to the scattered track in many pure organic liquids and observed the presence of another colour separated from the incident colour[3,4]. This was the culmination of seven years of intense research by Raman and his many coworkers on light scattering.

The above discussion points out that the spectrum of scattered light contains valuable information on the 'imprints' of different forms of fluctuations in the medium. The four quantities which contain the knowledge of the fluctuations and can be determined experimentally are: (1) the frequency shift (2) the intensity of the scattered radiation (3) spectral linewidth and (4) polarization.

The plan of the paper is as follows. In Section II, we present the important contributions of the Raman school to Rayleigh-Brillouin scattering from liquids, crystals and glasses. Under this heading, the topics to be briefly reviewed are:

i) Intensity of the total scattered light from the liquids.
ii) Brillouin scattering from liquids, deviation of intensity ratio of Rayleigh to Brillouin lines from the Landau-Placzek ratio.
iii) Brillouin scattering from viscous liquids and glasses.
iv) Light scattering from glasses—the concept of 'frozen-in' fluctuations, depolarization of scattered light in terms of Krishnan ratio, and Brillouin scattering.
v) Brillouin scattering from crystals.

Section III deals with Raman scattering. A very large number of systems were studied for the first time by Raman and his coworkers to probe structure, symmetry and dynamical properties. We shall not give a catalogue of all those investigations but briefly

discuss only the following: (i) use of Raman spectroscopy in chemical analysis, (ii) resonance Raman scattering, (iii) symmetry and Raman selection rules, (iv) crystal dynamics and (v) phase transitions and the soft mode.

2. Rayleigh-Brillouin scattering from liquids, crystals and glasses

2.1 Scattering from liquids

Historically speaking, Smoluchowski[5] invoked the idea of density fluctuations to explain the phenomenon of critical opalescence. Later, Einstein[6] developed the statistical theory of light scattering based on fluctuations in density for a pure liquid along with concentration fluctuations in multi-component systems.

Let I_0 be the intensity of incident light of wavelength λ. The total scattered intensity by a volume element v reaching the detector at a distance L is given by

$$I_s = \frac{I_0 \, v^2}{L^2} \, \frac{\pi^2}{2\lambda^4} \, \langle (\delta\epsilon_q)^2 \rangle \, (1 + \cos^2 \theta) \tag{1}$$

where $\delta\epsilon_q$ is the qth Fourier component of fluctuations in dielectric constant. The wavevector $\vec{q} = \vec{K}_i - \vec{K}_s$ and θ is the angle between $\vec{K}_i$ and $\vec{K}_s$ which are the wavevectors of the incident and scattered light. The brackets, $\langle \ \rangle$, denote the average over the equilibrium ensemble.

Taking ϵ to be a function of pressure P and entropy S,

$$\langle (\delta\epsilon)^2 \rangle = \left(\frac{\partial\epsilon}{\partial P} \right)_s^2 \, \langle (\delta P)^2 \rangle + \left(\frac{\partial\epsilon}{\partial S} \right)_P^2 \, \langle (\delta S)^2 \rangle \tag{2}$$

where subscript q has been dropped for the sake of convenience. We can write

$$\left(\frac{\partial\epsilon}{\partial P} \right)_s^2 \, \langle (\delta P)^2 \rangle = \left(\frac{\partial\epsilon}{\partial\rho} \right)_s^2 \, \langle (\delta\rho)^2 \rangle;$$

$$\left(\frac{\partial\epsilon}{\partial S} \right)_P^2 \, \langle (\delta S)^2 \rangle = \left(\frac{\partial\epsilon}{\partial T} \right)_P^2 \, \langle (\delta T)^2 \rangle; \tag{3}$$

$$\left(\frac{\partial\epsilon}{\partial T} \right)_P = \left(\rho\frac{\partial\epsilon}{\partial\rho} \right)_T \, \alpha_v + \left(\frac{\partial\epsilon}{\partial T} \right)_\rho .$$

From the theory of thermodynamic fluctuations[7]

$$\langle (\delta\rho)^2 \rangle = \rho^2 \, k_B \, T \, \beta_s / v,$$

$$\langle (\delta T)^2 \rangle = \frac{k_B \, T^2}{C_P \, \rho v} . \tag{4}$$

Here ρ and T are density and temperature, β_s the adiabatic compressibility, C_v the specific heat at constant volume, α_v the volume thermal expansion coefficient and k_B the Boltzmann constant. Using eqns (2)–(4) in eqn (1), one gets (for $\theta = 90°$)

$$I_s = \frac{I_0 \cdot v}{L^2} \quad \frac{\pi^2}{2\lambda^4} \left[\left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_s^2 \beta_s k_B T \right.$$

$$+ \frac{k_B T^2}{C_p \rho} \left\{ \alpha_v^2 \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 + \left(\frac{\partial \epsilon}{\partial T} \right)_\rho^2 \right\} \left. \right]. \tag{5}$$

It can be shown[8] that if

$$\frac{T \alpha_v^2}{C_p \beta_s \rho} \left[\left(\frac{1}{\alpha_v} \frac{\partial \epsilon}{\partial T} \right)_P + \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T \right] \ll \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T, \tag{6}$$

eqn (5) goes over to the Einstein formula:

$$I_s = \frac{I_0 v}{L^2} \quad \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 \beta_T k_B T, \tag{7}$$

where β_T is the isothermal compressibility.

