

Chapter 2

Basics and Brillouin Light Scattering

In this chapter, first the basic expressions of elasticity will be introduced, especially with regard to the propagation of elastic waves in isotropic media and their description as spherical waves. Then the general principles of light scattering will be presented and applied to the special case of Brillouin light scattering, including the discussion of its technical realization.

2.1 Elastic Waves in Condensed Matter

2.1.1 Elasticity Theory Basics

In this part, fundamental concepts of the theory of elasticity are briefly introduced, following mostly the notation of the excellent textbook of Landau and Lifschitz [1].

Essential terms are the strain and stress tensors. To introduce them, we first define the displacement vector $\mathbf{u}$ that shifted a point P that can be found by following the vector $\mathbf{r}$ (with the three components $x_1 = x$, $x_2 = y$, and $x_3 = z$ in a Cartesian system) from the origin of the coordinate system to the point P' with coordinates given by the vector $\mathbf{r}'$, i.e.,

$$\mathbf{u} = \mathbf{r} - \mathbf{r}'. \quad (2.1)$$

The distance between any two infinitesimally adjacent points dl is given by

$$dl = \sqrt{dx_1^2 + dx_2^2 + dx_3^2} = \sqrt{dx_i^2}, \quad (2.2)$$

using the Einstein summation convention behind the second equal. After a deformation it becomes

$$dl' = \sqrt{dx_1'^2 + dx_2'^2 + dx_3'^2} = \sqrt{dx_i'^2} \quad (2.3)$$

Therefore, it is possible to write

$$dl'^2 = dx_i'^2 = (dx_i + du_i)^2 = dl^2 + 2 \frac{\partial u_i}{\partial x_k} dx_i dx_k + \frac{\partial u_i}{\partial x_k} \frac{\partial u_i}{\partial x_l} dx_k dx_l \quad (2.4)$$

substituting $du_i = \frac{\partial u_i}{\partial x_k} dx_k$ in the last step. With $\frac{\partial u_i}{\partial x_k} dx_i dx_k = \frac{\partial u_k}{\partial x_i} dx_i dx_k$ and swap of i and l in the last term, finally we get

$$dl'^2 = dl^2 + 2u_{ik} dx_i dx_k. \quad (2.5)$$

The strain tensor u_{ik} is therein defined as

$$u_{ik} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} + \frac{\partial u_l}{\partial x_k} \cdot \frac{\partial u_l}{\partial x_i} \right) \approx \frac{1}{2} \left(\frac{\partial u_i}{\partial x_k} + \frac{\partial u_k}{\partial x_i} \right). \quad (2.6)$$

The last approximation is valid if second order terms can be neglected. Obviously, u_{ik} is a symmetric tensor. Each symmetric tensor can be diagonalized in any point. With the diagonal elements $u^{(1)}$, $u^{(2)}$, $u^{(3)}$ the strain in any point can be written as the sum of three independent terms, which give the strain in three orthogonal main directions.

$$dl'^2 = (1 + 2u^{(1)})dx_1^2 + (1 + 2u^{(2)})dx_2^2 + (1 + 2u^{(3)})dx_3^2. \quad (2.7)$$

For $u^{(i)} \ll 1$ and if higher order terms are neglected, the relative change of elongation becomes

$$\frac{dx_i' - dx_i}{dx_i} = \sqrt{1 + 2u^{(i)}} - 1 \approx u^{(i)}. \quad (2.8)$$

With that approximation we can write the relative volume change of an infinitesimal small volume element $dV \rightarrow dV'$ as the sum of the diagonal elements of the strain tensor [1].

$$\frac{dV' - dV}{dV} = u_{ii}. \quad (2.9)$$

The resulting force $\mathbf{F}$ on any partial volume of an elastic body can be written as the integral over the forces on any element of the volume $\int \mathbf{F} dV$. Because of the identity of actio and reactio for all forces between any two points within the volume the resulting force can also be written as the sum over the integrals of the three components F_i , $\int F_i dV$, which can be translated into an integral over the surface:

$$\int F_i dV = \int \frac{\partial \sigma_{ik}}{\partial x_k} dV = \oint \sigma_{ik} df_k. \quad (2.10)$$

Here, F_i is expressed as divergence of a second rank tensor, the stress tensor σ_{ik} :

$$F_i = \frac{\partial \sigma_{ik}}{\partial x_k} \quad (2.11)$$

In Eq. 2.10, df_i are the components of a vector that is always oriented in the direction normal to the surfaces. The nature of the stress tensor is visualized in Fig. 2.1. When placing the surfaces of the volume element in the principal plane of the coordinate system (xy , yz , or xz), the component σ_{ab} of the stress tensor equals to the a -component of the force that is normal to that x_b -axis.

The work δw that is achieved to perform a deformation is

$$\delta w = -\sigma_{ik} \delta u_{ik}. \quad (2.12)$$

For reversible, elastic deformations it follows for the free energy A ($A = U - TS$, $dU = TdS - \delta w$, S : entropy) that

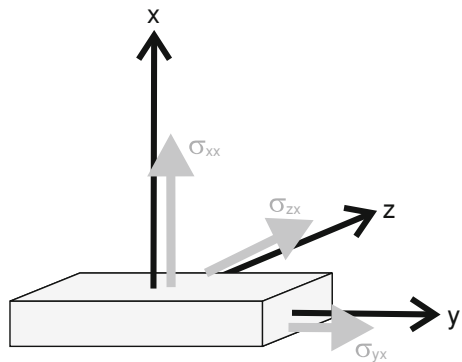
$$\sigma_{ik} = \left(\frac{\partial A}{\partial u_{ik}} \right)_T. \quad (2.13)$$

It can be shown that the free energy after an elastic isothermal deformation of an isotropic body can be expressed after series expansion and neglecting higher order terms as

$$A = A_0 + \frac{\lambda}{2} u_{ii}^2 + \mu u_{ik}^2, \quad (2.14)$$

introducing the Lamé coefficients λ and μ . Note that λ and μ are force constants. Since it was already shown that the volume change during a deformation is expressed by the sum of the diagonal elements u_{ii} , it is obvious that, if the term containing the u_{ii} becomes zero, the last term expresses a pure shear deformation. Therefore, μ is also called the shear modulus, sometimes denoted by G .

Fig. 2.1 Illustration of the stress tensor for the σ_{ax} -components working on a surface normal to the x -axis. The picture is analogously valid for the other six components when applied to the surfaces normal to the y - and z -axis



By writing the following identity

$$u_{ik} = \left(u_{ik} - \frac{1}{3} \delta_{ik} u_{ll} \right) + \frac{1}{3} \delta_{ik} u_{ll} \quad (2.15)$$

with $u_{ik} = \text{const} \cdot \delta_{ik}$ it follows directly that every deformation can be written as a sum of a pure shear deformation and a homogeneous dilatation. The term in brackets is surely a pure shear deformation, because the sum of the diagonal elements vanishes ($\delta_{ii} = 3$) and the other term is related to the homogeneous dilatation.

For a perfectly elastic body, Hook's law can be generalized to state that each component of the stress tensor is linearly related to each component of the strain tensor:

$$\sigma_{ik} = c_{iklm} u_{lm}. \quad (2.16)$$

Here, c_{iklm} is the fourth-rank stiffness tensor with $3^4 = 81$ components. Taking into account the symmetry of the strain and stress tensors, it is possible to reduce the number of coefficients to $6^2 = 36$. However, these 36 components are not independent. In the general case the following symmetry relations are valid:

$$c_{iklm} = c_{kilm} = c_{ikml} = c_{kml i}. \quad (2.17)$$

That is in an anisotropic body there are at most 21 independent components, which are usually noted in a matrix notation, which uses the itemized identities to abbreviate the tensor notation and to replace the tensor by a 6×6 -matrix with only two indices per component. The following rules are adopted for the indices:

Tensor notation	11	22	33	23, 32	13, 31	12, 21
Matrix notation	1	2	3	4	5	6

With that notation one can rewrite Eq. 2.16 as

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix}. \quad (2.18)$$

While the discussion of the stiffness matrix for different crystal symmetries is done in specialized treatments, here only the isotropic case, which is a good approximation for many cases, including also most polymer systems, should be discussed in the rest of this section. For an isotropic body, it can be shown that

due to further symmetry considerations the stiffness matrix in Eq. 2.16 has the following form [2]:

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \\ u_3 \\ u_4 \\ u_5 \\ u_6 \end{bmatrix}. \quad (2.19)$$

Because the three remaining constants are related by the following relation

$$C_{11} = C_{12} + 2C_{44}, \quad (2.20)$$

there are, indeed, only two independent constants remaining. These two constants can be identified with the Lamé coefficients

$$\lambda = C_{12} \quad \text{and} \quad \mu = C_{44}, \quad (2.21)$$

while C_{11} is also called the longitudinal modulus. Beside the shear modulus $G = \mu$, some other elastic parameters are often encountered, namely the bulk modulus, the Young's modulus, or the Poisson's ratio.

