# X-ray and Neutron Scattering

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**Abstract.** The series of lectures focuses on experimental techniques using X-rays and neutrons. We will discuss differences and similarities between these two probes and consider various scattering and spectroscopic techniques based on X-rays and neutrons. The material is selected in such a way that it complements the traditional condensed matter courses and gives a deeper understanding of scattering techniques. The main focus lies in scattering from interfaces and disordered systems.

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### 1 Introduction: X-rays, neutrons, and electrons

In order to study the atomic structure of matter by scattering, one has to use the probe with a wavelength comparable with interatomic distances, i.e.  $\lambda \sim 1$  Å. The most common probes are photons, neutrons, and electrons with the following dispersion relations (Fig. 1.1)

• X-rays:

$$E = \hbar\omega = \frac{2\pi\hbar c}{\lambda} = \frac{12398}{\lambda[\text{Å}]} [\text{eV}]; \qquad (1.1)$$

• Neutrons:

$$E = \frac{2\pi^2 \hbar^2}{m_n \lambda^2} = \frac{81.8204}{\lambda^2 [\text{Å}^2]} [\text{meV}]; \qquad (1.2)$$

• Electrons (non-relativistic):

$$E = \frac{2\pi^2 \hbar^2}{m_e \lambda^2} = \frac{150.442}{\lambda^2 [\text{\AA}^2]} [\text{eV}].$$
(1.3)

Further on, we will often describe the wave properties of these particles using the wave vector  $\mathbf{k} = \mathbf{p}/\hbar$ , where  $\mathbf{p}$  is the momentum of the particle, and the absolute value of the wave vector is

$$\mathbf{k}| = k = \frac{2\pi}{\lambda}.\tag{1.4}$$

X-rays and neutrons interact relatively weakly with atoms. Therefore they can be used to study bulk samples. In contrast, electrons interact strongly, so it is practically impossible to study the sample with a thickness larger than a few hundreds of nanometers.

#### 1.1 Interaction of X-ray photons with matter

The interaction of photons with matter is based on movement of charges caused by the electrical component of the electro-magnetic wave. Due to a very high frequency of X-rays, only the lightest particles, i.e. electrons are able to react to the electrical field. Protons, which are 1836 times heavier than the electrons, essentially do not move.

The following processes may happen when an X-ray photon hits an atom:

- Classical scattering: an X-ray photon transfers its energy to the atom, and the electrons start to oscillate in the electric field. Oscillating electrons generate a secondary electromagnetic wave with the same frequency (i.e. the same energy). As a result, the outcoming photon has the same energy as the incoming photon but a different direction (Fig. 1.2). An elastic scattering of an X-ray photon by a single electron is described by the Thomson formula (Section 1.1.3). The classical scattering from an atom will be considered later in section 1.1.6.
- **Compton scattering**: an X-ray photon partially transfers its energy to electrons of an atom. (Fig. 1.3). The easiest case is the Compton scattering on a free electron. Since an electron is not as heavy as a whole atom, one has to take into account recoil velocity of the electron, which it obtains during the scattering process. This leads to the increase of the photon wavelength by

$$\Delta \lambda = \frac{2\pi \hbar c}{m_e} (1 - \cos 2\theta) = \lambda_e (1 - \cos 2\theta), \qquad (1.5)$$



Fig. 1.1: Energy-wavelength relationship for photons, neutrons and electrons



Fig. 1.2: Classical scattering



Fig. 1.3: Compton scattering



Fig. 1.4: Photoelectric effect

where  $2\theta$  is the scattering angle between the directions of the incident and outcomming photons and  $\lambda_e = 2.43 \cdot 10^{-2}$  Å is the Compton wavelength of the electron. Relativistic consideration of an X-ray photon scattered by a single electron is given by the Klein-Nishina formula. In the limit of low recoil velocity of the electron,  $v/c \to 0$ , the Klein-Nishina formula transforms to the Thomson non-relativistic formula. The Compton scattering from an atom with one and many electrons will be considered in section 1.1.7.

• Photoelectric absorption: an X-ray photon completely transfers its energy to an electron which leaves the atom (Fig. 1.4). In the X-ray regime, the energy of the photon is high enough to remove electrons from the inner shells of the atom. In this case, a metastable corehole is created. An electron in the outer shell can recombine with this core-hole, and the excess energy can be emitted in a form of a fluorescent photon with the energy equal to the difference between the energy levels of the core-hole and the recombinating electron (Fig. 1.5). It is also possible, that the excess energy is transferred to a third electron which leaves the atom, so-called Auger process (Fig. 1.6). Auger process dominates in light atoms with  $Z \gtrsim 35$  [1].

X-ray photons scattered classically have the same frequency as the incident photons. Moreover, their phases are fixed with the respect to the phases of the incident photons. This means, that the classically scattered photons are able to interfere with each other, as long as the incident radiation is coherent. Therefore classical scattering is often referred as *coherent scattering*. In contrast to that, Compton scattering and fluorescence are called *incoherent scattering* and often are treated as a backgroung in scattering experiments.

Unless otherwise indicated, for the purpose of this course, we will focus on classical scattering. This is justified, since we will typically detect only the scattered X-ray photons (and not electrons), and these are dominated by classical scattering (at least after background subtraction in our energy range of around 10 keV). In certain cases, of course, we will make use of characteristic transitions, such as in X-ray standing waves (XSW) or anomalous scattering.

#### 1.1.1 Differential scattering cross-section

The probability of various scattering processes are usually quantified using scattering cross-sections (Fig. 1.7). By definition, the differential scattering cross-section is

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{I_{sc}}{\Phi_0 \cdot d\Omega},\tag{1.6}$$

where  $I_{sc}$  is a flux of the photons scattered into a solid angle  $d\Omega$  (photons per second) and  $\Phi_0$  is the density of the incoming flux (photons per second per square meter). To calculate the total scattering cross-section one has to integrate the differential cross-section over all possible angles

$$\sigma = \int_{4\pi} \left(\frac{\partial\sigma}{\partial\Omega}\right) d\Omega. \tag{1.7}$$



Fig. 1.5: X-ray fluorescence



Fig. 1.6: Auger process



Fig. 1.7: Differential scattering cross-section



Fig. 1.8: Attenuation of X-rays

#### 1.1.2 Attenuation of X-rays

The atomic scattering cross-section can be represented as a sum of total scattering cross-sections of the processes described above

$$\sigma_{atom} = \sigma_{classical} + \sigma_{compton} + \sigma_{absorption}.$$
 (1.8)

An X-ray beam passing through the material slab of thickness dx is attenuated due to the scattering and absorption (Fig. 1.8), so the intensity of the beam is decreased by

$$dI = I \cdot \mu \cdot dx,\tag{1.9}$$

where  $\mu$  is the linear absorption coefficient

$$\mu = \rho_{at} \cdot \sigma_{atom} = \left(\frac{\rho_{mass} \cdot N_A}{M}\right) \sigma_{atom}.$$
 (1.10)

Here  $\rho_{at}$  is numeric density of the atoms (atoms per cubic meter),  $\rho_{mass}$  is mass density (g/cm<sup>3</sup>),  $N_A = 6.022 \cdot 10^{23} \text{ mol}^{-1}$  is the Avogadro number, and M (g/mol) is the atomic mass.