So far $(\delta \epsilon)$ is taken to be a scalar which is the case when molecules comprising the medium are optically isotropic. On the assumption that molecules are freely rotating, Rayleigh and Gans have shown that the optical anisotropy makes an additional contribution $(6+6r)/(6-7r)$ to the scattering where r is the depolarization ratio given by $r = I_H/I_V$, $I_H(I_V 2)$ is the scattered intensity with polarization parallel (perpendicular) to the scattering plane. The total scattered light due to density and anisotropy fluctuations is given by

$$I_s = \frac{I_0 v}{L^2} \quad \frac{\pi^2}{2\lambda^4} \left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T^2 \beta_T k_B T \quad \frac{(6+6r)}{(6-7r)}. \tag{8}$$

In order to compare eqn (8) with experiments, it is necessary to know $(\rho \partial \epsilon / \partial \rho)_T$. Einstein used the Lorentz-Lorenz formula connecting ϵ and ρ:

$$\frac{\epsilon - 1}{\epsilon + 2} = C' \rho \tag{9}$$

where C' is a constant. Differenting (9),

$$\left(\rho \frac{\partial \epsilon}{\partial \rho} \right)_T = (\epsilon - 1) \frac{(\epsilon + 2)}{3} \tag{10}$$

After substituting (10) in (9) to get I_s, it was found that the computed scattered intensities are appreciably larger than the measured values. The discrepancy was reduced by Ramanathan[9]. He used the relation, $\epsilon - 1 = $ (constant)ρ by arguing that $(\epsilon + 2)$ in eqn (9) arises due to the action of molecules located outside the small sphere (the Lorentz sphere) surrounding the molecule under observation. The influence of fluctuations of ϵ in the material outside the Lorentz sphere on the change of field inside the sphere will be small and hence the term $(\epsilon + 2)$ can be regarded as constant. Then one gets

$$I_s = \frac{I_0 \cdot v}{L^2} \quad \frac{\pi^2}{2\lambda^4} \quad (\epsilon - 1)^2 \; \beta_T k_B T \cdot \left(\frac{6 + 6r}{6 - 7r} \right) \tag{11}$$

The agreement of eqn (11) with experiments, though satisfactory for a number of liquids, is still not good. Venkateswaran[10] suggested that the limitation involved in adopting any relation between ϵ and ρ is removed by using the experimentally determined values of adiabatic piezoelectric coefficients $(\rho\partial\mu/\partial\rho)_s$ (μ = refractive index = $\sqrt{\epsilon}$) obtained by Raman and Venkataraman[11]. The contributions of Krishnan[12], Raman and Rao [13], Ramanathan[14] and Ananthakrishnan[15] are noteworthy for the measurements of scattered intensities in a number of liquids. Rao[16] investigated the dependence of the scattered intensities on temperature for liquids and interpreted his results in terms of eqn (11).

Raman and Krishnan[17], and Cabannes and Daure[18] discovered that a depolarised continuous background appears which extends out ~ 150 cm^{-1} from the unshifted line and even further. This arises as result of the rapid temporal changes of the fluctuations of the anisotropy. In recent times, this broad wing has been investigated extensively to study rotational-relaxation mechanisms.

2.2 Brillouin scattering from liquids and Landau-Placzek ratio

As mentioned in the introduction, the density fluctuations at constant entropy give rise to Brillouin lines shifted by frequency

$$\omega_B = \pm v_e q \tag{12}$$

where v_e is the appropriate sound velocity and $q = (4\pi\mu \sin \theta/2)/\lambda$. Here μ is the refractive index of the medium.

The sum of the intensities $(2I_B)$ of the two Brillouin components is given by the first term in eqn (5) and the other terms in the equation contribute to Rayleigh line intensity (I_R). Landau and Placzek[19] showed that, under certain assumptions,

$$\frac{I_R}{2I_B} = \frac{\beta_T - \beta_s}{\beta_s} = \frac{C_p - C_v}{C_v} = \gamma - 1. \tag{13}$$

Even though the prediction of the shifted lines was made by Brillouin[2] in 1922, the first experimental observation was made by Gross[20] in liquids after the discovery of the Raman Effect. Krishnan[21] in his review article on Brillouin scattering mentions that the

most satisfactory patterns of the Doppler-shifted Brillouin components in liquids were recorded by Rao[22]. Extensive work was done by Venkateswaran[23] and Sunanda Bai[24].

Venkateswaran[23] was the first to demonstrate the failure of Landau-Placzek relation, eqn (13), in many liquids. Cummins and Gammon[25] attributed this discrepancy due to the neglect of dispersion of the thermodynamic quantities in the hypersonic region. The quantities involved in the expression for I_R correspond to the static value ($\omega = 0$) whereas the quantities in $2I_B$ should be those in the hypersonic frequency range ($\omega \sim 10^{10}$ Hz). The correction for the dispersion does not remove the discrepancy completely, the observed $I_R/2I_B$ is always higher than the theoretical values[25]. For example, the observed value of $I_R/2I_B$ in benzene is 0.84, eqn (13) gives 0.43 and after correction for dispersion, it is 0.66.