The bulk modulus K measures a substance's resistance to uniform compressions. It is defined as the ratio of the hydrostatic pressure to the fractional volume change,

$$K = -\frac{\partial p}{\partial u_{ii}} = \lambda + \frac{2}{3}\mu. \quad (2.22)$$

K should not be confused with the longitudinal bulk modulus

$$M = C_{11}. \quad (2.23)$$

The Young's modulus E , also known as modulus of elasticity or tensile modulus, is a measure of the stiffness of an isotropic elastic material. It is given by the ratio of longitudinal stress (which has units of pressure) and the dimensionless longitudinal strain,

$$E = \frac{\sigma_{11}}{u_{11}} = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}. \quad (2.24)$$

The ratio of the lateral strain to the longitudinal strain defines the Poisson's ratio,

$$\sigma = -\frac{u_{22}}{u_{11}} = \frac{\lambda}{2(\lambda + \mu)}. \quad (2.25)$$

2.1.2 Elastic Waves in Isotropic Media

When a body is deformed, the deformation usually goes along with changes in the temperature. However, the heat transport is normally much slower compared to periods of vibrations in the body. Therefore, one can regard the movements as (quasi)adiabatic. It can be shown that in the adiabatic case the values for the Young's modulus and the Poisson's ratio, given above for the isothermal case, change into

$$E_{\text{adiabatic}} = E + E^2 \frac{T\alpha^2}{9C_p} \quad \text{and} \quad \sigma_{\text{adiabatic}} = \sigma + (1 + \sigma)E \frac{T\alpha^2}{9C_p}, \quad (2.26)$$

where $\alpha = (\partial V / \partial T)_p$ and C_p is the specific heat at constant pressure [1]. In the following, σ and E mean their adiabatic values.

The general equation of movement can be written as

$$\varrho \frac{\partial^2 u_i}{\partial t^2} = \frac{\partial \sigma_{ik}}{\partial x_k} \quad (2.27)$$

with mass density ϱ . For the isotropic elastic medium the equation of movement becomes

$$\varrho \frac{\partial^2 \mathbf{u}_i}{\partial t^2} = \frac{E}{2(1 + \sigma)} \nabla^2 \mathbf{u} + \frac{E}{2(1 + \sigma)(1 - 2\sigma)} \text{grad div} \mathbf{u}. \quad (2.28)$$

Regarding a plane elastic wave in x -direction in an infinite medium, i.e., the deformation $\mathbf{u}$ depends only on the x -coordinate (all derivatives with respect to y and z become zero), the components of the vector $\mathbf{u}$ become

$$\frac{\partial^2 u_x}{\partial x^2} - \frac{1}{c_l^2} \frac{\partial^2 u_x}{\partial t^2} = 0; \quad \frac{\partial^2 u_y}{\partial x^2} - \frac{1}{c_t^2} \frac{\partial^2 u_y}{\partial t^2} = 0; \quad \frac{\partial^2 u_z}{\partial x^2} - \frac{1}{c_t^2} \frac{\partial^2 u_z}{\partial t^2} = 0. \quad (2.29)$$

The Eq. 2.29 are one-dimensional wave equations, c_l and c_t are their velocities of propagation. Obviously, the propagation in x -direction is different from that in the other directions. If the displacement u_x lies in the direction of propagation of the wave, the wave is called a longitudinal wave with longitudinal sound velocity c_l :

$$c_l = \sqrt{\frac{E(1 - \sigma)}{\varrho(1 + \sigma)(1 - 2\sigma)}} = \sqrt{\frac{\lambda + 2\mu}{\varrho}} = \sqrt{\frac{C_{11}}{\varrho}}. \quad (2.30)$$

In the other directions, the displacement (u_y, u_z) lies in a plane normal to the direction of propagation of the wave. Such a wave is called a transverse wave with transverse sound velocity c_t :

$$c_t = \sqrt{\frac{E}{2\varrho(1 + \sigma)}} = \sqrt{\frac{\mu}{\varrho}} = \sqrt{\frac{C_{44}}{\varrho}}. \quad (2.31)$$

Accordingly, from Eqs. 2.21 and 2.23 it is clear that we can express longitudinal and shear modulus simply by

$$M = \varrho c_l^2 \quad (2.32)$$

and

$$G = \varrho c_t^2, \quad (2.33)$$

respectively, while the bulk modulus K depends on the longitudinal as well as on the transverse sound velocity, since after Eqs. 2.20 and 2.22 it becomes

$$K = M - 2G + \frac{2}{3}G = M - \frac{4}{3}G = \varrho \left(c_l^2 - \frac{4}{3}c_t^2 \right). \quad (2.34)$$

The longitudinal sound velocity is always larger than the transverse sound velocity. For $\sigma \leq 0.5$,

$$c_l > c_t \sqrt{2}. \quad (2.35)$$

One should note that the transverse wave has two possible polarizations, which are orthogonal to each other. Furthermore, it is notable that longitudinal waves involve changes in the volume of the medium, i.e., dilatation or compression of a local volume element, while the transverse waves cause no volume change.

2.1.3 Spherical Waves

Because this thesis treats in many parts experiments on colloids acting as spherical scatterers, it is meaningful to introduce briefly the principle solution of the elastic wave equation for an isotropic medium. The equations presented here will be required again in the discussion of the vibrational eigenmodes of spherical particles.

In general, for a harmonic elastic wave of angular frequency ω , the displacement vector $\mathbf{u}$ can be written as

$$\mathbf{u}(\mathbf{r}, t) = \Re[\mathbf{u}(\mathbf{r}) \exp(-i\omega t)]. \quad (2.36)$$

Using that one can write the general equation of motion in the following time-independent form [3]:

$$(\lambda + 2\mu)\nabla(\nabla \cdot \mathbf{u}) - \mu\nabla \times \nabla \times \mathbf{u} + \varrho\omega^2\mathbf{u} = 0. \quad (2.37)$$

In a spherical coordinate system, the displacement vector can be written as the sum of three vectors $\mathbf{u} = \mathbf{l} + \mathbf{m} + \mathbf{n}$ such that Eq. 2.37 can be broken into three independent vector Helmholtz equations [4]

$$(\nabla^2 + k_l^2)\mathbf{l} = 0, \quad (\nabla^2 + k_t^2)\mathbf{m} = 0, \quad (\nabla^2 + k_t^2)\mathbf{n} = 0, \quad (2.38)$$

where $\mathbf{l}$ represents the displacement associated with longitudinal wave and $\mathbf{n}$ and $\mathbf{m}$ represent the transverse displacements, which are orthogonal to each other. These three vectors can be related to scalar functions φ, ψ , and χ that are solutions of a scalar Helmholtz equation $(\nabla^2 + k^2)f = 0$:

$$\mathbf{l} = \frac{1}{k_l} \nabla \varphi, \quad (2.39)$$

$$\mathbf{m} = \nabla \times \mathbf{r} \psi, \quad (2.40)$$

$$\mathbf{n} = \frac{1}{k_t} \nabla \times \nabla \times \mathbf{r} \chi. \quad (2.41)$$

The transverse displacement vectors $\mathbf{m}$ and $\mathbf{n}$ are herein expressed as the product of the constant position vector $\mathbf{r}$ and the scalar functions mentioned above [4]. In polar coordinates the solution of the scalar Helmholtz equation is known. It is

$$f_{lm}(r, \theta, \phi) = R_l(kr) Y_{lm}(\theta, \phi). \quad (2.42)$$

$R_l(kr)$ are n -th order spherical Bessel functions, which represent the radial displacement. $Y_{lm}(\theta, \phi)$ are the n -th order spherical harmonics (Legendre functions) with $l = 0, 1, 2, 3, \dots$ and m being an integer $-l \leq m \leq +l$. Knowing this, the vector solutions of Eq. 2.38 can be written as

$$\mathbf{l}_{lm}(R, k_l) = \frac{1}{k_l} \nabla [R_l(k_l r) Y_{lm}(\hat{r})]; \quad l = 0, 1, 2, 3, \dots, \quad (2.43)$$

$$\mathbf{m}_{lm}(R, k_t) = \nabla \times [\mathbf{r} R_l(k_t r) Y_{lm}(\hat{r})]; \quad l = 1, 2, 3, \dots, \quad (2.44)$$

$$\mathbf{n}_{lm}(R, k_t) = \frac{1}{k_t} \nabla \times \nabla \times [\mathbf{r} R_l(k_t r) Y_{lm}(\hat{r})]; \quad l = 1, 2, 3, \dots \quad (2.45)$$