The solution of Eq. (1.9) leads to the exponential decay of the beam intensity known as the Beer-Lambert law:

$$I = I_0 \cdot e^{-\mu x}.$$
 (1.11)

The characteristic length  $1/\mu$  over which the intensity decays to  $1/e \approx 1/2.72 \approx 0.37$  is called the attenuation length. Some typical values of the attenuation length are given in Table 1.

## 1.1.3 Classical scattering by a single free electron (polarization factor)

In the following sections we will consider classical elastic scattering starting from a single free electron (so-called Thomson scattering) and then gradually increasing the complexity of the system to the scattering from an atom.

Let us first consider a movement of an electron caused by the electric field  $E_x = E_0 e^{-i\omega t}$  of a plane monochromatic wave (see the schematic in Fig. 1.9). The electron at the origin of the coordinate system oscillates along the *x*-axis with the phase shift  $\pi$  with respect to the wave:

$$x = -\frac{eE_0}{m_e\omega^2}e^{-i\omega t},\tag{1.12}$$

where e is the negative charge of the electron. Therefore it produces an electromagnetic field at the observation point **R** at the time t, which in dipole approximation can be written as [3]

$$\begin{aligned} \mathbf{H}(\mathbf{R},t) &= \frac{1}{c^2 R} \begin{bmatrix} \ddot{\mathbf{d}} |_{t-\tau} \times \mathbf{n} \end{bmatrix}, \\ \mathbf{E}(\mathbf{R},t) &= \frac{1}{c^2 R} \begin{bmatrix} \begin{bmatrix} \ddot{\mathbf{d}} |_{t-\tau} \times \mathbf{n} \end{bmatrix} \times \mathbf{n} \end{bmatrix}, \end{aligned} \tag{1.13}$$

where  $\mathbf{n} = \mathbf{R}/R$  is a unit vector pointing to the point of the observation  $\mathbf{R}$  and the time derivative of the dipole moment  $d_x = e \cdot x$  is taken at the moment of time  $t - \tau$ , where the delay  $\tau = R/c = Rk/\omega$  is needed for the electromagnetic field to travel from the electron located at the origin to the point of the observation  $\mathbf{R}$  (see retarded potential in any book on classical electrodynamics).

	E = 8.04  keV	E = 16  keV
	$(\operatorname{Cu-}K_{\alpha})$	
$N_2$ (air)	$0.9\cdot 10^6$	$5.5 \cdot 10^6$
Be	5352	22961
С	1053	7765
$\mathrm{SiO}_2$	132	1016
Si	71	536
Ca	38	262
Cu	22	18
Pb	4	6

Table 1: Characteristic absorption length  $1/\mu$  for some materials. The values are given in micrometers. Data are taken from [2].



Fig. 1.9: Coordinate system for derivation of the polarization factor (up) and the resulting distribution of intensity (bottom). The incoming photon propagates along z-axis and has linear horizontal polarization (electric field  $\mathbf{E}_0$  is always parallel to x-axis).

The resulting magnitude of the electric field and the corresponding intensity of the scattered electromagnetic wave at  $\mathbf{R}$  can be written as

spherical

wave

$$E(\mathbf{R},t) = -r_e \cdot \underbrace{E_0 \frac{e^{ikR-i\omega t}}{R}}_{R} \cdot \underbrace{P(2\theta,\varphi)}_{R} , \qquad (1.14)$$

polarization factor

$$I(\mathbf{R}) = \frac{r_e^2}{R^2} E_0^2 P^2(2\theta, \varphi), \qquad (1.15)$$

where

$$r_e = \frac{e^2}{mc^2} \approx 2.82 \cdot 10^{-5} \,\text{\AA},$$
 (1.16)

is the so-called classical radius of electron and

$$P^{2}(2\theta,\varphi) = \cos^{2} 2\theta + \sin^{2} 2\theta \sin^{2} \varphi \qquad (1.17)$$

is the polarization factor (see the schematic in Fig. 1.9).

In the case of vertical scattering ( $\varphi = \pi/2$ ), the polarization factor is constant and equal to unity,  $P^2 = 1$ , and in the case of horizontal scattering ( $\varphi = 0$ ), it has the anisotropic distribution of a dipole antenna,  $P^2 = \cos^2 2\theta$ . In the case of non-polarized incidence photons, the polarization factor should be averaged over  $\varphi$ , which leads to  $P^2 = \frac{1}{2}(1 + \cos^2 2\theta)$ .

The results can be easily rewritten in terms of the differential scattering cross-section using the following relation:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{E^2 R^2}{E_0^2} = r_e^2 \cdot P^2(2\theta,\varphi) , \qquad (1.18)$$

which can be obtained from the definition given in Eq. (1.6).

#### 1.1.4 Classical scattering by a single bound electron

When the electron is bound, its equation of motion can be written as

$$\ddot{x} + \gamma \dot{x} + \omega_0^2 x = \frac{E_0 e}{m_e} e^{-i\omega t}, \qquad (1.19)$$

where  $\omega_0$  is the natural frequency of the bound electron (eigenfrequency),  $\gamma$  is an effective damping coefficient, and the right-hand side represents the external force created by an incident electromagnetic wave. In this case, similar to Eq. (1.12), the electron oscillates around its equilibrium position:

$$x = A \cdot e^{-i\omega t},\tag{1.20}$$

but the amplitude A is now a complex number

$$A = \frac{\frac{E_0 e}{m_e}}{\omega_0^2 - \omega^2 - i\gamma\omega} = |A|e^{-i\Delta\varphi}, \qquad (1.21)$$

with a magnitude

$$|A| = \frac{\frac{E_0 e}{m_e}}{\sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2}}$$
(1.22)

and the phase

$$\tan\Delta\varphi = \frac{\gamma\omega}{\omega^2 - \omega_0^2}.$$
 (1.23)

The dependence of the magnitude |A| and the phase  $\psi$  on the frequency of the incident electromagnetic field is shown in Fig. 1.10.



Fig. 1.10: Magnitude and the phase of the bound electron oscillations as a function of the frequency of the incoming field. The resonance happens when the natural frequency of the electron matches the frequency of the driving force,  $\omega = \omega_0$ .