The relatively small calculated values of $I_R/2I_B$ point out that there are other mechanisms contributing to the Rayleigh intensity. These can be understood in the hydrodynamic theory of light scattering by Mountain[26]. He pointed out that the spectral distribution contains a non-propagating mode in addition to the usual thermal and phonon modes which give rise to the central and two shifted-Brillouin components. This new mode called the fourth component arises from the exchange of energy between the internal vibrational modes and translation modes of the molecules and dissipates with relaxation time τ. It gives rise to the appearance of a broad line of unshifted frequency with a width $\Delta\omega_{FC} \simeq \tau^{-1}$ and integrated intensity $(1 - v_0^2/v_\infty^2)\gamma^{-1}$, where v_0 and v_∞ are the low- and high-frequency sound velocities. The fourth component is polarised in the same plane as the Brillouin components. Figure 1 shows a schematic of the spectrum of scattered light. The presence of the fourth component also makes Brillouin lines asymmetric, and this can depend on temperature due to the dependence of the relaxation time τ (and hence $\Delta\omega_{FC}$) on T. Since the fourth component is mainly present over the central component, the measured ratio of $I_R/2I_B$ will be higher than that estimated from eqn (13) even after applying correction for the dispersion.
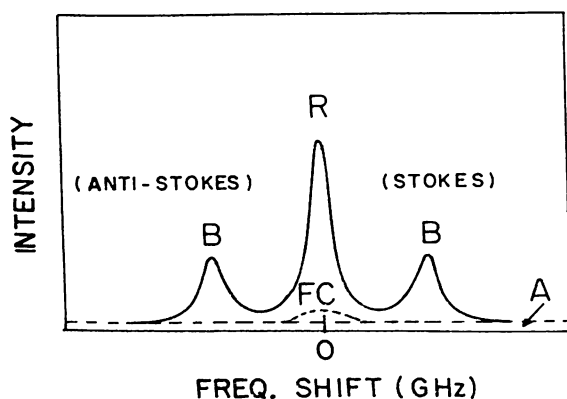

FIG. 1. Schematic illustration of the spectrum of the scattered light from a liquid. R and B stand for Rayleigh and Brillouin components. A is the background due to orientational fluctuations and FC is the fourth component proposed by Mountain[26].

Knapp et al[27] have argued that in addition to the thermal relaxation process introduced by Mountain in frequency-dependent bulk viscosity, other relaxation processes described by frequency-dependent shear viscosity or elastic modulii would give rise to velocity dispersion and hence to the presence of the fourth component. Their experiments on glycerine as a function of temperature show that the broad intense background arises due to the structural relaxation occurring predominantly in associated liquids (which tend to form ordered molecular aggregates over various volumes).

2.3 Brillouin scattering from viscous liquids and glasses

A finite damping of the sound waves in a viscous medium contributes to the linewidth, $\Delta\omega_B$, of the Brillouin lines[8,19]:

$$\Delta\omega_B = \Gamma q^2 = 2\alpha v_e \tag{14}$$

where

$$\Gamma = \frac{1}{\rho}\left[\frac{4}{3}\eta_s + \eta_v + \frac{\sigma}{C_p}(\gamma - 1)\right]. \tag{15}$$

Here η_s and η_v are the shear and bulk viscosities, σ the thermal conductivity and α the absorption coefficient for the sound waves in the medium. The term $\sigma(\gamma - 1)/C_p$ is usually very small as compared to viscosity terms in eqn (15). The peak of the Brillouin line is also shifted from ω_B given by eqn (12) as

$$\omega'_B = (\omega_B^2 - 2\alpha^2 v_e^2)^{1/2}. \tag{16}$$

It appears that when η_v and η_s are large (in viscous liquids), $\Delta\omega_B$ will be very large and the shift ω'_B will go to zero, suggesting that the Brillouin lines should not be seen in viscous liquids and glasses. Contrary to this, Venkateswaran[23] observed the Brillouin lines in a number of viscous liquids, including glycerine and castor oil. The shifted components were seen in glycerine up to a viscosity of 120.4 poise and for castor oil, up to 6.04 poise (for comparison, the viscosity of water at room temperature is ~ 0.01 poise).

A number of unsuccessful attempts were made before 1950 by Gross, Ramm, Raman and Rao, Venkateswaran, Velichkina, and Rank and Douglas to detect Brillouin lines in glasses. The first successful observation was reported by Krishnan[28] in fused quartz by using 2536 Å excitation from mercury vapour lamp. The Brillouin shift was ± 1.5 cm^{-1} which agreed well with the calculated ± 1.65 cm^{-1} from the elastic constants.

Let us now see how we can qualitatively understand Venkateswaran's observations in viscous liquids and Krishnan's result on fused quartz. The argument that the absorption coefficient α is proportional to the viscosity η cannot be valid for the entire range of η because, if this were the case, the glasses (for which $\eta \sim 10^{13}$ poise) cannot be good conductors of sound. In reality, glasses are good conductor of sound even at high frequencies. This happens because of the relaxation processes due to which α increases with increase in viscosity up to a definite maximum, after which it falls off with continued in-

crease in η. The difficulty in detecting Brillouin lines in earlier observations can be understood by realising that $I_B \propto \beta_s$ [see eqn (5)] and $\beta_s = (\rho v_{HS})^{-1}$ where v_{HS} is the hypersonic velocity. In relaxation theory, at higher frequencies ($\omega\tau \gg 1$) when a system with a large value of η relaxes, $v_\infty - v_0$ will also be large i.e., the liquid will behave like a solid at high frequencies. The large dispersion in velocity will make β_s and hence I_B small as compared to that in the low-viscous liquids.

2.4 Light scattering from glasses

In this section, we shall highlight the fundamental contributions in the following: i) Concept of 'frozen-in' fluctuations in glasses; and ii) Krishnan Effect.