2.2 Light Scattering Basics

This section is a brief introduction into the basic principles of light scattering. While the derivation of scattering theory on the basis of quantum field theory is possible, herein the scattering medium as well as the light are treated classically, leading to practically the same results within the scope of this thesis. Of course there are light scattering effects, as for example in the well-known Raman scattering technique, which deals with rotational and vibrational transitions of single atoms or molecules, i.e., effects in a quantum length scale, that must be treated (at least partially) quantum mechanically. However, this thesis deals with the investigation of phonons by Brillouin light scattering (Sect. 2.3) in condensed

matter. Thus the investigated phonons are classical waves with wavelengths in the order of some nanometer up to micrometer, it is fully justified to apply a classic theory.

The classical theory of light scattering in dense media developed by Einstein [5] and Smoluchowski considers the sample as divided into small volume elements large enough to contain many molecules (i.e., following classical physics), but of linear dimension small compared to the wavelength of light. An incident light wave induces a dipole moment in each volume element, which becomes the source of scattered radiation. Provided that the induced polarization is constant through the medium, the net scattered radiation in all directions but the forward will be zero due to destructive interference, because the wavelets scattered from each subregion differ only by a phase factor that depends on the relative position of the small volumes. Therefore, neglecting small surface effects, it is possible to pair each small volume with another small volume whose scattered field is identical in amplitude but opposite in phase, thus they cancel out [4, 6, 7].

However, in real media there will always be small random fluctuations in the local dielectric constant due to the thermal motion of the atoms and molecules in the sample. Because these fluctuations should be uncorrelated from one volume element to the next, these regions are optically different, and therefore also the amplitudes of the scattered light are uncorrelated. That means that now light is also scattered in other directions than forward due to only partial interference.

The local dielectric constant at a point at position $\mathbf{r}$ and time t , $\epsilon(\mathbf{r}, t)$, is generally described by the dielectric constant fluctuation tensor $\delta\epsilon(\mathbf{r}, t)$. It describes the relation between the local and the average dielectric constant ϵ_0 ,

$$\epsilon(\mathbf{r}, t) = \epsilon_0 \mathbf{I} + \delta\epsilon(\mathbf{r}, t). \quad (2.46)$$

$\mathbf{I}$ is the second-rank unit tensor.

When the incident light is a plane wave with field amplitude E_0 , angular frequency ω_i , and incident propagation vector $\mathbf{k}_i$, the incident electric field can be written as

$$\mathbf{E}_i(\mathbf{r}, t) = \mathbf{n}_i E_0 \exp i(\mathbf{k}_i \cdot \mathbf{r} - \omega_i t) \quad (2.47)$$

with $\mathbf{n}_i$ being the unit vector in the direction of the incident field.

At large distance $\mathbf{R}$ from the scattering volume, the scattered electric field $\mathbf{E}_s(\mathbf{R}, t)$ can be obtained from the fact that the Maxwell equations must hold for the total electric field, the incident electric field and as well for the scattered electric field, where the total field is just the sum of the two others:

$$\mathbf{E} = \mathbf{E}_i + \mathbf{E}_s. \quad (2.48)$$

Indeed, the same should be valid for the electric displacement field $\mathbf{D}$ and the magnetizing field $\mathbf{H}$. The solution of the Maxwell equations is lengthy and

performed elsewhere [7]. In the end it follows for the component of the scattered electric field $E_s(R, t)$ that

$$E_s(R, t) = \frac{E_0}{4\pi R\epsilon_0} \exp i k_s R \int_V d^3 r \times \exp i(\mathbf{q} \cdot \mathbf{r} - \omega_i t [\mathbf{n}_s \cdot [\mathbf{k}_s \times (\mathbf{k}_s \times (\delta\epsilon(\mathbf{r}, t) \cdot \mathbf{n}_i)]]), \quad (2.49)$$

where $\mathbf{n}_s$ is the polarization, $\mathbf{k}_s$ is the propagation vector and ω_s is the frequency of the scattered plane wave field that reaches the detector, while V indicates that the integral is over the whole scattering volume. The scattering wave vector $\mathbf{q}$ is defined as the difference between incident and scattered propagation vector,

$$\mathbf{q} = \mathbf{k}_i - \mathbf{k}_s. \quad (2.50)$$

The angle between $\mathbf{k}_i$ and $\mathbf{k}_s$ is called the scattering angle θ (see Fig. 2.2).

Figure 2.2b makes clear that the magnitude of the scattering wave vector q can be computed as

$$q^2 = |\mathbf{q}|^2 = k_i^2 + k_s^2 - 2\mathbf{k}_i \cdot \mathbf{k}_s. \quad (2.51)$$

When—like in most light scattering experiments— $k_i \approx k_s$, i.e., the scattering is quasi-elastic, the cosine rule becomes applicable and Eq. 2.51 becomes

$$q^2 = k_i^2 + k_s^2 - 2\mathbf{k}_i \cdot \mathbf{k}_s = 2k_i^2(1 - \cos \theta) = 4k_i^2 \sin^2 \frac{\theta}{2}. \quad (2.52)$$

Or, with $k_s = k_i = 2\pi n/\lambda$, where the length of the incident wave vector is written as function of the refractive index $n(n = \sqrt{\epsilon_0})$ and the incident wave length λ :

$$q = 2k_i \sin \frac{\theta}{2} = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}. \quad (2.53)$$

This is the Bragg condition.

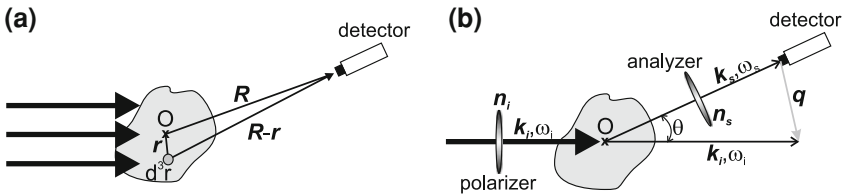


Fig. 2.2 **a** At the detector, the total radiated field is the sum of all fields radiated from any infinitesimal volume $d^3 r$ at position $\mathbf{r}$ from the center O of the illuminated volume. The detector is at position $\mathbf{R}$. **b** General light scattering setup: incident light of polarization $\mathbf{n}_i$, frequency ω_i , and wave vector $\mathbf{k}_i$ is scattered. Although it is scattered in all directions (not shown for clarity), the figure shows only the light with $\mathbf{n}_s$ and wave vector $\mathbf{k}_s$ that can reach the detector after passing an analyzer. The wave vector $\mathbf{q}$ is shown in gray as $\mathbf{k}_i - \mathbf{k}_s$ (according to [7])

Using the spatial Fourier transform of the dielectric fluctuation

$$\delta\epsilon(\mathbf{q}, t) = \int_V d^3r \exp i\mathbf{q} \cdot \mathbf{r} \delta\epsilon(\mathbf{r}, t), \quad (2.54)$$

Eq. 2.49 can be rewritten as

$$E_s(R, t) = \frac{E_0}{4\pi R\epsilon_0} \exp i(k_s R - \omega_i t) [\mathbf{n}_s \cdot [\mathbf{k}_s \times \mathbf{k}_s \times (\delta\epsilon(\mathbf{q}, t) \cdot \mathbf{n}_i)]]. \quad (2.55)$$

This can be simplified [7]:

$$E_s(R, t) = \frac{-k_s^2 E_0}{4\pi R\epsilon_0} \exp i(k_s R - \omega_i t) \delta\epsilon_{is}(\mathbf{q}, t), \quad (2.56)$$

where

$$\delta\epsilon_{is}(\mathbf{q}, t) \equiv \mathbf{n}_s \cdot \delta\epsilon(\mathbf{q}, t) \cdot \mathbf{n}_i \quad (2.57)$$

is the component of the dielectric constant fluctuation tensor along the initial and final polarization direction.