#### 1.1.5 Interference effects for the scattering by multiple electrons

Let us first consider scattering by an electron located at the point  $\mathbf{r} \neq 0$ , which is different from the situation described in section 1.1.3. The scheme for this experiment is shown in Fig. (1.11). To evaluate the scattered wave in this case, we just need to modify Eq. (1.14) and take into account two following factors:

- The electrical field of the incoming wave at the point r equals to  $E_0 \exp(i\mathbf{k}_{in}\mathbf{r} i\omega t)$ . This results in a phase shift  $\mathbf{k}_{in}\mathbf{r}$  of the driving force which causes the oscillations of the electron (note the phase difference  $\mathbf{k}_{in}\mathbf{r}$  of the incoming wave between the origin O and the point  $\mathbf{r}$  in Fig. (1.11).
- Another phase shift occurs in the spherical wave generated by the oscillating electron, because the origin of this wave is located at the point **r**.

Therefore, the electric field at the point of observation  $\mathbf{R}$  can be written as

$$E(\mathbf{R},t) = -r_e \cdot E_0 e^{i\mathbf{k}_{in}\mathbf{r} - i\omega t} \frac{e^{ik_{out}|\mathbf{R}-\mathbf{r}|}}{|\mathbf{R}-\mathbf{r}|} \cdot P(2\theta,\varphi).$$
(1.24)

For the far field diffraction (Fraunhofer diffraction), when r is much smaller than both R and the wavelength  $\lambda$ , the change in the distance in the denominator can be neglected,  $|\mathbf{R} - \mathbf{r}| \approx R$ , and the phase  $ik_{out}|\mathbf{R} - \mathbf{r}|$  in the nominator can be approximated by  $ik_{out}R - i\mathbf{k}_{out}\mathbf{r}$ . Thus, Eq. (1.24) can be written as

$$E(\mathbf{R},t) = -\frac{r_e}{R} E_0 e^{ik_{out}R - i\omega t} \cdot e^{-i\mathbf{q}\mathbf{r}} \cdot P(2\theta,\varphi), \qquad (1.25)$$

where

$$\mathbf{q} = \mathbf{k}_{out} - \mathbf{k}_{in}$$

$$q = \frac{4\pi}{\lambda} \sin \theta$$
(1.26)

is the scattering vector. The result obtained in Eq. (1.25) differs from Eq. (1.14) by just a pure phase factor  $e^{i\mathbf{qr}}$ .

According to the principle of superposition, the electromagnetic wave scattered by N electrons located at the positions  $\mathbf{r}_n$  will be just a sum of the spherical waves similar to the one in Eq. (1.25)

$$E(\mathbf{R},t) = -\frac{r_e}{R} E_0 e^{ik_{out}R - i\omega t} \cdot P(2\theta,\varphi) \cdot \sum_{n=1}^N e^{-i\mathbf{q}\mathbf{r}_n}.$$
 (1.27)

The sum in this equation describes the interference effects occurring between the spherical waves scattered by different electrons. Similarly, we can also write a differential scattering cross-section as

$$\left[\left(\frac{\partial\sigma}{\partial\Omega}\right) = r_e^2 \cdot P^2(2\theta,\varphi) \cdot \left|\sum_{n=1}^N e^{-i\mathbf{q}\mathbf{r}_n}\right|^2\right].$$
 (1.28)

#### 1.1.6 Classical (elastic) X-ray scattering by an atom

In an atom, the electrons are distributed around the nucleus with the probability density  $\rho_e(\mathbf{r}) = |\psi(\mathbf{r})|^2$ . Therefore instead of calculating the sum as in



Fig. 1.11: Scattering of the electromagnetic wave by an electron displaced by vector  $\mathbf{r}$  from the origin of the coordinates O. Bold red and blue lines shows additional path  $\mathbf{k}_{in}\mathbf{r}/k_{in} - \mathbf{k}_{out}\mathbf{r}/k_{out}$  that the incident and the scattered wave need to travel when the electron is located not in the origin O. The corresponding phase shift equals to  $\mathbf{k}_{in}\mathbf{r} - \mathbf{k}_{out}\mathbf{r} = -\mathbf{qr}$ .



Fig. 1.12: Scattering of the electromagnetic wave by several electrons. The incoming photons of the incidence plane monochromatic wave are in phase, while the scattered photons have the phase shift of  $-\mathbf{qr}_n$ .

Eq. (1.27), one has to evaluate the integral called an X-ray scattering form factor of an atom:

$$\sum_{n=1}^{N} e^{i\mathbf{q}\mathbf{r}_n} \to f(\mathbf{q}) = \int \rho_e(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}, \qquad (1.29)$$

which is a Fourier transform of the electron density  $\rho_e(\mathbf{r})$ . Typical angularly averaged X-ray atomic form factors for several atoms are shown in Fig. 1.13. From comparing Eqs. (1.14) and (1.27), it follows that the atomic X-ray form factor is a ratio of electrical field scattered by an atom to the electrical field scattered by a single free electron. In other words, it shows how much the scattering by an atom differs compared to a single free electron.

In practice, f(q) for all atoms are already calculated and parameterized (see, for example, parameterization by Cromer-Mann [4] and Waasmaier-Kirfel [5]). In case of the forward scattering, the X-ray atomic form factor equals to the total amount of electrons in the atom:

$$f(q \to 0) = \int \rho_e(\mathbf{r}) d\mathbf{r} = Z. \tag{1.30}$$

In real atoms, electrons are not free: they interact with the nucleus and each other. Strong resonance effects will happen when the energy of the incoming photon matches the electron biding energy. To take these effects into account, one has to calculate the X-ray atomic scattering form factors using a quantum approach, i.e. by evaluating the matrix elements  $f(\mathbf{q}) \sim \langle \mathbf{k} + \mathbf{q} | \hat{V}_{int} | \mathbf{k} \rangle$ , which happen to be complex numbers (see section 1.1.4 for the illustration). In result, to the calculated above elastic X-ray scattering atomic form factor  $f_0(q)$  one should add corrections that depend on energy of the photon  $\hbar\omega$ :

$$f(q,\hbar\omega) = f_0(q) + f_1(\hbar\omega) + if_2(\hbar\omega).$$
(1.31)

The dispersion corrections are tabulated<sup>1</sup> for most of the chemical elements [1, 2], and some examples are shown in Fig. 1.14.

