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THEORY OF RAYLEIGH AND BRILLOUIN SCATTERING NEAR THE PHASE TRANSITION

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Résumé. — Après avoir exposé les principes de la diffusion de la lumière et mentionné quelques résultats relatifs au cas de la transition liquide-gaz d'un simple liquide monoatomique, nous discu-
tons du spectre de la lumière diffusée par les modes acoustiques en portant tout spécialement notre attention au couplage du mode acoustique et du mode « doux » optique. Nous donnons un aperçu d'une théorie de la composante centrale du spectre de diffusion de la lumière. Ce pic quasi élastique est dû aux fluctuations de la densité de phonons et devrait être observé du fait du couplage anhar-
monique avec le mode « doux » et du couplage direct de la lumière avec cette excitation collective.

Abstract. — After giving a basic outline of the theory of light scattering and mentioning a few results for the case of a simple monoatomic liquid at the liquid-gas transition, the spectrum of light scattered from acoustic modes is discussed with special emphasis on the coupling of the acoustic mode to the soft optical mode. A theory of a central component in the light scattering spectrum is outlined. This quasi-elastic peak arises from phonon density fluctuations and in general should be observed through anharmonic coupling to the soft mode and through direct coupling of light to this collective excitation.

I. Introduction. — The method of light scattering has been established in the past as a valuable tool to investigate critical phenomena. The measurement of the total scattered intensity gives information on static properties of the system and the magnitudes of the fluctuations in it. The modern laser techniques and the sophisticated detection systems developed recently, allow the observation of the spectrum of scattered light, which is a result of the dynamics of the fluctuations. The dynamical properties of the collective excitations are important for an understanding of the phase transition.

II. Spectrum of scattered light in simple systems. — An incident plane wave electric field of wave vector $k_0$ and frequency $\omega_0$ is being scattered by fluctuations in the optical dielectric constant, which have wave vector $q$ and frequency $\omega$ [1]:

$$\delta \varepsilon_{sp}(r, t) = \varepsilon_{sp}(r, t) - \bar{\varepsilon}_{sp} = \delta \varepsilon_{sp}(q, \omega) \exp[i(q, \cdot r - \omega t)]. \quad (1)$$

Here, $\bar{\varepsilon}_{sp}$ is the dielectric constant at optical frequencies in the absence of the thermally induced fluctuation in the system. The incoming field induces an oscillating dipole moment, which radiates electromagnetic energy. The far-field solution gives the scattered radiation (wave vector $k_s$ and frequency $\omega_s$). The spectrum of the scattered light is given by

$$I(q, \omega) = \frac{c}{4 \pi} \left( \frac{\omega_0}{c} \right)^4 \frac{E_0^2}{(4 \pi R)} \times \left[ \int_{-\infty}^{\infty} dt \ e^{-\omega t} < B(q, t), B(-q, 0) > \right]. \quad (2)$$

$E_0$ is the amplitude of the incoming light and $R$ the distance of the detector from the scattering volume. The brackets appearing in the integrand indicate a canonical ensemble average. The transfer of wave vector and frequency from the light to the medium are given by

$$k_0 = k_s + q \quad |q| \approx 2 k_0 \sin(\theta/2) \quad \text{and} \quad \omega_0 = \omega_s \pm \omega \quad \text{where} \ \theta \text{the angle between} \ k_0 \text{and} \ k_s \text{and the upper signs in eq. (3) refer to Stokes scattering (emission of an excitation), whereas the lower sign leads to Anti-Stokes scattering (absorption of an excitation). Finally,}$$

$$B(q, t) = \hat{k}_s \times (\hat{k}_s \times \delta(q, t), \hat{E}_0). \quad (4)$$

$\hat{k}_s$ is a unit vector in the direction of the scattered light and $\hat{E}_0$ the polarization direction of the incoming radiation.

In order to calculate the spectrum of scattered light one must know how the fluctuations in the dielectric constant are induced by the fluctuations in the thermo-
dynamic variables of the system.