The time-correlated function of E_s can then be written as

$$\langle E_s^*(R, 0) E_s(R, t) \rangle = \frac{k_s^4 |E_0|^2}{16\pi^2 R^2 \epsilon_0^2} \langle \delta\epsilon_{is}(\mathbf{q}, t) \rangle \exp(-i\omega_i t). \quad (2.58)$$

Then, the spectral density

$$I_E(\omega) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau \langle E^*(t) E(t + \tau) \rangle \exp(-i\omega\tau) \quad (2.59)$$

of light reaching the detector with $\mathbf{n}_s$, $\mathbf{k}_s$, and ω_s can be computed as

$$I_{is}(\mathbf{q}, \omega_s, R) = \left(\frac{I_0 k_s^4}{16\pi^2 R^2 \epsilon_0^2} \right) \frac{1}{2\pi} \int_{-\infty}^{+\infty} dt \langle \delta\epsilon_{is}(\mathbf{q}, 0) \delta\epsilon_{is}(\mathbf{q}, t) \rangle \exp(i(\omega) t) \quad (2.60)$$

with $I_0 \equiv |E_0|^2$ and

$$\omega \equiv \omega_i - \omega_s. \quad (2.61)$$

The latter means that the spectral density (the intensity measured by the detector) depends only on the difference between the incident and the scattered frequency. Furthermore from Eq. 2.60 one can learn that $I_{is} \propto k_s^4$ (i.e., $I_{is} \propto \lambda^{-4}$) and $I_{is} \propto R^{-2}$. The λ^{-4} dependence means that electromagnetic radiation with short wavelengths is scattered more than that with longer wavelength, as, e.g., apparent in the blue color of the sky. The R^{-2} dependence is expected, because it just expresses the attenuation of a spherical wave.

For a given experiment, the coefficient in Eq. 2.60 becomes a constant, and the scattering intensity is then only affected by the spectral density of the dielectric constant fluctuations, i.e., the integral

$$I_{is}(\mathbf{q}, \omega) \propto \int_{-\infty}^{+\infty} dt \langle \delta\epsilon_{is}^*(\mathbf{q}, 0) \delta\epsilon_{is}(\mathbf{q}, t) \rangle. \quad (2.62)$$

The integral of Eq. 2.62 over frequency, the integrated intensity at all frequencies, provides information about the $\mathbf{q}$ -dependent mean-square fluctuations ϵ :

$$I_{is}(\mathbf{q}) = \langle |\delta\epsilon_{is}(\mathbf{q})|^2 \rangle. \quad (2.63)$$

Harking back on the definition of the scattering wave vector $\mathbf{q}$ (Eq. 2.50) and the frequency shift ω (Eq. 2.61), the scattering event can be considered in terms of energy and momentum conservation. Most generally, during a scattering process, the scattered photon sustains an energy change from $\hbar\omega_i$ to $\hbar\omega_s$ and a momentum change from $\hbar\mathbf{k}_i$ to $\hbar\mathbf{k}_s$. This must be related to the creation or annihilation of an excitation in the scattering medium. It is:

$$\hbar\omega = \hbar\omega_s - \hbar\omega_i \quad (2.64)$$

$$\hbar\mathbf{k} = \hbar\mathbf{k}_s - \hbar\mathbf{k}_i. \quad (2.65)$$

Note that in these equations the energy and momentum of the excitation can have both positive and negative sign.

2.3 Brillouin Light Scattering

Brillouin light scattering (BLS) is the inelastic scattering of monochromatic laser light by phonons in the GHz frequency range. The required high resolution is obtained by the use of multipass tandem Fabry–Pérot interferometers. In BLS spectroscopy of transparent samples, the desired dispersion relations are obtained by recording the phonon frequencies as a function of the scattering wave vector $\mathbf{q}$, which varies with the scattering angle. However, in samples exhibiting strong multiple light scattering, as for the dry colloidal crystals (opals), $\mathbf{q}$ is ill-defined and hence $\mathbf{q}$ -dependent acoustic-like modes become inaccessible. Though, localized in space, i.e., $\mathbf{q}$ -independent modes can be recorded in the BLS spectrum as it was demonstrated for sub-micron colloidal silica [8] and polymer crystals [9]. These $\mathbf{q}$ -independent frequencies have been identified as the resonance modes of the individual colloidal particles, i.e., BLS can record numerous thermally excited elastic resonances in one measurement (Chap. 4). These eigenfrequencies are uniquely defined by the geometrical and elastic characteristics of the particles. Based on these data, the elastic properties of the materials can be calculated at the nanoscale. Thus the combination of $\mathbf{q}$ -independent BLS spectroscopy of multiply

light scattering (opaque) samples and the dispersion relations from the $\mathbf{q}$ -dependent BLS spectroscopy on transparent samples is a powerful methodology to investigate the elastic behavior of nanostructured materials.

This section will introduce the basic principles of BLS following a simple approach. Further important results obtained by thermodynamical considerations will be introduced very briefly. Then a description of the BLS setup with selective attention on the main principles of the tandem Fabry–Pérot interferometer is given.

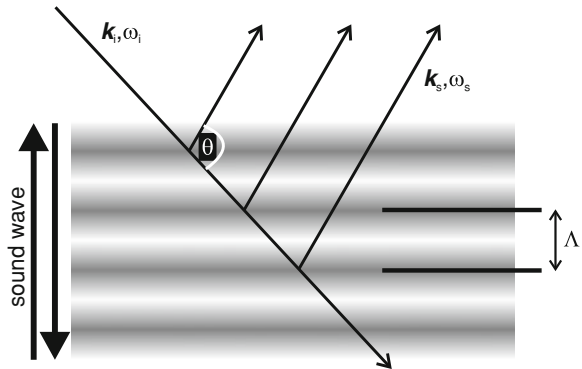
2.3.1 BLS Basics

The main principle of BLS is the scattering of photons on sound waves and the constructive interference of the multiply reflected light beam as sketched in Fig. 2.3. A plane elastic wave creates a periodic change of density and hence of the local dielectric constant in a medium, symbolized by the black/white layers. The typical velocity of an acoustic wave is between 10^3 and 10^4 ms^{-1} , while the velocity of the probing light c is $\approx 3 \times 10^8 \text{ ms}^{-1}$. Because of this great discrepancy the dielectric inhomogeneities can be regarded as a quasi-static (i.e., ‘frozen’) lattice on which the photons of the probing light are scattered. Thus, it is justified to treat the medium as a periodic multilayer stack with periodicity Λ , the wavelength of the phonon, as shown in Fig. 2.3. The probing laser light is multiply reflected (under the scattering angle θ) on these layers and the reflected light interferes on the detector, whose distant to the sample R is much larger than the periodicity of the scattering planes ($R \gg \Lambda$). The reflected intensity reaches its maximum when the interference is constructive, i.e.,

$$2n\Lambda \sin \frac{\theta}{2} = \lambda \quad (2.66)$$

with refractive index n and wavelength of light λ .

Fig. 2.3 BLS scattering process: the probing light beam is multiply reflected on the planes of a quasi-static periodic multilayer stack of modulated local dielectric constant with periodicity Λ . Only reflected beams that interfere constructively account for the scattering intensity



Insertion of Eq. 2.66 in the Bragg condition (Eq. 2.53) leads to

$$\frac{2\pi}{\Lambda} = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2} \quad (2.67)$$

and

$$q = \frac{2\pi}{\Lambda}. \quad (2.68)$$

That is to say the scattering wave vector $\mathbf{q}$ is equivalent to the wave vector $\mathbf{k}$ of the sound wave ($k = 2\pi/\Lambda$), viz. by changing θ , $\mathbf{q}$ can be chosen, too, and at every q the corresponding sound waves are probed selectively. The identity $\mathbf{q} = \mathbf{k}$ shows that the momentum conservation (cf. Eq. 2.64) during the scattering process is realized by a momentum transfer between the sound wave and the photon. From this point of view it is clear that the scattered light changes its angular frequency from ω_i to ω_s by inelastic interaction, in which a phonon, the acoustic quantum, can be either created (Stokes process) or annihilated (anti-Stokes process), depending on the direction of motion of the acoustic wave. In terms of energy conservation considerations (Eq. 2.65) it is obvious that the exchanged energy $\hbar\omega$ comes from the angular frequency of the phonon, $\omega_{\text{phonon}} = |\omega| = \omega_s - \omega_i$, which is related to the phonon wavelength and the velocity c of the acoustic wave by

$$\omega_{\text{phonon}} = \omega = \frac{2\pi c}{\Lambda}. \quad (2.69)$$

Therefore the frequency $f = \frac{\omega}{2\pi}$ undergoes a Doppler shift:

$$f_s = f_i \pm \frac{cq}{2\pi} = f_i \pm \frac{c}{2\pi} \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}, \quad (2.70)$$

using the definition of q given in Eq. 2.53. Here, the minus corresponds to a motion of the acoustic wave away from the detector leading to a frequency decrease (or phonon creation; Stokes), and the plus corresponds to a propagation direction of the acoustic waves towards the detector leading to an increasing photon frequency (or phonon annihilation; anti-Stokes). Obviously, it is

$$\omega = \omega_s - \omega_i = \pm cq. \quad (2.71)$$

Therefore the BLS spectrum consists of doublets centered at the elastic frequency with frequencies $f = \pm cq/2\pi$ (frequency shifts).