2.4.1 'Frozen-in' fluctuations in glasses

Young Rayleigh[29] (John William Strutt) conjectured that accidental inclusions and incipient crystallization occurring within the glass were responsible for scattering the light. It was first shown by Raman[30] that light scattering from glasses has its origin in true molecular scattering arising from local fluctuations of composition and of molecular orientation, as in a liquid. He arrived at this important conclusion after measuring scattered intensities for fourteen different types of silicate glasses with refractive indices varying from 1.4933 to 1.7782. The measured intensities relative to liquid benzene varied from 0.11 to 0.63 while the depolarization ratio ranged from 0.045 to 0.295. Raman's conclusions were reinforced later by Krishnan[31], Krishnan and Rao[32], Rank and Douglas[33], Debye and Bueche[34] and Maurer[35].

In all these studies, it was found that the value of the measured scattered intensity is almost an order of magnitude larger than the calculated intensity on the basis of equilibrium density fluctuations. Raman[30] proposed that the increased measured intensity was due to the 'freezing-in' (thermal arrest) of concentration fluctuations. Later, Müller[36] extended this idea to the 'frozen-in' density fluctuations. Fabelinskii[8] has quoted the work of Vladimirskii (in 1940) which suggested the possibility of freezing of orientation fluctuations. In order to amplify the above point regarding the discrepancy between the observed and calculated intensities, we shall quote the results of Velichkina on fused quartz as reported by Fabelinskii[8].

The measured scattering coefficient R, defined as $R = I_s L^2 / I_0 v$, for fused quartz in transverse direction ($\theta = 90°$) at a temperature of $-70°C$ was 1.86×10^{-6} cm^{-1}. In order to calculate the scattered intensity, glass was considered either as a liquid or as a crystal with an infinite number of symmetry axes. Using eqn (8) and taking T to be the temperature of measurements, Velichkina estimated $R = 2.3 \times 10^{-7}$ cm^{-1}. The scattering coefficient for the cubic crystal for the transverse scattering, when incident light is unpolarized, is given by[8]

$$R = \frac{\pi^2}{2\lambda^4} \; \mu^8 \, k_B \, T \cdot \left[\frac{p_{12}^2}{C_{11}} + (p_{11} - p_{12})^2, \right.$$

$$\left. \left\{ \frac{1}{4C_{11}} + \frac{1}{2(C_{11} - C_{12})} \right\} \right] \tag{17}$$

This expression was obtained by Leontowitsch and Mandelstamm in 1932. Here C_{ij} are the elastic constants and p_{ij} are Pockel's elasto-optical constants. The first term, p_{12}^2/C_{11}, arises due to density fluctuations and the other terms are due to anisotropy or orientation scattering. For isotropic solid, $p_{11} - p_{12} = 2p_{44}$ and $C_{11} - C_{12} = 2C_{44}$. Using eqn (17), Velichkina calculated $R = 1.8 \times 10^{-7}$ cm^{-1} for fused quartz. Therefore, the calculated scattering coefficients for fused quartz using either liquid state theory or based on crystals are an order of magnitude larger than the measured value.

2.4.1.1 Freezing-in density fluctuations

Applying this idea to fused quartz, Velichkina assumed that the scattering in fused quartz is determined by the density fluctuations close to the glass-transition temperature $Tg \sim 2100$ K. Then, using eqn (8) and taking $T = Tg$, $R = 1.5 \times 10^{-6}$, is in good agreement with the experiment.

The density fluctuations can be either isobaric or adiabatic:

$$\langle (\delta \rho)^2 \rangle = \left(\frac{\partial \rho}{\partial S} \right)_P^2 \; \langle (\delta p)^2 \rangle + \left(\frac{\partial \rho}{\partial P} \right)_S^2 \; \langle (\delta S)^2 \rangle. \tag{18}$$

The isobaric density fluctuations are dissipated with a time-constant

$$\tau_\rho = (\chi q^2)^{-1} \tag{19}$$

where $\chi = \sigma/\rho C_p$ is the thermal diffusivity. For visible light and $\theta = 90°$, $q \sim 5 \times 10^5$ cm^{-1} and taking for glasses, $\chi \sim 3 \times 10^{-3}$ cm^2/s, $\tau_\rho \sim 10^{-9}$ s. Hence the isobaric fluctuations of the density are quite fast and it is likely that such fluctuations may or may not freeze during cooling.

The adiabatic fluctuations of density move with the speed of hypersound (giving rise to Brillouin scattering). From the fact that Brillouin components exist in glasses[28], the freezing of adiabatic density fluctuations is clearly ruled out.

2.4.1.2 Freezing-in concentration fluctuations

The time constant associated with the concentration fluctuations is

$$\tau_C = (Dq^2)^{-1} \tag{20}$$

where D is the diffusion coefficient. For ordinary liquids, $D \sim 10^{-5}$ cm²/s and hence $\tau_C \sim 10^{-10}$ s. But near the glass-transition temperature, D decreases by many orders of magnitude (recall $D \alpha \, 1/\eta$). Taking $D \sim 10^{-9}$ cm²/s, $\tau_C \sim 10^{-3}$ s and hence one can expect the arrest of the concentration fluctuations in liquid to glass transition.