#### 1.1.7 Coherent and incoherent X-ray scattering

As it was briefly discussed in the beginning of section 1.1, when one considers scattering of an X-ray photon by a free electron, one has to take into account the recoil energy of the electron, which leads to the change of the wavelength of the scattered X-ray photon (Eq. 1.5). Therefore, the classical scattering can be considered as a limiting case of Compton scattering when the recoil velocity of the electron is negligible. But strictly speaking, elastic scattering of an X-ray photon on a free electron is not possible.

The situation is different, when one considers X-ray scattering from an atom. Because the atom is heavy, its recoil energy,  $E_{\text{recoil}} = \hbar^2 q^2 / (2M) \ll \hbar \omega$  is much smaller than the energy of the X-ray photon  $\hbar \omega$ . Therefore this energy change can be neglected,<sup>2</sup> and the elastic scattering is a much better approximation for the scattering by an atom, as compared to the scattering by a electron.

From a quantum mechanical point of view, the elastic scattering of X-rays by an atom means, that the electrons of the atom remain in the same state



Fig. 1.13: X-ray scattering atomic form factors for several chemical elements [4].



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Fig. 1.14: Dispersion corrections  $f_1(\hbar\omega)$  and  $f_2(\hbar\omega)$  for several chemical elements [2].

<sup>&</sup>lt;sup>1</sup>In the tables for the dispersion correction, the atomic form factors are given for q = 0and usually the real and imaginary parts are tabulated for different  $\hbar\omega$ :  $f(q = 0, \hbar\omega) =$  $f'(\hbar\omega) + if''(\hbar\omega)$ . In this case, the correction  $f_1(\hbar\omega)$  in Eq. (1.31) can be calculated as  $f_1(\hbar\omega) = f'(\hbar\omega) - Z$  (see Eq. (1.30)).

 $<sup>^{2}</sup>$ For the deeper understanding of recoil energy we refer to the Mössbauer effect, the quantum theory of which is given, for example, in [6]

before and after the scattering process. In contrast, the Compton scattering includes partial transfer of the X-ray energy to the electrons, so the electrons are in an excited state after the scattering process.

Elastic X-ray scattering is usually referred as *coherent* scattering, because the elastically photons have the same energy and therefore they can form a diffraction pattern. Compton scattering is usually referred as *incoherent* scattering, because the final energy of the photon is not fixed (it depends on which exactly electron state was excited), so the incoherently scattered photons cannot form a diffraction pattern. This terminology is different from what is called neutron coherent and incoherent scattering (see section 1.2.2).

The total X-ray scattering cross section by an atom can be written as a sum of coherent and incoherent counterparts [7, 8]:

$$\begin{pmatrix} \frac{\partial\sigma}{\partial\Omega} \end{pmatrix} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} + \left(\frac{\partial\sigma}{\partial\Omega}\right)_{inc} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |f(q)|^2 + \left(\frac{\partial\sigma}{\partial\Omega}\right)_{KN} \cdot s(q) \\ \approx \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |f(q)|^2 + \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot s(q).$$
(1.32)

Here f(q) is the atomic form factor (Eqs. (1.29),(1.31)), and s(q) is so-called incoherent scattering function. The classical differential cross-section  $\left(\frac{\partial\sigma}{\partial\Omega}\right)_e$ is given by Eq. (1.18) (Thomson scattering from a single electron). For the X-ray energies relevant for a diffraction experiment ( $\hbar\omega \leq 100$  keV), the Klein-Nishina differential cross-section  $\left(\frac{\partial\sigma}{\partial\Omega}\right)_{KN}$  is very close to the nonrelativistic classical cross-section, so in the following we will use  $\left(\frac{\partial\sigma}{\partial\Omega}\right)_{KN} \approx \frac{k_{in}}{k_{out}} \cdot \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \approx \left(\frac{\partial\sigma}{\partial\Omega}\right)_e$ . The sketch of coherent, incoherent and total X-ray scattering cross-sections for helium atom is shown in Fig. 1.15

The incoherent scattering function s(q) can be calculated using different approximations and it is tabulated for many chemical elements [7]. Generally, it is significantly non-zero (i.e. cannot be neglected) for light elements and for the large values of the scattering vector q (Fig. 1.15).

To better illustrate the difference between the coherent and incoherent scattering, let us consider N atoms positioned at  $\mathbf{r}_n$  scattering the incident beam of monochromatic X-ray photons. Each atom can scatter X-ray photon elastically (coherently) or inelastically (incoherently) with certain probabilities, defined by the atomic form factor f(q) and the incoherent scattering function (Eq. (1.32)). The photons scattered elastically will have the same wavelength (equal to the initial wavelength of the incoming photons). Therefore, the elastically scattered photons will interfere with each other and form an interference pattern, as it was shown in Eq. (1.28). In contrast, each incoherently scattered photon will have its individual wavelength, different from all other incoherently scattered photons. Therefore, incoherently scattered intensity will be a sum over all intensities of the incoherent photons. This can be written as the following equation for the total scattering cross-section from N atoms:

$$\begin{pmatrix} \frac{\partial \sigma}{\partial \Omega} \end{pmatrix} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{coh} \left| \sum_{n=1}^{N} e^{-i\mathbf{q}\mathbf{r}_n} \right|^2 + \left( \frac{\partial \sigma}{\partial \Omega} \right)_{inc} \cdot N$$

$$= \left( \frac{\partial \sigma}{\partial \Omega} \right)_e \cdot |f(q)|^2 \cdot \sum_{n,m=1}^{N} e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)} + \left( \frac{\partial \sigma}{\partial \Omega} \right)_e \cdot s(q) \cdot N.$$

$$(1.33)$$

A similar equation can be written for neutron scattering (compare with Eq. (1.50)), although the coherent and incoherent scattering has a different nature for neutrons.

In the special case of X-ray scattering by an atom with a single electron, the incoherent scattering function s(q) can be evaluated exactly. To illustrate



Fig. 1.15: Coherent, incoherent and total Xray scattering cross-section for He atom with Z = 2 electrons. The cross-sections are normalized to the Thomson scattering  $\left(\frac{\partial \sigma}{\partial \Omega}\right)_e$ (see Eq. (1.32)). The X-ray scattering form factor f(q) and the incoherent scattering function sq were calculated with Eqs. (B.20) and (B.30) under the assumption that two electrons in He atom are independent and each of them can be described by the single-electron wave function  $\phi(\mathbf{r}) = e^{-r/a}/(\pi a^3)^{1/2}$  with a = 0.32 Å.

this, let us first consider elastic X-ray scattering by an atom with a single electron, and then consider the inelastic X-ray scattering.