Equations 2.64 and 2.65 can now be rewritten for the Brillouin scattering process as follows:

$$\hbar\omega_s - \hbar\omega_i = \pm\hbar\omega \quad (2.72)$$

$$\hbar\mathbf{k}_s - \hbar\mathbf{k}_i = \pm\hbar\mathbf{q}. \quad (2.73)$$

Note that in these equations momentum and energy (frequency) of the acoustic wave are positively defined and plus- and minus-signs correspond again to anti-Stokes and Stokes process, respectively.

So far, this easy approach explains satisfactorily the appearance of the doublet as well as the position of the frequency shifts. However, when performing BLS experiments a central line always appears that is not explained by the above considerations. Also the intensity of the signals can not be predicted. To elucidate these features of a BLS spectra it is necessary to take some ideas from thermodynamics into account.

The total scattering intensity of a Brillouin spectrum was first derived by Einstein in 1910 [5, 6]. He started with considering ϵ as a function of density and temperature $\epsilon = \epsilon(q, T)$. For q and T are statistically independent, one can write the total differential

$$d\epsilon = \left(\frac{\partial \epsilon}{\partial q} \right)_T dq + \left(\frac{\partial \epsilon}{\partial T} \right)_q dT. \quad (2.74)$$

Then

$$\langle (d\epsilon)^2 \rangle = \left(\frac{\partial \epsilon}{\partial q} \right)_T^2 \langle (dq)^2 \rangle + \left(\frac{\partial \epsilon}{\partial T} \right)_q^2 \langle (dT)^2 \rangle. \quad (2.75)$$

Using the assumption

$$\left(\frac{\partial \epsilon}{\partial q} \right)_T \gg \left(\frac{\partial \epsilon}{\partial T} \right)_q \quad (2.76)$$

and

$$\frac{\langle (dq)^2 \rangle}{q^2} = \frac{k_B T \beta_T}{v} \quad (2.77)$$

for the mean-square fluctuation in density in the volume element v , where k_B is Boltzmann's constant and β_T is the isothermal compressibility, Eq. 2.75 becomes

$$\langle (d\epsilon)^2 \rangle \approx \left(\frac{\partial \epsilon}{\partial q} \right)_T^2 \langle (dq)^2 \rangle = \left(q \frac{\partial \epsilon}{\partial q} \right)_T^2 \frac{k_B T \beta_T}{v}. \quad (2.78)$$

Comparison with Eq. 2.63 shows the main result of these calculations,

$$I \propto \beta_T, \quad (2.79)$$

i.e., the total scattering intensity depends on the isothermal compressibility. Without going into details, the full vectorial expression for $I(\mathbf{q})$ is given by [7]

$$I_{is}(\mathbf{q}) = (\mathbf{n}_i \cdot \mathbf{n}_s)^2 \left(\frac{\partial \epsilon}{\partial q} \right)_T^2 V q^2 k_B T \beta_T \quad (2.80)$$

with scattering volume V . If $V(\theta) \approx \text{const}$, which may be valid depending on the experimental details, the total scattering intensity is also independent from the scattering angle.

Although Eq. 2.80 gives the total scattering intensity, experiments showed that only a part of the intensity belongs to the Brillouin doublets while the rest makes for a central line. These findings could be explained by Landau and Placzek regarding $\epsilon(S, p)$ as function of entropy S and pressure p [1]. In analogy to Eq. 2.75 one can write

$$\langle (d\epsilon)^2 \rangle = \left(\frac{\partial \epsilon}{\partial S} \right)_p^2 \langle (dS)^2 \rangle + \left(\frac{\partial \epsilon}{\partial p} \right)_S^2 \langle (dp)^2 \rangle \quad (2.81)$$

because fluctuations in S and p are independent, too.

The first term, also called the Rayleigh term, represents local entropy fluctuations, which do not propagate in normal liquids and are the source of the unshifted component of the scattered light with intensity I_C . The other term, the Brillouin term, represents the isoentropic pressure fluctuations, ergo, sound waves that contribute to the Brillouin doublet. With

$$\langle (dp)^2 \rangle = \frac{k_B T}{v \beta_S}, \quad (2.82)$$

where β_S is the adiabatic compressibility, and by writing

$$\left(\frac{\partial \epsilon}{\partial p} \right)_S = \left(\frac{\partial \epsilon}{\partial q} \right)_S \left(\frac{\partial q}{\partial p} \right)_S = \left(\frac{\partial \epsilon}{\partial q} \right)_S q \beta_S \quad (2.83)$$

the Brillouin term can be transformed into

$$\left(\frac{\partial \epsilon}{\partial p} \right)_S^2 \langle (dp)^2 \rangle = \left(\frac{\partial \epsilon}{\partial q} \right)_S^2 q^2 \beta_S^2 \frac{k_B T}{v \beta_S} = \left(q \frac{\partial \epsilon}{\partial q} \right)_S^2 \frac{k_B T \beta_S}{v}. \quad (2.84)$$

It becomes clear that the intensity of the Brillouin doublet $2I_B$ depends on the adiabatic compressibility β_S .

After further simplifications it can be shown that the ratio between total scattering intensity ($I_C + 2I_B$) and the intensity of the Brillouin doublet is simply given by the ratio of isothermal and adiabatic compressibility or of the specific heats at constant pressure or volume [1, 6, 7]:

$$\frac{I_C + 2I_B}{2I_B} = \frac{\beta_T}{\beta_S} = \frac{C_p}{C_v}. \quad (2.85)$$

In the form

$$\frac{I_C}{2I_B} = \frac{\beta_T - \beta_S}{\beta_S} = \frac{C_p - C_v}{C_v} = \gamma - 1 \quad (2.86)$$

it is known as the Landau–Placzek equation.

2.3.2 BLS Instrumentation

It was already pointed out that the relative shift of the photon frequency in BLS spectroscopy ($\sim 10^8$ to 10^{11} Hz) is quite subtle compared to the initial frequency of the probing light (10^{14} Hz) or to the resolution obtained by Raman spectroscopy, where frequency shifts in the order of 10^{13} Hz are measured frequently by diffraction grating spectrometers. In order to achieve such high resolution, Fabry–Pérot interferometers (FPs) are used in BLS. In combination with an highly monochromatic laser light source a single FP or, even better, a design composed of two FPs with multiple light pass can give excellent results. Here the FP principle is elucidated and the construction details of the used tandem FP as well as the general features of the whole BLS setup are illuminated.