2.4.1.3 *'Fictive temperature' in a glass*

The concept of frozen-in fluctuations proposed by Raman is one of the key points in glass physics. The introduction of a 'fictive temperature'[37,38] is a useful concept. At a fictive temperature T_f, density fluctuations are arrested so that upon lowering the temperature further no structural rearrangement is possible. Therefore, T_f becomes the governing temperature for the molecular structure of a glass. Another fictive temperature T_f' is associated with thermally arrested concentration fluctuations, and in general, $T_f' \neq T_f$. Since $\tau_C \gg \tau_\rho$, concentration fluctuations are 'arrested' at a relatively higher temperature than the density fluctuations *i.e.*, $T_f' > T_f$. Usually, T_f is taken[37] to be the temperature at which the liquid viscosity is $\sim 10^{13.5}$ poise or the glass-transition temperature T_g. Typically, $\tau_C/\tau_\rho \sim 10^6$ and therefore T_f' may be taken to be the temperature at which the liquid viscosity is $\sim 10^7 - 10^8$ poise[39].

2.4.2 *Krishnan Effect*

The Krishnan Effect, discovered by R. S. Krishnan, relates to the state of polarization of the scattered radiation by condensed matter in a direction normal to the incident beam. As shown in fig. 2, four possible scattering intensities can be measured: $I_s(VV)$, $I_s(VH)$, $I_s(HV)$ and $I_s(HH)$, where H and V refer to the polarization parallel and perpendicular
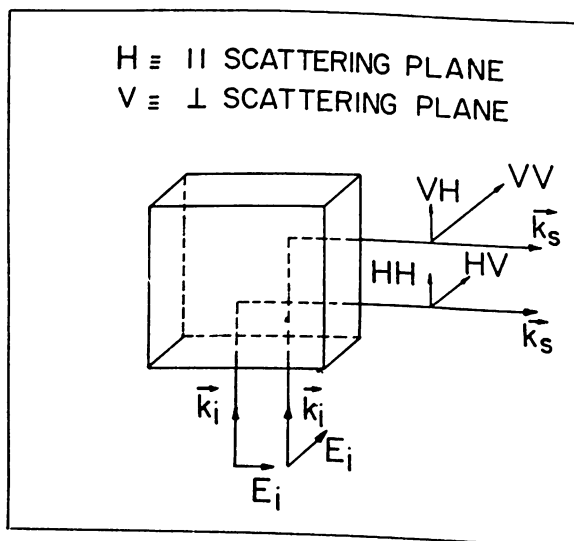

FIG. 2. Schematic representation of the polarized components of the scattered light.

to the scattering plane, respectively. The first letter in brackets (e.g., V in I_s(VH)) refer to the polarization of the incident radiation and the second one corresponds to the polarization of the scattered radiation. The depolarization ratios are defined by

$$\rho_H = \frac{I_s(\text{HV})}{I_s(\text{HH})} \qquad (21)$$

and

$$\rho_V = \frac{I_s(\text{VH})}{I_s(\text{VV})} . \qquad (22)$$

The relation $I_s(\text{VH}) = I_s(\text{HV})$ is true for all materials (not optically active) and is called Rayleigh-reciprocity relation as was shown by Krishnan[40].

For isotropic fluids consisting of molecules with dimension much less than wavelength of light,

$$I(\text{VH}) = I(\text{HV}) = I(\text{HH}).$$

The Krishnan Effect is the observation that in a number of liquids and solids,

$$\rho_H < 1. \qquad (23)$$

The Krishnan Effect has been demonstrated for critical liquid mixtures, associated liquids like formic and acetic acids, emulsions, colloids, proteins[40−46], cholesteric liquid crystals[47] and a number of glasses[31,39,48,49]. The effect observed in colloids could be explained with Mie theory of light scattering from medium consisting of non-spherical particles (or 'clusters') with linear dimensions of the order of wavelength of incident light wherein the phase differences between the waves emitted from different points of the particle must be taken into account. It may be noted that the intensities referred to in ρ_H are for the unshifted component (Rayleigh) as the Brillouin components are very weak in these systems.

There have been a number of attempts to understand Krishnan Effect in glasses. Prompted by the effect in colloids, Krishnan proposed that there are 'clusters' of dimension $\sim \lambda$ in glasses which scatter light. Gans[50] gave a theory based on the optical anisotropy of clusters which have to be necessarily strongly aspherical. Gans' theory[50] usually predicts $\rho_H > 1$ in contrast to the observation that $\rho_H < 1$. The next theoretical work was that of Müller[36] who questioned the cluster hypothesis of Krishnan in light of the X-ray investigation of Warren. Müller proposed a theory of Krishnan Effect based on strain scattering in glasses in which it is assumed that the equipartition of energy is not obeyed. The strain energy is stored more in the longitudinal modes than in the transverse modes. The Krishnan ratio becomes

$$\rho_H = \frac{U_T}{U_L} \frac{C_{11}}{2C_{44}} = \frac{U_T}{U_L} \frac{(1 - \sigma_P)}{(1 - 2\sigma_P)} \qquad (23)$$

where U_T and U_L are the energy densities of the transverse and the longitudinal strain waves and σ_P the Poisson ratio. If the equipartition energy principal is used, $U_T = U_L = k_B T/2v$ then $\rho_H = C_{11}/2C_{44}$ which is the same as in an isotropic solid. To explain $\rho_H < 1$, Müller argued that $U_L = k_B T_f/2v$ and $U_T < U_L$. This assumption is definitely unappealing because the transverse waves should as well play an important role as the longitudinal waves in the glass transition. Further, for glasses like fused quartz[39], $\rho_H \sim 1$. Müeller theory does not specify on what grounds one expects $\rho_H \sim 1$ in some glasses. Further, according to theory[36],

$$\rho_V = \frac{1}{4} \frac{U_T}{U_L} \left(\frac{1-\sigma_P}{1-2\sigma_P} \right) \cdot \left(1 - \frac{q}{P} \right)^2 \tag{24}$$

where q and p are Neumann's constants related to p_{ij} by $p_{11} = 2q/\mu$, $p_{12} = 2p/\mu$. From eqns (23) and (24),

$$\frac{\rho_V}{\rho_H} = \frac{1}{4} \left(1 - \frac{q}{P} \right)^2. \tag{25}$$

In general, $q < p$ and, therefore, the maximum value of ρ_V/ρ_H is 0.25 in Müller's theory. The experimental results on many glasses[48,49] do not agree with eqn (25).