For the elastic scattering, the electron remains in its initial (ground) state  $|0\rangle$ , and according to the perturbation theory (Fermi's golded rule), the probability of such process is defined by the matrix element  $M_{00} = \langle 0 | \hat{V} | 0 \rangle$ , where  $\hat{V} \propto e^{-i\mathbf{q}\mathbf{r}}$  is the operator of interaction between the X-ray photon and the electron. This matrix element has been already calculated in Eq. (1.29), although we have never explicitly considered quantum perturbation theory. More specifically, the X-ray coherent scattering cross-section is

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |M_{00}|^2 = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |f(q)|^2 \tag{1.34}$$

where  $f(q) = M_{00}$ , and  $\left(\frac{\partial \sigma}{\partial \Omega}\right)_e$  is the differential cross-section for X-ray scattering by a single free electron (Thomson scattering given by Eq. (1.14)).

In a non-elastic Compton scattering process, the X-ray photon loses part of its energy (see Eq. (1.5)), and this energy is absorbed by the electron of the atom. This leads to the transition of the electron from the ground state  $|0\rangle$  to some excited state  $|\nu\rangle$ . The probability of such a process is proportional to the matrix element  $|M_{0\nu}|^2$ .

To obtain the total *incoherent* scattering cross-section (Compton scattering), one has to sum over all possible final states  $|\nu\rangle$ :

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{inc} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot \sum_{\nu>0} |M_{0\nu}|^2, \qquad (1.35)$$

where the sum runs over all possible states of the electron  $|\nu\rangle$ , except of the ground state  $|0\rangle$ . The total scattering cross-section is then

$$\begin{pmatrix} \frac{\partial\sigma}{\partial\Omega} \end{pmatrix} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} + \left(\frac{\partial\sigma}{\partial\Omega}\right)_{inc} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{e} \left[|M_{00}|^{2} + \sum_{\nu>0} |M_{0\nu}|^{2}\right] = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{e} \sum_{\nu\geq0} |M_{0\nu}|^{2},$$
(1.36)

where the sum runs now over all possible states of the electron  $|\nu\rangle$ . Since the set of wave functions  $|\nu\rangle$  is complete, one can use closure relation<sup>3</sup> and show that

$$\sum_{\nu \ge 0} |M_{0\nu}|^2 = \sum_{\nu \ge 0} \langle 0| \, \hat{V}^* \, |\nu\rangle \, \langle \nu| \, \hat{V} \, |0\rangle = \langle 0| \, \hat{V}^* \hat{V} \, |0\rangle = 1, \tag{1.37}$$

where we used that  $\hat{V}^*\hat{V} = e^{i\mathbf{q}\mathbf{r}}e^{-i\mathbf{q}\mathbf{r}} = 1$ . Thus, for an atom with a single electron,

$$\begin{pmatrix} \frac{\partial \sigma}{\partial \Omega} \end{pmatrix} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{coh} + \left( \frac{\partial \sigma}{\partial \Omega} \right)_{inc} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{e},$$

$$\begin{pmatrix} \frac{\partial \sigma}{\partial \Omega} \end{pmatrix}_{coh} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{e} \cdot |f(q)|^{2},$$

$$\begin{pmatrix} \frac{\partial \sigma}{\partial \Omega} \end{pmatrix}_{inc} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{e} \cdot \left( 1 - |f(q)|^{2} \right).$$

$$(1.38)$$

This means, an atom with a single electron will scatter in total as much as a single free electron (Thomson scattering). A certain fraction the scattered

$$\sum_{\nu'} \left\langle \nu \right| \hat{A} \left| \nu' \right\rangle \left\langle \nu' \right| \hat{B} \left| \nu \right\rangle = \left\langle \nu \right| \hat{A} \hat{B} \left| \nu \right\rangle$$

<sup>&</sup>lt;sup>3</sup>if the wave functions  $|\nu'\rangle$  form a complete orthonormal set of eigenfunctions, the following identity is true:  $1 = \sum_{\nu'} |\nu'\rangle \langle \nu'|$ . Thus, for any operators  $\hat{A}$  and  $\hat{B}$  the identity (closure relation) is true:

photons will be coherent (elastic scattering) and the rest of the scattered photons will be incoherent (inelastic scattering).

The X-ray scattering by a many-electron atom has two main complications. First, one has to consider many-electron wave functions. Second, the interaction operator  $\hat{V} = \sum_{n=1}^{Z} e^{-i\mathbf{qr}_n}$  is now a sum over all electrons n = 1, 2, ..., Z in the atom. In this case, one can still calculate the intensity of coherent scattering as it was done before via the total atomic scattering form factor given by Eq. (1.29). Equations (1.34-1.36) are still valid, but the sum (1.37) cannot be easily evaluated. An approximation for X-ray scattering from a many-electron atom is discussed in Appendix B.

#### **1.2** Interaction of neutrons with matter

Neutrons are not charged, but they have a magnetic moment  $\mu_n \approx -1.9\mu_N$ , where  $\mu_N = |e|\hbar/(2m_pc)$  is the nuclear magneton. Therefore, neutrons can interact with both the electrical charge and the magnetic moment of the nuclei. Apart from these processes, which will be discussed in more details below, also a resonant neutron scattering through an intermediate excited state may happen.

Also a neutron capture is possible resulting in creation of a new stable isotope. This processs occurs with the probability inversely proportional to the neutron speed. Below we will consider an elastic scattering of a neutron by an atom.

#### 1.2.1 Elastic scattering of a neutron by a nucleus

The straightforward way to analyze elastic scattering of neutron on a nucleus is to consider the stationary Schrödinger equation for neutrons

$$-\frac{\hbar^2}{2m_n}\nabla^2\psi(\mathbf{r}) + \hat{V}_N(\mathbf{r})\psi(\mathbf{r}) = \frac{\hbar^2k^2}{2m_n}\psi(\mathbf{r}), \qquad (1.39)$$

where  $\hat{V}_N(\mathbf{r})$  is the interaction potential between the nucleus and the neutron. (Fig. 1.16). The potential  $\hat{V}_N(\mathbf{r})$  is non-zero only at very short range (order of the size of the nucleus, ~  $10^{-5}$  Å, as shown in Fig. 1.17).

Let us put the origin of coordinates at the position of the nucleus. In the following consideration we will assume that the heavy nucleus does not move.<sup>4</sup> Assuming that the incident neutrons can be described by a plane wave,  $e^{i\mathbf{k}_{in}\mathbf{r}}$ , it can be shown that far away from the scattering center the neutron wave function can be represented as a sum of the incident wave and the spherical divergent scattered wave:

$$\psi(\mathbf{r}) \approx \underbrace{e^{i\mathbf{k}_{in}\mathbf{r}}}_{\text{incident}} + \underbrace{f_n(\Omega)\frac{e^{ikr}}{r}}_{\text{scattered}} . \tag{1.40}$$

Here  $f_n(\Omega)$  has units of length and is called the scattering amplitude. It is directly related to the differential scattering cross-section:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = |f_n(\Omega)|^2. \tag{1.41}$$



Fig. 1.16: Neutron scattering by a nucleus.