In principle, a single FP is not much more than an etalon as it is used in laser resonant cavities. The FP consists of two plane mirrors with reflectivity R mounted accurately parallel to one another. The spacing between the mirrors is given by d and can be varied by moving one of the mirrors. When the laser light enters the etalon through the first mirror, which is usually a plane glass plate with a thin layer of metal on the inner side, it is reflected numerously between the two mirrors. However, the light with intensity I_I is already reflected when it enters the etalon, so that we have only the intensity $I_0 = I_I(1 - R)$ inside the FP before the first internal reflection. During the reflections within the FP, the intensity decreases after x reflections to

$$I_x = I_0 R^x = I_I(1 - R)R^x, \quad (2.87)$$

because every time a part of the light is also transmitted; a typical value for BLS experiments is $R \approx 0.93$. Note that Eq. 2.87 is not fully true as it does not take into account the dissipation of energy, which is usually considered by the absorptance A , i.e., $R + T + A = 1$, with transmittance T . Anyhow, it implies that with increasing reflectivity the number of reflections inside the FP increases rapidly, and this is important for the working principle of the system. When the light is reflected many times between the mirrors, the reflected beams interfere. Only light that fulfills the equation

$$m\lambda = 2n_{\text{FP}}d \cos \theta_{\text{FP}}, \quad (2.88)$$

with m being an integer and n_{FP} being the refractive index inside the FP, and θ_{FP} being the angle between the light in the FP and the normal to the mirrors, is transmitted losslessly due to constructive interference. Thus usually the interferometry is performed by moving one of the mirrors, there is just air between the mirrors. (The other possibility would be to vary n during a measurement.) With normal incidence ($\cos 0 = 1$) and $n = 1$ we can therefore simplify to

$$\lambda = \frac{2d}{m}. \quad (2.89)$$

That means that only light with wavelength $2d/m$ is transmitted, and the transmitted λ can be easily scanned when scanning different d s by moving a mirror,

e.g., by a piezo transducer. The separation between two adjacent transmission maxima for a given d is called the free spectral range ($\text{FSR}_\lambda = \Delta\lambda$). Differentiating Eq. 2.89 leads to

$$\frac{\Delta\lambda}{\lambda} = \frac{\Delta m}{m} \quad (2.90)$$

with initial wavelength λ . For $m \pm 1$ it follows in the described setup (normal incidence, $n_{\text{FP}} = 1$)

$$\text{FSR}_\lambda = \frac{\lambda^2}{2d}, \quad (2.91)$$

or in the frequency domain

$$\text{FSR} = \frac{v}{2d}, \quad (2.92)$$

with v being the velocity of light in vacuum.

The linewidth of the transmitted line depends strongly on R . As denoted above, the more often the beam is reflected before it transmits the second beam of the FP (or the first, but this light is uninteresting for the further analysis) the more often it can interfere with itself. Therefore the destructive interference will be enforced for wavelengths not satisfying Eq. 2.89 with increasing reflectivity and the function $I(\lambda)$ becomes more narrow.

Indeed, the phase difference δ_p between each succeeding reflection is

$$\delta_p = \frac{2\pi}{\lambda} 2d. \quad (2.93)$$

The transmission function of the etalon $T(\delta_p)$ is found to be (http://en.wikipedia.org/wiki/Fabry_Perot, April 2009)

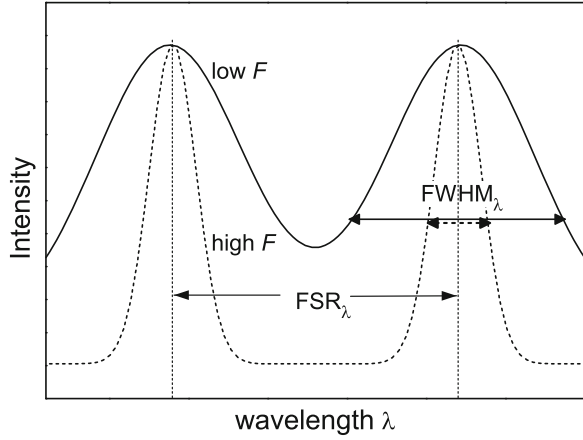
$$T(\delta_p) = \frac{(1 - R)^2}{1 + R^2 - 2R \cos \delta_p} = \frac{1}{1 + c_F \sin^2 \frac{\delta_p}{2}}, \quad (2.94)$$

where c_F is the so-called coefficient of finesse F :

$$c_F \equiv \frac{4R}{(1 - R)^2}. \quad (2.95)$$

F is defined as the ratio between FSR_λ and the full width at half maximum (FWHM $_\lambda$) of a transmission peak in the $T(\lambda)$ -function, i.e., F gives the relative separation between nearest transmission peaks (cf. Fig. 2.4) and is also the most important parameter for the practical resolution of a spectrometer. As it is approximately

Fig. 2.4 High and low finesse, FWHM_λ at fixed FSR_λ



$$\text{FWHM}_\lambda \approx \frac{4}{\sqrt{c_F}}, \quad (2.96)$$

the finesse is found to be

$$F = \frac{\text{FSR}_\lambda}{\text{FWHM}_\lambda} \approx \frac{\pi\sqrt{c_F}}{2} = \frac{\pi\sqrt{R}}{1-R}. \quad (2.97)$$

However, in real experiments the ‘practical finesse’ depends not only on the reflectivity of the mirrors but also, e.g., on the mirror flatness. In general, a high F is intended, but by practical limitations it cannot be made much greater than about 100 [10].

Single-pass FPs have been used to realized the first measurements of traveling acoustic waves in solids and liquids. However, it turned out quite early that the contrast was too low to resolve weaker signals and also the interference between neighboring orders could create easily very complicated spectra. Both problems were solved by John Sandercock when he introduced his multi-pass tandem Fabry–Pérot interferometer (multi-pass modes are also possible in single FPs).

The idea behind is quite simple: two FPs with slightly different FSR are connected in series (tandem). An intelligent use of additional mirrors assures that the light passes each FP several times (multi-pass). In the tandem operation, both FPs must transmit the same wavelength simultaneously by an appropriate scanning technique. Due to the differing FSRs of both individual FPs, always one of the FPs blocks the neighboring interferences. Let us assume FP1 to have a free spectral range $\text{FSR}_{\lambda 1}$ and FP2 $\text{FSR}_{\lambda 2}$. Then only wavelengths are transmitted that simultaneously satisfy

$$\lambda_{\text{trans}} = 2pd_1 \text{ and } \lambda_{\text{trans}} = 2qd_2, \quad (2.98)$$

where d_1 and d_2 are the mirror distances in FP1 and FP2 and p and q are integers. The effect of the tandem operation is sketched in Fig. 2.5b. The next order of light

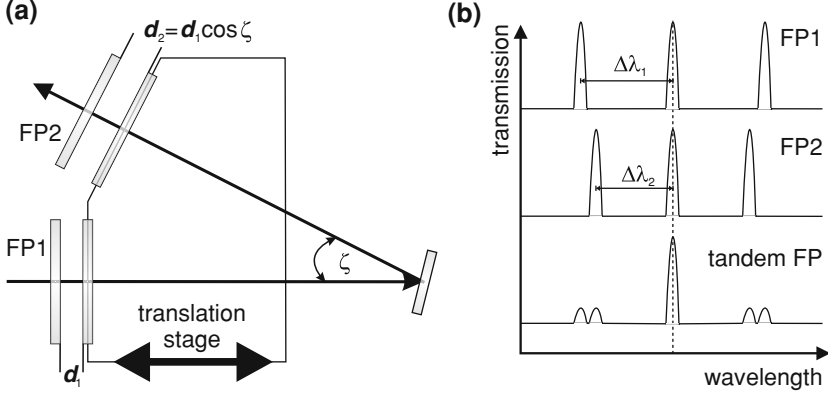


Fig. 2.5 **a** Basic mechanism of a Sandercock multipass tandem Fabry-Pérot interferometer. The light passes FP1 and then FP2. Two mirrors (one of FP1 and one of FP2) are moved simultaneously on a piezoelectric translation stage. The angle ζ of the light path between the two FPs is chosen in that way that the ratio between d_1 and d_2 is constant. **b** Effect of the multi-pass through two FPs: the neighboring orders (viewed from the harmonized central signals) that can pass each single FP are suppressed. Only the common multiples of $\Delta\lambda_1$ and $\Delta\lambda_2$ will be transmitted gainlessly

transmitted through FP1 (i.e., $\Delta p = 1$) is nearly completely suppressed by FP2 and vice versa, depending on the reflectivity of the mirrors. In our case the transmittance of wrong wavelengths is about 10^{-3} . According to that, the total FSR of the tandem interferometer is the distance between the common multiples of $\Delta\lambda_1$ and $\Delta\lambda_2$. Therefore, with tandem FPIs much higher finesses can be achieved.

Although the principle idea is not complicated at all, the technical realization was problematic. Both FPs have to be scanned synchronously, and from Eqs. 2.89 and 2.98 it is clear that the ratio between the mirror distances in both FPs must be constant. With other words

$$\frac{\Delta d_1}{\Delta d_2} = \frac{d_1}{d_2}. \quad (2.99)$$

Indeed, this condition was hard to satisfy as the total scanning distance is usually below $1 \mu\text{m}$ and the scan is repeated many times during one measurement, so that even very small asymmetries in the nanometer-range would disable the experiment.