The most simple and probably one of the best understood systems is the gas-liquid phase transition. The order parameter of this transition is the density change and therefore $\delta \varepsilon(r, t)$ is considered to arise from density fluctuations $\delta \rho(r, t)$. Choosing the density $\rho$ and the temperature $T$ as the independent thermo-
dynamic variables, one usually neglects $\partial \varepsilon / \partial T$ and decomposes the remaining density fluctuations into adiabatic pressure waves (which correspond to ordinary sound waves) and isobaric entropy fluctuations. The first give rise to Brillouin scattering and the second...
to Rayleigh scattering. The ratio of the integrated intensities of Rayleigh and Brillouin scattering is given in this approximation by the Landau-Placzek ratio
\[ \frac{I_R}{I_B} = \frac{C_p(C_v - 1)}{C_v}, \]
where \( C_p \) and \( C_v \) are the specific heats at constant pressure and at constant volume, respectively. Since \( C_p \) diverges at the phase transition we get the well-known phenomenon of critical opalescence. Furthermore, simple hydrodynamics allows to calculate the width of the Rayleigh (or central) component to be
\[ \Gamma_R = D_T q^2, \]
where the thermal diffusivity \( D_T = \lambda / \rho C_p \) is given by the thermal conductivity \( \lambda \) and the specific heat \( C_p \).

Hydrodynamics, which leads to eq. (5) breaks down near \( T_c \), since the range of the fluctuations \( \xi \) diverges at \( T_c \), so that \( \xi \) becomes larger than the wavelength \( q^{-1} \) of the excitation. There are several theories \([2]\) which allow an extension into the critical region \( q \xi > 1 \). These result in modifications of the hydrodynamic expressions like eq. (5) and allow a determination of the correlation length \( \xi \) by a light scattering experiment \([3]\).

Many of the static and dynamical properties of the system are singular at \( T_c \). Light scattering is one way to estimate the exponents of the most singular terms in the expansion of the relevant quantities in terms of \( \epsilon = | T - T_c | / T_c \). It is of particular importance that the method of light scattering also allows to measure dynamical properties, such as thermal conductivity.

III. Scattering from acoustic modes. — In solids such as ferroelectrics the situation is more complicated than at the liquid-gas transition. So far the Landau theory of phase transitions has been used to describe the ferroelectric transition, but it is now established that for temperatures near \( T_c \) the Landau theory is not applicable. One example is the result by Müller and Berlinger \([4]\), according to which the rotation angle \( \varphi \) of the oxygen octahedra in SrTiO\(_3\) varies as \( \varphi \sim \epsilon^\beta \) with \( \beta \approx 1/3 \). Whereas the more general theories for critical behaviour, which go beyond the mean field approximation, allow to put a number of different phase transitions (liquid-gas, ferromagnetic, binary mixtures, superfluid helium) on the same basis, it is not at all clear, how the ferroelectric transition fits into this picture. The recent observation of a central component in the spectra of light \([5]\) and of neutron scattering \([6]\) may be a beginning in this direction.

Typical solid state effects which make light scattering more complicated are the presence of other fluctuations besides density fluctuations, and the existence of selection rules for the coupling of light to these fluctuations. In a solid the fluctuations in the optical dielectric constant or the polarizability arise from all possible nuclear motions. We, therefore, expand the susceptibility fluctuations in powers of the normal coordinates \( A(qj\omega) \) of the nuclear motions up to the second order
\[ \delta A_{ab}(qj\omega) = \sum_j P_{1,ab}(qj) A(qj\omega) + \sum_{\lambda_1,\lambda_2} P_{2,ab}(\lambda_1, \lambda_2) A(\lambda_1 \omega) A(\lambda_2 \omega), \]
Here \( \lambda = (qj) \) stands for wave vector \( q \) and branch index \( j \). If \( j = \text{ac} \) refers to an acoustic branch, \( P_1 \) is related to the elasto-optic tensor (or Pockels coefficients) and gives rise to Brillouin scattering \([7]\). For Raman scattering \( j = \text{op} \) denotes an optical branch and \( P_1 \) is related to the Raman tensor. In the case of polarized 90° scattering, it follows from eq. (4) and (2) that only correlations of \( \delta A_{ac} \) need to be considered. Working with the polarizability and introducing the retarded Green function of two operators \( A \) and \( B \)
\[ G'_\omega(A | B) = i \theta(t) \langle [A(t), B(0)] \rangle, \]
the spectrum of scattered light for the case under consideration is essentially given by
\[ S(q, \omega) = (n(\omega) + 1) \Im G'_\omega(\delta(q, \omega) | \delta(-q, 0)), \]
where \( n(\omega) \) is the Bose function and \( G'_\omega \) is the Fourier transform of \( G_t \).