Schroeder[39] has established a connection between concentration fluctuations and the Krishnan Effect by measuring ρ_H in a number of xK$_2$O·$(100-x)$SiO$_2$ and xNa$_2$O·$(100-x)$SiO$_2$ glasses. Figure 3 shows his data on ρ_H versus x. The minima in ρ_H mostly arises from a pronounced maxima in I_s(HH) rather than any anomalous behaviour in I_s(VH)[39,48,49]. The above silicate glasses undergo phase separation as a function of temperature and it has been observed that ρ_H is the minimum at those concentrations of alkali oxides which are close to the critical composition. This establishes that I_s(HH) reflects some aspect of the critical phase-separation process. This is further corroborated
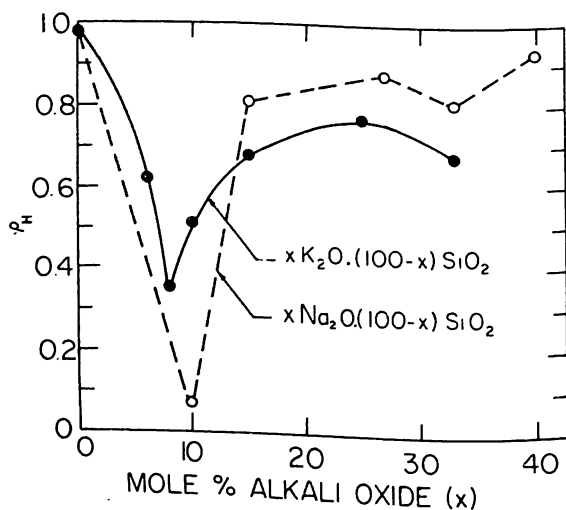

FIG. 3. Krishnan ratio ρ_H versus concentration of alkali oxides in glasses. Data are taken from Schroeder's work[39].

by Schroeder by observing that ρ_H increases from ~ 0.2 to ~ 0.5 as $(T - T_s)$ is increased from 50 to 150°C (here T is the temperature at which each particular sample was heat-treated and T_s is the spinodal temperature). Schroeder has suggested that the isotropic composition fluctuations (described by a scalar) which increase near the critical temperature must be coupled to the longitudinal 'frozen-in' fluctuations of the dielectric susceptibility (a tensorial quantity) and a mode-mode coupling approach may provide the key to the Krishnan Effect.

The effect in the glassy state of polybutadiene and polypropylene glycol has been attributed to the frozen-in fluctuations of the anisotropy[48,49].

2.5 Brillouin scattering from crystals

In a crystal, three pairs of Doppler-shifted components can occur due to three types of elastic waves which can propagate with different velocities in any general direction. For a symmetry direction the waves can be pure longitudinal or pure transverse. The Brillouin lines were first observed in a solid like quartz by Gross[51] and later by Raman and Venkateswaran[52] in gypsum. Chandrasekharan[53] showed that for a birefringent crystal, there should be twelve Doppler components. A number of crystals like diamond, calcite and alkali halides were studied by Krishnan and coworkers[21].

3. Raman scattering

Contributions of Indian scientists to Raman spectroscopy have been reviewed recently by Krishnan[54]. We shall mention here only a few of them.

3.1 Use in chemical analysis

The extensive use of Raman spectroscopy in chemical analysis is based on the fact that every chemical bond in a molecule has its characteristic Raman fingerprints which are not affected much by the other parts of the same molecule. By examining a homologous series of compounds commencing from its earlier member, it is possible to trace the development of Raman spectra with increasing complexity of the molecule and to locate these frequencies which are characteristic of particular groups or linkages. This important conclusion was reached by Bhagavantam, Venkateswaran and Ganesan along with others like Dadien and Kohrausch (for detailed references, see the review article by Bhagavantam[55]).

3.2 Resonance Raman scattering

When the incident radiation is close to an electronic transition in the medium, the Raman cross-section shows an enormous enhancement, defying the usual ν^4 law. This is called resonance Raman scattering and was discussed by Placzek in his masterly theory of Raman scattering[56]. With the advent of tunable dye lasers, resonance Raman scattering has become an important technique to understand electron-phonon interactions in crystals, especially semiconductors[57], and in conformational analysis of biomolecules.

The first observations which gave clear indication of resonance enhancement were made by Sirkar[58] in CCl_4 and nitrobenzene. He also showed that the depolarization characteristics of the Raman lines also change as the incident radiation frequency approaches the absorption frequency in liquids.

3.3 Symmetry and Raman selection rules

A vibration is said to be Raman active when it produces a change of polarizability in the vibrating system. The deformations produced by the vibrations in the polarizability ellipsoid of the crystal depend upon the symmetry of the given vibration and the symmetry of the crystal. Placzek[56] has given tables of selection rules for various types of vibrations belonging to any of the 32 point groups of crystal symmetry. However, Saxena[59] gave a lucid exposition of the subject based on the geometrical reasoning and cleared up certain discrepancies between the theoretical works of Placzek and Cabannes who give different tensors for degenerate vibrations in systems possessing only one axis of three-fold symmetry. Pioneering work was done by Bhagavantam and Venkatarayudu who gave a clear group-theoretical analysis of vibrations in crystals based on the unit-cell approach[60,61].