This problem was solved in 1987 by a new, elegant design, presented in Fig. 2.5a [11]. The two FPs used in Sandercock's 'parallelogram geometry' consist of one fixed mirror and one movable mirror, each. The two movable mirrors are placed on a shared panel, the translation stage, which is the part of the setup moved during the scan. Thus, both FPs change the mirror distance always at the same time. The FPs are mounted that the two mirrors of each would touch at the same time if the translation stage would be moved to the very left. In order to satisfy Eq. 2.99 the relative orientation of the two FPs is chosen that way that the

angle ζ between FP1 and FP2 is fixed and the mirror distances have then to be adjusted in a way that

$$d_2 = d_1 \cos \zeta. \quad (2.100)$$

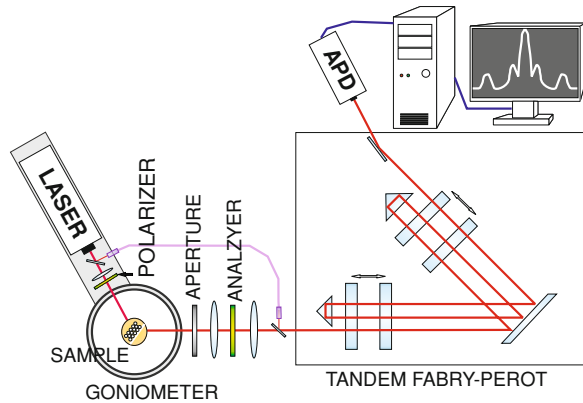
A movement of the translation stage to the right shifts the spacings between the mirrors simultaneously by Δd_1 and $\Delta d_1 \cos \zeta$, i.e., the ratio keeps constant.

In my experiments, a six-pass tandem Fabry–Pérot interferometer was used. The path of the light inside the FP as well as the other details of the applied BLS setup are sketched in Fig. 2.6. The sample is mounted in the center of a goniometer (Huber) in a custom-made sample holder with or without oven. A solid state pumped frequency-doubled Nd:YAG laser (coherence; 150 mW at 532 nm) is fixed on the goniometer and can be rotated so that scattering angles between 0° and $\sim 160^\circ$ can be chosen either in transmission or reflection geometry. In difference to pure BLS backscattering techniques, i.e., $\theta = 180^\circ$, this technique has the advantage that not only the components of $\mathbf{q}$ but the whole wave vector is changed according to Eq. 2.53.

Before the light reaches the sample, it passes a Glan polarizer (extinction ratio 10^{-5}) with vertical polarization (V), i.e., perpendicular to the scattering plane, to ensure fully polarized incident light. Behind the sample the light scattered in the direction of the detector is collected by an aperture and focused into the entrance pinhole of the tandem Fabry–Pérot interferometer (JRS Scientific Instruments) by some lenses. Before entering the FP, a Glan–Thompson analyzer (extinction ratio 10^{-8}) is passed that selects either vertically (V), i.e., perpendicular to the scattering plane, or horizontally, i.e., parallel to the scattering plane, polarized light (or, of course, everything in between). After passing the FP the transmitted light is detected by an avalanche photo diode (APD) and processed by an multi-channel analyzer with 1,024 channels. The further processing is performed by a computer software.

The stability of the alignment is greatly enhanced by the use of a reference beam. Therefore, a small amount of the laser light is diverted via the reflection

Fig. 2.6 BLS setup with six-pass tandem Fabry–Pérot interferometer. Electronic stabilization over days to weeks is achieved by permanent compensation using a diverted part of the unscattered light as reference beam. The goniometer allows to record dispersion relations with continuous $\mathbf{q}$ -range. For the eigenmode spectra the scattering angle is not relevant [12]



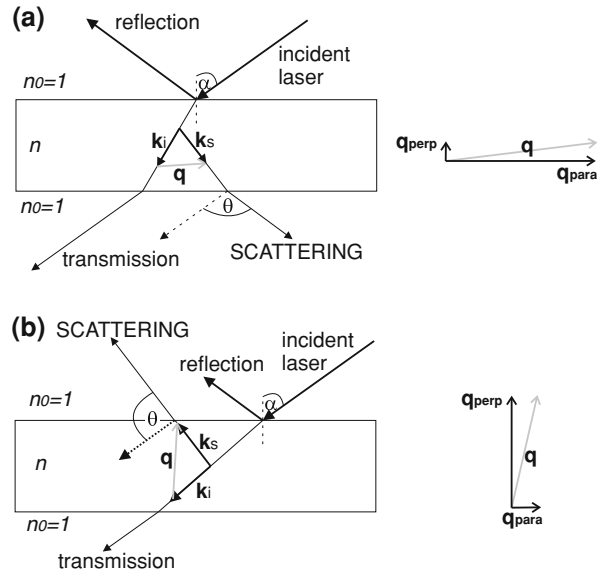
(5%) of a parallel plate on a beam splitter and an optical fiber from the incident laser beam and introduced as a reference beam that gives the central line via an optical fiber. Therefore, a mechanical shutter is used, which switches periodically the entrance to the FP between reference beam and scattered light and excludes the central elastic line. In order to avoid mechanical disruptions the whole setup is placed on an optical table with active vibration damping.

In some experiments dealing with temperature-dependent effects, e.g., glass transition experiments (Sect. 4.3.1 in Chap. 4) or measurements on kinetically stable organic glasses (Chap. 6), an oven is used in order to control the temperature of the sample in the range between ca. 10 and 200 °C. The oven is a metal cylinder with filament and coolant tubes in the wall [13]. A small slit at the height of the laser and a cylindrical quartz glass insert in order to avoid heat transfer through the slit allow the light to reach the sample and the detector afterwards. The temperature is controlled electronically (built in-house) by two Pt-100 temperature sensors inside the wall and inside the heat chamber, close to the sample. The temperature can be stabilized within better than ± 0.2 K in the given range.

Most experiments in this thesis deal with samples on a plane substrate, i.e., ‘films’. When performing the BLS experiment on such samples, there are in principle two different scattering geometries, the transmission and the reflection geometry. In transmission geometry the light scattered on the other side of the film than that of the incident laser beam is investigated, while in reflection geometry the light scattered on the side of the incident beam is regarded.

The two geometries are sketched in Fig. 2.7 and a full geometrical derivation is given in Appendix.

Fig. 2.7 Principle BLS scattering geometries for a film sample (view atop the scattering plane). **a** Transmission geometry, **b** reflection geometry. On the right side the vector decomposition for the wave vector $\mathbf{q}$ in its components perpendicular ($\mathbf{q}_{\text{perp}}$) and parallel to the film plane ($\mathbf{q}_{\text{para}}$)



In the transmission case, it is found that the magnitude of the scattering wave vector becomes

$$q = \frac{4\pi n}{\lambda} \sin \left[\frac{1}{2} \left(\sin^{-1} \left(\frac{1}{n} \sin (\theta - \alpha) \right) + \sin^{-1} \left(\frac{1}{n} \sin \alpha \right) \right) \right] \quad (2.101)$$

with the angles α and θ given in Fig. 2.7a. It is shown in the appendix that the length of the component of the scattering wave vector parallel to the film, q_{para} , is

$$q_{\text{para}} = \frac{2\pi}{\lambda} (\sin \alpha + \sin (\theta - \alpha)). \quad (2.102)$$

Obviously, in this equation the refractive index n of the sample is eliminated.

A special transmission geometry in which $q = q_{\text{para}}$ exists for $\theta = 2\alpha$. In this case q is given simply by

$$q = q_{\text{para}} = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (\text{for } \theta = 2\alpha). \quad (2.103)$$

To use this special geometry is advantageous in several ways, indeed nearly all the experiments in this thesis are performed using it. First of all, it facilitates the calculation of q , as the refractive index of the sample has not to be taken into account. Although n of most ‘standard materials’ (e.g., typical polymers like polystyrene) is well-known, the exact determination of n for unknown materials or, even more, for composite materials, as they are widely used in this thesis, may become complicated and time consuming. The second great benefit of this geometry is that in this case the direction of q is well defined parallel to the film. When discussing colloidal crystals [14] it is important to know which crystallographic direction is probed by the BLS experiment.

In the reflection geometry the general expression for q as a function of n , θ , and α becomes

$$q = \frac{4\pi n}{\lambda} \cos \left[\frac{1}{2} \left(\sin^{-1} \left(\frac{1}{n} \sin \alpha \right) + \sin^{-1} \left(\frac{1}{n} \sin (\theta + \alpha) \right) \right) \right]. \quad (2.104)$$

Also for the reflection case there is a special scattering geometry. If $\alpha = \frac{180^\circ - \theta}{2}$ the scattering wave vector is identical to its component perpendicular to the film, i.e., $q = q_{\text{perp}}$ in Fig. 2.7b.