Fig. 1.17: Typical interaction potential  $\hat{V}_N(\mathbf{r})$  between the nucleus and a neutron.

<sup>&</sup>lt;sup>4</sup>If the nucleus is free, one has to consider the scattering process in the center-of-mass system. In this case, the result will be the same as derived in the text, but the neutron mass  $m_n$  has to be replaced by reduced mass  $\mu = m_n M/(m_n + M)$ , where M is the nucleus mass.

An analogous quantity for X-ray scattering would be the product  $r_e f(\mathbf{q})$  which also has units of length.

To consider the scattering in a given solid angle  $\Omega$ , or, in other words, in the direction of  $\mathbf{k}_{out}$ , we can select the portion of the scattered wave propagated in this direction and approximate it with a plane wave  $e^{i\mathbf{k}_{out}\mathbf{r}}$ .

One of the easiest approaches to finding the scattering amplitude  $f_n(\Omega)$ is to use the first Born approximation, as described in section 2.7.2), which is essentially the first order perturbation theory (see also: Fermi's golden rule). Strictly speaking, this approximation can not be applied to the nuclear scattering of thermal neutrons, because the nuclear potential is not small (Fig. 1.17). However, the first Born approximation still gives the qualitatively correct result (independence of the scattering amplitude on the direction), and one can even obtain the quantitatively correct result by replacing the actual attracting nuclear potential  $\hat{V}_N(\mathbf{r})$  by a short-range repulsive pseudo-potential  $\hat{V}_N^{ps}(\mathbf{r}) = \alpha \delta(\mathbf{r})$  [9, 10]. The approximation with a delta function is justified by the fact, that the range of the nuclear potential  $\sim 10^{-5}$  Å is much smaller than the thermal neutron wavelength  $\lambda = 2\pi/k \sim 1$  Å.

Using this pseudo-potential, we can find  $f_n(\Omega)$  as a matrix element:

$$f_n(\Omega) = -\frac{m_n}{2\pi\hbar^2} \cdot \langle e^{i\mathbf{k}_{out}\mathbf{r}} | \hat{V}_N^{ps}(\mathbf{r}) | e^{i\mathbf{k}_{in}\mathbf{r}} \rangle = -\frac{m_n}{2\pi\hbar^2} \int \hat{V}_N^{ps}(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
  
$$= -\frac{m_n}{2\pi\hbar^2} \int \alpha \delta(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} = -\frac{m_n}{2\pi\hbar^2} \alpha = -b$$
 (1.42)

where  $\mathbf{q} = \mathbf{k}_{out} - \mathbf{k}_{in}$ . Thus, we obtain that the neutron scattering amplitude is independent on the scattering vector  $\mathbf{q}$  and equals to -b (note the sign convention). The constant b is called the bound neutron scattering length and is positive for the majority of the isotopes.<sup>5</sup>

The neutron scattering length does not depend on the scattering vector  $\mathbf{q}$  (unlike X-rays), but it strongly depends on type of the nucleus (both chemical element and isotope). The latter fact is illustrated in Fig. 1.18. For the purpose of our calculations of the neutron scattering from condensed matter, knowledge of this one number, the *q*-independent scattering length *b* for a given isotope (and spin orientation), is sufficient, and our considerations will be based on this.

Since the neutron scattering amplitude does not depend on the scattering angle, the total scattering cross-section can be easily calculated as

$$\sigma = 4\pi b^2. \tag{1.43}$$

#### 1.2.2 Coherent and incoherent neutron scattering

In the previous section 1.2.1, we ignored the interaction between the nuclear spin  $\mathbf{I}$  and the spin  $\mathbf{S}$  of a neutron. If the nuclear spin is zero, I = 0, the

For an average mass number  $\langle A \rangle \approx 100$  Turchin estimates an approximately 3 % probability for a negative scattering length [12], which makes plausible that they do occur in the table of isotopes, but are rather the exception (e.g., b < 0 for <sup>1</sup>H, <sup>48</sup>Ti, <sup>55</sup>Mn, <sup>62</sup>Ni).



Fig. 1.18: Neutron scattering length  $b_{coh}$  for natural isotopes of different elements with Z =1 - 95 [13].

<sup>&</sup>lt;sup>5</sup>If we want to understand the origin of the scattering length b in some more detail, we consider the scattering of a thermal neutron from a nucleus, which we model as a potential well V(r) with depth  $V_0$  (typically several 10 MeV deep) and spatial extension  $R_0$  (typically only a few fm).

For the full calculation we refer to textbooks [11, 12]. In fact, this is a typical problem in quantum mechanics, and from matching the wave function inside (typically strongly curved for typical  $V_0$ ) and outside the potential (typically very slowly varying or indeed essentially constant on the scale of femtometers if the neutron wavelength is  $\sim 1\text{\AA}$ ) at  $r = R_0$  we finally obtain a certain scattering phase  $\delta_0$  (for the scattering from the individual nucleus), which is then used to determine the scattering length.

scattering amplitude does not depend on the direction of the neutron spin and the scattering length can be calculated by Eq. (1.42).

If the nuclear spin is non-zero,  $I \neq 0$ , one has to consider spin-spin interaction. Since S = 1/2, there are only two possible orientations of the neutron spin **S** and the nuclear spin **I**:

- the spin of neutron **S** is parallel to the nuclear spin **I**, so the total angular momentum has the absolute value  $J_+ = I + 1/2$ . The total amount of  $N_+ = 2J_+ + 1 = 2I + 2$  wave functions correspond to the parallel orientation of **S** and **I**.
- the spin of neutron **S** is anti-parallel to the nuclear spin **I**, so the total angular momentum has the absolute value  $J_{-} = I 1/2$ . The total amount of  $N_{-} = 2J_{-} + 1 = 2I$  wave functions correspond to the anti-parallel orientation of **S** and **I**.