A restriction to one-phonon processes alone in eq. (6) allows to write
\[ S(q, \omega) = (n(\omega) + 1) \times \sum_{j, j'} P_1(qj) P_1(-qj') \Im G'_\omega(A_j | A_{j'}). \]
In the diagonal case, \( j = j' \), we have ordinary first-order Brillouin (\( j = \text{ac} \)) or Raman (\( j = \text{op} \)) scattering. In this case
\[ \Im G'_\omega(A_j | A_j) = \frac{4 \omega \Omega_{\omega j} G_j}{(\omega^2 - \omega_\omega^2)^2 + 4 \omega_\omega^2 G_j^2} \]
and the spectrum consists of a Lorentzian of half width \( G_j \) centered at frequency \( \omega_j \). But in many cases this one-mode picture is not sufficient since the mode under consideration is coupled to other modes.

The case of two coupled modes has been of particular interest \([j, j' = 1, 2]\) in this case
\[ S(q, \omega) = (n(\omega) + 1) \times \Im \{ P_1^2(1) G_{11} + 2 P_1(1) P_2(2) G_{12} + P_2^2(2) G_{22} \}. \]
As long as the two modes (1) and (2) are far away from each other, coupling will be weak, \( G_{12} \approx 0 \), and the light couples to mode (1) via \( P_1(1) \) and to mode (2) via \( P_2(2) \); the functions \( G_{11} \) and \( G_{22} \) give rise to two Lorentzians in the spectrum. If the coupling gets stronger, \( G_{11} \) and \( G_{22} \) are modified to renormalized function \( \tilde{G}_{11} \) and \( \tilde{G}_{22} \) and furthermore, \( G_{12} \) is finite. These coupled functions are solutions of a matrix Dyson equation
\[ \begin{pmatrix} \tilde{G}_{11} & \tilde{G}_{12} \\ \tilde{G}_{21} & \tilde{G}_{22} \end{pmatrix} = \begin{pmatrix} G_{11} & 0 \\ G_{12} & 0 \end{pmatrix} \times \begin{pmatrix} I - \omega_{\text{p},\omega} G_{11} & G_{12} \\ G_{21} & I - \omega_{\text{p},\omega} G_{22} \end{pmatrix}, \]
where \( I \) is the 2 \times 2 unit matrix and \( \omega_{\text{p},\omega} \) expresses the coupling (which in general is complex and also may have diagonal elements).
For instance, we have
\[ \tilde{G}_{11} = \frac{G_{11}}{1 - \pi_{12}^2 G_{11} G_{22}}. \] (13)

Suppose, light couples much more strongly to mode (1) than to mode (2), but that the two modes are strongly coupled together through \( \pi_{12} \). In this case the spectrum of light shows peaks at the peaks of \( \text{Im} \tilde{G}_{11} \). As can be seen from eq. (13), instead of a simple Lorentzian \( G_{11} \), we now have a spectrum which is determined also by \( G_{22} \). This effect has been considered in the past mostly for the anharmonic coupling of two optic branches.

Here we will mention the case of the piezoelectric coupling of an acoustic mode (1) to the soft optic mode (2), as it has been studied in detail for KDP [8], BaTiO\(_3\) [9] and DKDP [10]. The Brillouin scattering study on KDP illustrates eq. (13), which allows to calculate the renormalization of the velocity of the \( X'_\perp \) transverse acoustic mode due to the interaction (\( \pi_{12} \sim a_{36} \)) with the overdamped soft mode:
\[ \tilde{v}_{ac} = v_{ac} - \frac{\pi_{12}^2}{q^2 \omega_{op}^2} \left( 1 - \frac{1}{2} \frac{\omega_{op}^2}{\omega_{ac}^2} \right), \] (14)

where \( v_{ac} \) and \( \omega_{op} \) denote the uncoupled frequencies and \( \Gamma_{op} \) is the half width of the soft optical mode. Since \( \omega_{op} \) decreases for \( T \to T_c \), the acoustic mode becomes soft (\( \tilde{v}_{ac} \to 0 \)), as has been demonstrated in the experiments by Brody and Cummins [8].

Another interesting case is the observation by Fleury and Lazey [9] of the coupling of the TA [101] phonon in BaTiO\(_3\) to the soft optical mode (\( \pi_{12} \sim a_{15} \)). The Raman spectrum for \( \pi_{12} = 0 \) is determined by \( G_{ac} \) alone, which is an overdamped mode. But because of the coupling one gets an additional \( \propto \) pole \( \propto \) into \( G_{op} \), resulting in a rather sharp peak on top of the very broad soft mode. It should be mentioned that the coupling of two anharmonic oscillators produces not only shifts in the uncoupled frequencies, but it also gives rise to line-shape anomalies such as antiresonances and interference dips, so that the spectrum looks much more complicated than a sum of single Lorentzians. An example is the case of BaTiO\(_3\) [9].