In a cylindrical sample, e.g., a liquid in a NMR-tube, q has simply the magnitude

$$q_{\text{cylinder}} = \frac{4\pi n}{\lambda} \sin \frac{\theta}{2}. \quad (2.105)$$

2.3.3 Vibrational Modes of Individual Particles

In the foregone section it was pointed out that the result of a BLS experiment is usually the plot of longitudinal or transverse [or mixed, especially in thin films, e.g., the so-called Lamb waves (http://en.wikipedia.org/wiki/Lamb_wave, May 2009)] sound waves as a function of the scattering wave vector q , while the frequencies $f(q)$ are given as a Doppler shift of the probing laser light around its elastic line. The phase sound velocities are given by the slope of the $f(q)$ -diagram. Thus, in the case of a nonlinear function $f(q)$, i.e., if the acoustic mode is dispersive, the result of the BLS experiment is the dispersion relation in the investigated q -range.

However, the appearance of a dispersion relation is only meaningful if it is possible to determine q . If strong multiple scattering occurs in a sample, q becomes ill-defined. In such samples $f(q)$ is no longer accessible. Anyhow, now the inelastic scattering from localized modes, i.e., the vibrational resonance modes, can lead to incoherent BLS in analogy to the Raman scattering.

Indeed, in BLS experiments such samples show a spectrum where scattering at all possible qs between zero degree incident and backscattering case contributes to the final result, independent from the experimental scattering angle θ . Furthermore, also the polarization information is lost.

Nevertheless, the Brillouin spectrum of multiple scattering samples with well defined shape still gives useful information, which are not accessible by other techniques. In Chap. 4 of this thesis, several experiments are discussed dealing with the detection of vibrational resonance modes of spherical colloidal samples. BLS spectra of such samples deliver many useful information about the individual colloids and, in case of hybrid materials, about the mechanical properties of the components, too. This section will give a short introduction into the mathematical description of the vibrations in spheres, their theoretical calculation, and their detection by BLS.

Under stress-free boundary conditions, the vibrational modes are usually called eigenmodes. The eigenmodes for free homogeneous elastic spheres have been derived by Lamb in the nineteenth century [15]. The modes can be classified as torsional and spheroidal ones, both labeled by the indices n , l , and m , which describe the radial (n) and the angular (l , m) dependence of the displacement (cf. Sect. 2.1.3). The torsional modes are fully tangential, i.e., they involve only shear motions and do not cause changes in the sphere volume—they do not contribute to the BLS intensity. The spheroidal modes involve usually both shear and stretching motions, and they can be fully specified by two indices in analogy to the atomic orbitals as the n -th order radial solution ($n = 1, 2, 3, \dots$) for angular momentum ‘quantum number’ l ($l = 0, 1, 2, \dots$) [4, 12, 16]. Only spheroidal modes with $l = 0$ have purely radial displacement (breathing modes) [17].

By solving the wave equation for elastic and isotropic media (Eq. 2.37), Lamb found the frequencies of the eigenmodes (n , l) to be (in a very general expression):

$$f(n, l) = \left(x(n, l) \sqrt{\frac{R(c_l, c_t)}{\varrho}} \right) / d, \quad (2.106)$$

with $x(n, l)$ being a constant for each individual mode, $R(c_l, c_t)$ being the rigidity, and d being the diameter of the sphere. The rigidity is a function of the longitudinal and transverse sound velocities and has the dimension of pressure, thus it is simply a modulus. Indeed, e.g., for the (1,2)-mode, R is identical with the shear modulus $\mu (=C_{44})$.

The experiments discussed in [Chap. 4](#) are all related to the vibrational modes of colloidal spheres in air. Because of the large density (and elastic) mismatch between air and the colloids, the boundary-conditions are quasi that of a stress-free, undamped vibration, thus these modes are practically real eigenmodes and the values calculated by Lamb's theory are a good approximation. However, in the more general case of a elastic vibrator embedded in an elastic matrix, some coupling should occur between the eigenmodes and the propagating acoustic waves in the matrix. The amount of coupling depends on the elastic mismatch between spheres and matrix. While the limit case of large mismatch corresponds to the free eigenmodes, where the elastic energy is totally localized in the spheres, the other limit case is a zero-mismatch, which means that all energy is coupled between sphere and matrix and an elastic wave can travel the system like a homogeneous medium.

To calculate the distinct vibrational modes of elastic spheres with radius r_s and density ϱ_s in an elastic matrix with density ϱ_m , one has to introduce boundary conditions. At the surface of the sphere, the displacement $\mathbf{u}$ has to be the same inside and outside the sphere [[4](#), [18](#)]:

$$\mathbf{u}^i|_{r=r_s} = \mathbf{u}^m|_{r=r_s}. \quad (2.107)$$

The same must be fulfilled for the surface traction $\boldsymbol{\tau} (\boldsymbol{\tau} = \boldsymbol{\sigma}(\mathbf{r}) \cdot \hat{\mathbf{r}}$, with stress tensor $\boldsymbol{\sigma}$ and outgoing unit vector normal to the sphere surface $\hat{\mathbf{r}}$) :

$$\boldsymbol{\tau}^i|_{r=r_s} = \boldsymbol{\tau}^m|_{r=r_s}. \quad (2.108)$$

The field can be written as a linear sum of spherical waves as discussed in [Sect. 2.1.3](#). The field inside the spheres becomes

$$\mathbf{u}^i(\mathbf{r}) = \sum_{lm} a_{lm}^L \mathbf{I}_{lm}(R, k_l^i) + a_{lm}^M \mathbf{m}_{lm}(R, k_l^i) + a_{lm}^N \mathbf{n}_{lm}(R, k_l^i) \quad (2.109)$$

with the coefficients a_{lm}^L , a_{lm}^M and a_{lm}^N . In the same way we can write for the field in the matrix

$$\mathbf{u}^m(\mathbf{r}) = \sum_{lm} b_{lm}^L \mathbf{I}_{lm}^m(R, k_l) + b_{lm}^M \mathbf{m}_{lm}(R, k_l^m) + b_{lm}^N \mathbf{n}_{lm}(R, k_l^m) \quad (2.110)$$

with the coefficients b_{lm}^L , b_{lm}^M and b_{lm}^N . With [Eqs. 2.43–2.45](#) one can write

$$\begin{aligned}
\mathbf{u}(\mathbf{r}) = & \sum_{lm} x_{lm}^L \frac{1}{k_l} \nabla [R_l(k_l r) Y_{lm}(\hat{\mathbf{r}})] + x_{lm}^M \nabla \times [\mathbf{r} R_l(k_l r) Y_{lm}(\hat{\mathbf{r}})] \\
& + x_{lm}^N \frac{1}{k_t} \nabla \times \nabla \times [\mathbf{r} R_l(k_t r) Y_{lm}(\hat{\mathbf{r}})],
\end{aligned} \tag{2.111}$$

where the x replace either the coefficients a inside or b outside the spheres and k_l and k_t are the longitudinal wavenumbers ($k = \omega/c$) inside (k^l) or outside (k^m) the sphere, respectively.

With Eq. 2.111 it becomes clear that Eqs. 2.107 and 2.108 are equivalent to three scalar equations, each, and the boundary conditions can be expressed as a system of six homogeneous equations with an infinite numbers of unknowns. Due to the orthonormality over the spherical surface of the Legendre functions Y_{lm} , it is possible to decompose each of these equations into l equations, but independent from m . That is also the coefficients a and b depend only on l , leading to a system of six equations with six unknowns for each l . It can be broken into two smaller systems, considering the orthogonality of $\mathbf{m}_{lm}$ to $\mathbf{n}_{lm}$ and $\mathbf{l}_{lm}$, which contain two equations involving the coefficients a_l^M and b_l^M and four equations containing the coefficients a_l^L , b_l^L , a_l^N , and b_l^N , respectively. Non-trivial solutions for both systems are only achieved if their determinants are zero, leading to a set of discrete modes with angular frequencies ω_l^n for each l and n -th order, corresponding to the expression given in Eq. 2.106.

The considerations presented in this section are the fundamental of theoretical methods dealing with the scattering of plane waves on single and multiple spheres presented in Sect. 3.4 in Chap. 3.

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