The neutron scattering length will be also different in these two cases:

$$b = \begin{cases} b_+ , & \text{for } \mathbf{S} \uparrow \uparrow \mathbf{I}, \\ b_- , & \text{for } \mathbf{S} \uparrow \downarrow \mathbf{I}. \end{cases}$$
(1.44)

If the neutron is not in a polarized state, the probabilities  $W_{\pm}$  to find the neutron in a parallel or anti-parallel states can be directly calculated from the total number of the corresponding wave functions:

$$W_{+} = \frac{N_{+}}{N_{+} + N_{-}} = \frac{I+1}{2I+1} , \text{ for } \mathbf{S} \uparrow\uparrow \mathbf{I},$$
  

$$W_{-} = \frac{N_{-}}{N_{+} + N_{-}} = \frac{I}{2I+1} , \text{ for } \mathbf{S} \uparrow\downarrow \mathbf{I}.$$
(1.45)

It can be seen, that  $W_+ > W_-$ , because there are more wave function corresponding to the parallel state ( $\mathbf{S} \uparrow \uparrow \mathbf{I}$ ) then to the anti-parallel state ( $\mathbf{S} \uparrow \downarrow \mathbf{I}$ ). The mean scattering length denoted as  $b_{coh}$  can be calculated as

$$b_{coh} \equiv \langle b \rangle = W_{+}b_{+} + W_{-}b_{-} = \frac{I+1}{2I+1}b_{+} + \frac{I}{2I+1}b_{-}.$$
 (1.46)

It is called the bound-*coherent* scattering length, because it describes the process in which all atoms scatter neutrons identically, i.e. coherently. In contrast to that, the bound-*incoherent* scattering length  $b_{inc}$  is defined as the standard deviation of the neutron scattering length:

$$b_{inc}^{2} \equiv \langle b^{2} \rangle - \langle b \rangle^{2} = W_{+}b_{+}^{2} + W_{-}b_{-}^{2} - (W_{+}b_{+} + W_{-}b_{-})^{2}$$
$$= (b_{+} - b_{-})^{2} \cdot \frac{I(I+1)}{(2I+1)^{2}}.$$
(1.47)

It describes the scattering processes that depend on the mutual orientation of the neutron spin  $\mathbf{S}$  and nuclear spin  $\mathbf{I}$ , and therefore the atoms are scattering individually, i.e. incoherently.

The difference between the coherent and incoherent scattering of neutrons can be further illustrated by considering the scattering of unpolarized neutron beam on N nuclei positioned at  $\mathbf{r}_n$ . We can write an expression for the differential cross-section similarly to Eq. (1.28), but taking into account that each atom scatters neutrons with the scattering length  $b_n$  and one has to average the result over all possible orientations of the neutron spins:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \left\langle \left|\sum_{n=1}^{N} b_n e^{-i\mathbf{q}\mathbf{r}_n}\right|^2 \right\rangle = \sum_{n,m=1}^{N} \langle b_n b_m^* \rangle e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)}, \quad (1.48)$$

where the asterisk denotes complex conjugation. For the majority of the isotopes, the scattering length is a real number, i.e.  $\mathfrak{Im}\{b\} \ll \mathfrak{Re}\{b\}$  [12, 14], so the complex conjugation can be omitted.

The mean values in sum (1.48) can be calculated separately for the diagonal terms (n = m) and off-diagonal terms  $(n \neq m)$ :

Two Eqs. (1.49) can be merged together and written in a single line as  $\langle b_n b_m \rangle = \langle b \rangle^2 + \delta_{nm} (\langle b^2 \rangle - \langle b \rangle^2)$ . Then the differential scattering cross-section in Eq. (1.48) can be written as

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \langle b\rangle^2 \sum_{n,m=1}^{N} e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)} + \underbrace{\left(\langle b^2 \rangle - \langle b \rangle^2\right)N}_{\text{incoherent scattering}}.$$
(1.50)

It is now explicitly shown that the interference between the neutrons scattered by different nuclei occurs only in coherent scattering, while the incoherent scattering does not depend on position of the nuclei. The scattering effects arising due to the presence of different orientations of nuclear and neutron spins in the sample are called spin-incoherent scattering.

The total neutron scattering cross-section also can be written as a sum of coherent and incoherent parts:

$$\sigma = 4\pi \langle b^2 \rangle = 4\pi \left( W_+ b_+^2 + W_- b_-^2 \right) = 4\pi \langle b \rangle^2 + 4\pi \left( \langle b^2 \rangle - \langle b \rangle^2 \right) = \sigma_{coh} + \sigma_{inc}.$$
(1.51)

As it was mentioned before, the neutron scattering lengths and cross-sections strongly depend not only on chemical element (see Fig. 1.18), but also on isotopes. The values for well-known examples hydrogen and carbon isotopes are given in Table 2 The presence of different isotopes in the sample leads to the so-called isotopic incoherent neutron scattering.

#### **1.2.3** Magnetic scattering of neutrons

Due to non-zero magnetic moments of neutrons, they also interact electromagnetically with electrons in partially filled atomic shells. The corresponding amplitude of neutron magnetic scattering is proportional the atomic form factor  $f(\mathbf{q})$  given in Eq. (1.29) and can be calculated as

$$f_m = 2r_e \gamma f(\mathbf{q}) \cdot \langle S'M' | \hat{V}_M | SM \rangle,$$
$$\hat{V}_M = (\mathbf{S}_{at} \mathbf{S}) - \frac{(\mathbf{q} \mathbf{S})(\mathbf{S}_{at} \mathbf{q})}{q^2}$$
(1.52)

Here  $\gamma = \mu_n/\mu_N = -1.9$  is the magnetic moment of neutrons in the units of nuclear magnetons, S and S' are the initial and final spin states of the neutron, M and M' are the initial and final states of the atomic spin  $\mathbf{S}_{at}$ (not the nuclear spin I). From the equation for  $\hat{V}_M$  it follows, that the magnetic scattering is determined by the component of the magnetic moment perpendicular to the momentum transfer  $\mathbf{q}$ .

The magnitude of the magnetic scattering is comparable with the nuclear scattering (see section 1.2.2), which leads to a noticeable interference

	$^{1}_{1}\mathrm{H}$	$^2_1\mathrm{D}$	$^{12}_{6}{ m C}$	$^{13}_{6}C$
Ι	1/2	1	0	1/2
c	99.985	0.015	98.90	1.10
$b_+$	10.85	9.53	-	5.89
<i>b_</i>	-47.52	0.95	-	7.12
$b_{coh}$	-3.74	6.67	6.65	6.19
$b_{inc}$	25.27	4.04	0	-0.52
$\sigma_{coh}$	1.76	5.59	5.56	4.81
$\sigma_{inc}$	80.28	2.05	0	0.03
$\sigma$	82.03	7.64	5.56	4.84

Table 2: Neutron scattering length and crosssections for some isotopes. In the second line the natural abundance c for the isotopes is given in per cents. The values for the scattering lengths are given in fm, for the crosssections - in barns (1 barn = 100 fm<sup>2</sup>). Data are taken from [14].

between these two scattering mechanisms. The resulting differential scattering cross-section is

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = b^2 + f_m^2 \pm 2b|f_m|, \qquad (1.53)$$

where b is the amplitude of nuclear scattering,  $f_m$  is the amplitude of magnetic scattering, and the sign of the interference term depends on the mutual orientation of the nuclear and atomic spins. The interference term  $2b|f_m|$  allows to produce polarized neutron beams via the scattering on ferromagnetics.