3.4 Crystal dynamics

Due to wavevector conservation, phonons near the Brillouin-zone centre ($q \sim 0$) can participate in the first-order Raman spectra and hence the detailed nature of the phonon-dispersion curves is not probed. In the second-order Raman scattering, however, two phonons of equal and opposite wavevectors, anywhere in the Brillouin zone, can participate. Hence the second-order spectra (SORS) consisting of a continuous background extending over a wide frequency range with sharp peaks superimposed on it are much more rich in information and have an important bearing on the theories of lattice dynamics. High-quality SORS were recorded by Krishnan for diamond, rock salt and alkali halides[62-65]. Prompted by this, Born and Bradburn[66] applied the Born-von Karman theory of lattice dynamics to calculated SORS of rock salt. Later, Birman[67] and Loudon[68] have pointed out the importance of van-Hove singularities in the one-phonon densities of states to explain the peaks in the intensity distributions of SORS.

Another important observation is in SORS of diamond by Krishnan[65]. Figure 4 shows the microphotometer record of the Raman spectra of diamond[65]. The peak at 1332 cm^{-1} is the first-order Raman mode. What is of significance is that the sharp peak at 2666 cm^{-1} observed in the second-order Raman spectra lies higher than twice the first-order line. Later, Solin and Ramdas[69] reexamined the Raman spectra of diamond with improved experimental accuracy using lasers and confirmed the results of Krishnan and also obtained temperature and polarization characteristics of 2666 cm^{-1} mode. These results prompted Cohen and Ruvalds[70] to propose the existence of two-phonon bound state which can be split off the top of the two-phonon continuum by anharmonic phonon-phonon interactions.
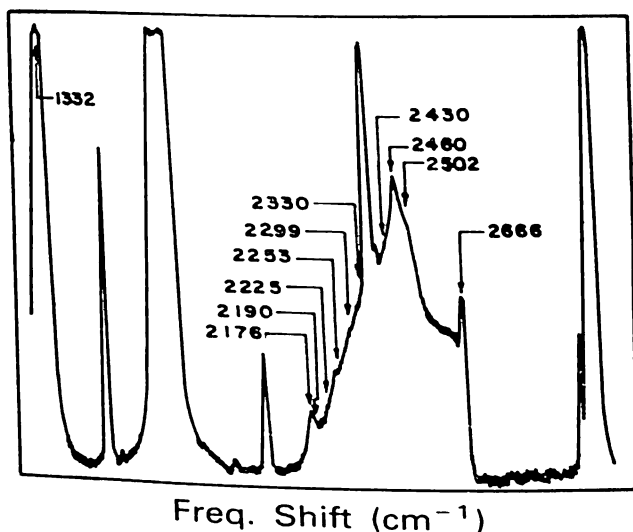
Freq. Shift (cm⁻¹)

FIG. 4. Microphotometer record of the Raman spectrum of diamond (after Krishnan)[65].

3.5 Phase transitions and 'soft mode'

The study of phase transitions has been one of the most pursued branch in condensed-matter physics. The concept of 'soft mode', formally proposed by Cochran[71] in 1959 but discovered much earlier by Raman and Nedungadi[72] in 1940, has played an increasingly dominant role in the understanding of solid-state phase transitions[73]. What is a soft mode? A soft mode is a collective excitation which may be either propagating or diffusive, whose frequency decreases substantially as the transition temperature T_0 (or pressure) is reached from above or below. Figure 5 shows the schematic behaviour of the soft mode for first- and second- order phase transitions. The static atomic displacements occurring in going from one phase to the other represent the frozen-in mode displacements of the unstable phonon.

The question of structural phase transition as the limit of stability against a particular mode of vibration was formally discussed by Cochran[71]. The basic idea and the first observation of the soft-mode were made by Raman and Nedungadi[72] in their Raman investigations of a solid-state structural phase transition from α(trigonal) to β(hexagonal) phase at ~ 573°C in crystalline quartz. They observed that "The 220 cm⁻¹ line behaves in an exceptional way, spreading out greatly towards the exciting line and becoming a weak diffuse band as the transition temperature is approached". Realising the importance of their results, they proposed that "The behaviour of the 220 cm⁻¹ line clearly indicates that the binding forces which determine the frequency of the corresponding mode of vibration of the crystal lattices diminishes rapidly with rising temperature. It appears therefore reasonable to infer that the increasing excitation of this particular mode of vibration with rising temperature and the deformations of the atomic arrangement resulting therefrom are in a special measure responsible for the remarkable changes in the properties of the crystal as well as for inducing the transformation from the α to the β form". This is an exceedingly beautiful description of a soft
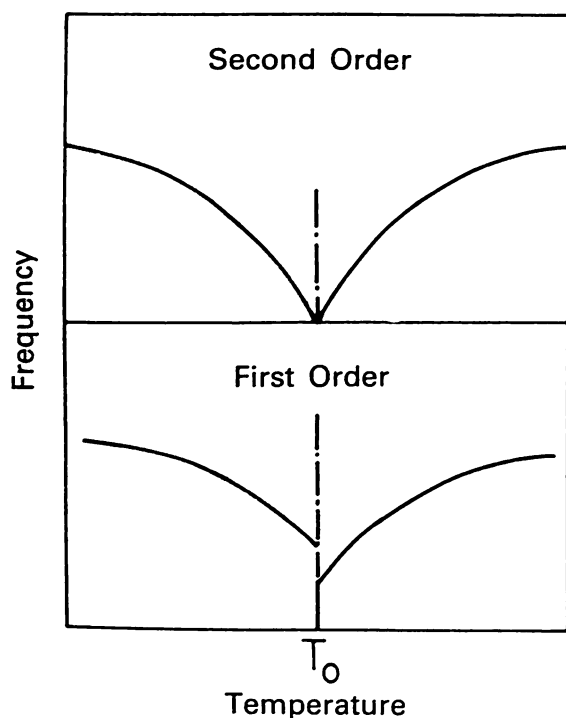
Fig. 5. Schematic representation of variation of soft-mode frequency with temperature for first- and second-order phase transitions.