**IV. Rayleigh scattering.** — In order to include into the theory possible low-frequency excitations like the Rayleigh component which was mentioned in the case of liquids, we have to extend the treatment outlined so far. We have to use for the dielectric an equation which plays the analogous role to the Navier-Stokes equation in the fluid-gas transition. This means that the phonon theory has to be extended to include transport effects. If the excitation is of very long wavelength and of very low frequency, one must take into account that the system of thermal phonons has sufficient time to adjust to a local thermodynamic equilibrium during one period of the excitation. These fluctuations in space and time of the thermal phonon density give rise in general to quasi-elastic scattering of light, i.e. a central or Rayleigh component.

In order to calculate the spectrum of scattered light from the low-frequency modes we have to extend the theory which was used for the problem of light scattering by second sound in dielectrics [11]. In the ferroelectric case we have to consider the soft optic mode instead of the longitudinal acoustic mode being coupled to the phonon density fluctuations [12]. This means that different coupling mechanisms apply.

Using the full expression for the susceptibility operator, eq. (6), in the calculation of \( S(q, \omega) \), we include also the direct coupling of light (\( P_2 \neq 0 \)) to the phonon density fluctuation. The low-frequency excitations enter the spectrum in two ways. Besides the direct coupling effect the transport modes also modify the soft-mode. This latter effect corresponds to the Landau-Placzek approximation mentioned earlier and was also considered by Cowley et al. [13] in a study of the dielectric response of KDA and CsDA. As long as \( P_2 = 0 \), light couples to the soft mode, but if phonon density fluctuations are taken into account, the shape of the soft mode and its position are no longer given by an expression like eq. (10). Instead, one has to use phonon transport theory [14], according to which the phonon self-energy at low frequencies has to take three-phonon vertex corrections into account. The latter can be calculated from an integral equation, which is the microscopic form of a Boltzmann transport equation, describing the dynamics of the fluctuations in the phonon density and in the temperature. This derivation results in a frequency dependent damping function in \( S(q, \omega) \).

The second effect of the low-lying excitations arises from the second term in eq. (6) which leads to higher order Green functions in eq. (8). These cannot be simply reduced to products of the one-phonon function. Instead, three-phonon and four-phonon vertex corrections have to be calculated from microscopic transport equations.

The spectrum \( S(q, \omega) \) consists therefore of a modified soft mode scattering, a direct scattering from the phonon density fluctuations and interference effects between the two. The result of the rather lengthy calculations can best be represented in the form of scattering from two coupled oscillators, similar to eq. (11):
\[ S(q, \omega) = (n(\omega) + 1) \times \]
\[ \times \text{Im} \left\{ P_1^2 G_{11} + 2 P_1 P_2 G_{12} + P_2^2 G_{22} \right\}. \] (15)

Here, \( P_1 \) is related to the Raman tensor of the soft mode and \( P_2 \) measures the direct coupling to the phonon density fluctuation. If the latter consists of temperature fluctuations, \( P_2 \) is proportional to \((\partial\varepsilon/\partial T)_c\). The effect of this temperature variation of the optical dielectric constant on the second sound problem was found to be quite important [11].
Eq. (15) describes scattering from two coupled modes, one being the soft optical phonon and the other one the collective phonon mode. The first contribution, Im \( \{ P_2 G_{11} \} \) consists of a peak from the soft mode, but because of the coupling to the collective mode additional intensity is introduced at low frequencies and is of the form of a Debye relaxation

\[
G_{11} = \frac{G_{op}}{1 - \pi_2^2 G_{op} G_{col} \tau^2}; \quad G_{col} \propto \frac{1 + i\omega\tau}{1 + \omega^2\tau^2}. \quad (16)
\]

The last term in eq. (15) describes the direct coupling to light of the phonon density fluctuation. Its contribution is of the form

\[
S_2(q, \omega) \propto \frac{\tau^2}{1 + \omega^2\tau^2}. \quad (17)
\]

The time \( \tau \) in eq. (16) and (17) is related to the transport relaxation time, which in general is different from a phonon lifetime [16].

In addition, there is the possibility of line-shape anomalies, like antiresonances, etc., depending on the details of the coupling between the oscillators and on their dampings.

The possibility of appearance of a quasielastic peak in the spectrum of a ferroelectric resembles the Rayleigh component as known from other phase transitions like the liquid-gas case. More work has to be done in order to establish the relation of the strength of the Rayleigh contribution to the soft mode as known from other phase transitions like antiresonances, etc., depending on the specific material under consideration.

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\[\text{References}\]