mode, almost twenty years ahead of Cochran's work. Saxena[74] carried out a lattice dynamic calculation of quartz and showed that one particular mode was unstable.

Figure 6 shows the data of Nedungadi[75] for α-quartz for two modes. The bars indicate the lower and upper limits of the Raman lines. Earlier it was confusing that the two modes at ~ 220 cm^{-1} and ~ 147 cm^{-1} show anomalous temperature dependence. Also, the 147 cm^{-1} was present in polarized α_{zz}-Raman spectra, in addition to the four modes predicted by group theory. The unambiguous assignment of this extra mode as the second-order (two-phonon) process was made by Scott and Porto[77]. Scott[76] showed that the soft-mode at ~ 220 cm^{-1} interacts very strongly with the two-phonon state via anharmonic interaction (Fermi-resonance). The soft-mode in quartz is then the feature at ~ 40 cm^{-1} close to T_0. The temperature dependence of the uncoupled mode deduced by Scott along with his data on quartz are shown in fig. 7. The soft-mode behaviour goes as $\omega \sim A(T_0 - T)^{0.3}$.

The concept of soft-mode initially given for the displacive phase transitions has been extended to order-disorder transitions like in hydrogen-bonded ferroelectrics. The soft-collective excitations in order-disorder transitions are not phonons but rather unstable pseudo-spin waves which occur in addition to all the phonon modes predicted by harmonic theory of crystal lattices. Further, the idea of lattice-vibrational soft-mode has been generalised by Schneider et al[78] to several other phase transitions (like superfluid transition) by combining the static aspects of phase transitions with the dynamic
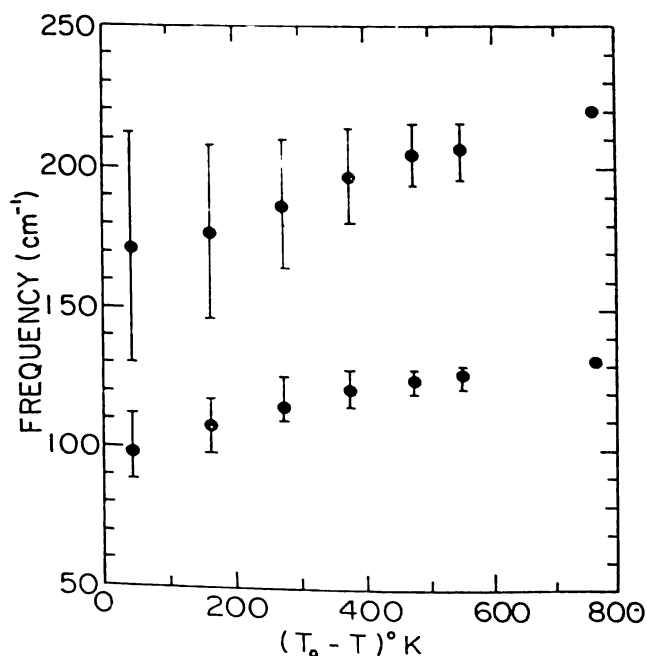
FIG. 6. Temperature dependence of modes in α-quartz. Data are taken from Nedungadi[75].
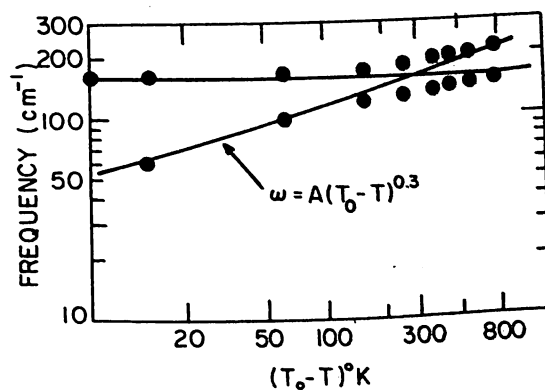
FIG. 7. Temperature dependence in α-quartz from the work of Scott[77]. The solid lines show the temperature dependence of uncoupled modes.

response of the system. To summarize, the concept of the soft-mode provides a unified view of the phase transitions and hence the early work of Raman and Nedungadi assumes a significant place in the study of the phase transitions.

4. Conclusion

We have attempted to bring out a few important contributions of Raman and his co-workers in all the fields of light scattering from condensed matter. Limitations of space did not allow us to include the interesting work of Raman and Ramdas on the scattering of light at the interface between two media and the famous Raman-Nath theory of diffraction of light by sound waves. Nor could we include post-laser work on the Raman study of ferroelectric phase transitions by P. S. Narayanan and his group.

To conclude, the work of Raman school on light scattering remains a guiding spirit in many of the present-day researches in condensed-matter physics.

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