#### 1.3 Interaction of electrons with matter

Electrons being electrically charged particles interact with the electrons of the atom as well as the nuclei. The resulting elastic atomic electron scattering form factors can be estimated by the Mott–Bethe formula [15]:

$$f_e(q) = \frac{2}{a_0} \cdot \frac{Z - f_x(q)}{q^2}.$$
 (1.54)

Here  $a_0 = 0.529$  Å is the Bohr radius, the scattering vector q is defined in Eq. (1.26), and  $f_x(q)$  is an elastic X-ray atomic scattering factor defined in Eq. (1.29). Note that traditionally the electron scattering form factor is defined as the scattering amplitude in quantum mechanics, i.e.  $\left(\frac{\partial \sigma}{\partial \Omega}\right) =$  $|f(\mathbf{q})|^2$ , so it has units of length. The comparison between the X-ray, neutron and electron form factor for Cu is shown as example in Fig. 1.19.

The most important point about electron scattering is, of course, that the scattering cross section is so high, that the single-scattering assumption is no longer valid. The single-scattering approximation works very well for X-ray and neutron scattering, which makes these techniques much much more straight-forward to analyze and allows one to use Fourier transfrom to calculate the scattering magnitudes (as for example in Eq. (1.29)). In this course, we will focus on single-scattering approximation, and mostly consider X-rays and neutrons, although one should remember that the electron diffraction is also broadly used in material science and allows to achieve incredible spatial resolution and "see" individual atoms in thin samples.

Of course, there are also electron inelastic scattering processes, the most important of which are thermal diffuse scattering, plasmon excitations, interband and intraband excitations, inner-shell excitations (for more details see [17]).



Fig. 1.19: Scattering length by copper atom for electrons  $(f_e(q))$ , X-rays  $(r_e f_x(q))$  and neutrons  $(b_{coh})$  [16].

## 2 Scattering from surfaces and interfaces

#### 2.1 Index of refraction

#### 2.1.1 X-ray index of refraction for electron gas

A detailed derivation of the index of refraction for electromagnetic waves, including X-rays, can be found for example, in [18, 19]. Here we will present a simplified approach, which nevertheless leads to the correct result.

Let us first consider a gas of free electrons with density  $n_e$ . When the electromagnetic field propagates through such a system, the electrons at position  $\mathbf{r}$  will be displaced by the electric field  $\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0 e^{i\mathbf{k}\mathbf{r}-i\omega t}$  from their initial positions by the value (compare with Eq. (1.12))

$$\Delta \mathbf{r} = -\frac{e\mathbf{E}_0}{m_e\omega^2} e^{i\mathbf{k}\mathbf{r}-i\omega t} = -\frac{e}{m_e\omega^2} \mathbf{E}.$$
(2.1)

The volumetric polarization (polarization of the unit of the volume) of the gas can then be calculated as

$$\mathbf{P} = n_e \cdot e \cdot \Delta \mathbf{r}.\tag{2.2}$$

This allows us to evaluate the electric displacement field D

$$\mathbf{D} = \mathbf{E} + 4\pi \mathbf{P} = \varepsilon \mathbf{E} \tag{2.3}$$

and write the permittivity as

$$\varepsilon = 1 + 4\pi \frac{\mathbf{P}}{\mathbf{E}} = 1 - 4\pi \cdot n_e \frac{e^2}{m_e \omega^2},\tag{2.4}$$

using the fact that all vectors **D**, **E** and **P** are collinear to each other. Using the relation  $kc = \omega$  for photons, it is easy to see that the second term in Eq. (2.4) is of the order of  $n_e r_e \lambda^2$ , where  $r_e$  is the classical radius of an electron. With the values typical for X-rays ( $\lambda \sim 1$ Å,  $r_e \approx 2.8 \cdot 10^{-5}$ Å,  $n_e \sim 1$ Å<sup>-3</sup>), this second term is just a small correction to unity. This allows us to use the Taylor series to evaluate the index of refraction for X-rays:

$$n = \sqrt{\varepsilon} \approx 1 - 2\pi \cdot n_e \frac{e^2}{m_e \omega^2}.$$
 (2.5)

One should note here that the value of the index of refraction is slightly below unity, meaning that the *phase velocity* of X-rays,  $c/n = \omega/k$  is slightly *above* the speed of light. There is, however, no contradiction to the theory of relativity, which limits the *group velocity*  $V_{gr} = \partial \omega/\partial k$  to be less than the speed of light. There is no restriction on the value of the phase velocity.

In the case of bound electrons, one should modify the equation for the displacement of electrons, as it was done in section 1.1.4. This leads to the following expression for the X-ray index of refraction:

$$n = 1 + 2\pi n_e \cdot \frac{e^2}{m_e} \cdot \frac{1}{\omega_0^2 - \omega^2 - i\gamma\omega}.$$
(2.6)

From this equation it is evident that the index of refraction has a real part (describing refraction) and an imaginary part (describing absorption).

The latter fact can be easily shown by writing the index of refraction as  $n = 1 - \delta + i\beta$  and substituting it into the equation for the electromagnetic wave propagating through the media with the index of refraction n:

$$E = E_0 e^{iknx - i\omega t} = E_0 \exp\left[i\frac{\omega}{c}(1 - \delta + i\beta)x\right] \exp[i\omega t]$$
  
=  $E_0 \exp\left[i\frac{\omega(1 - \delta)}{c}x\right] \exp[i\omega t] \exp\left[-\frac{\omega\beta}{c}x\right].$  (2.7)

Therefore for the intensity one can write

$$I \propto |E|^2 = I_0 \exp\left[-\frac{2\omega}{c}\beta x\right].$$
(2.8)

Comparing this result with Eq. (1.11) shows that the absorption coefficient  $\mu$  is proportional to the imaginary part of the index of refraction

$$\beta = \Im \mathfrak{m}\{n\} = \frac{c}{2\omega}\mu = \frac{\lambda}{4\pi}\mu.$$
(2.9)

#### 2.1.2 X-ray index of refraction for atoms

To write the expression for the X-ray index of refraction for the gas of atoms, let us rewrite Eq. (2.5) as

$$n = 1 - \frac{2\pi n_e r_e}{k^2},$$
(2.10)

and modify it in the following way. First, we should replace the electron density  $n_e$  with atomic density  $\rho_{at}$ . Second, we should replace the scattering amplitude corresponding to a single electron, i.e.  $r_e$ , with the scattering by an atom, i.e.  $r_e f(0)$ . Here we took into account the fact, that the index of refraction is very close to unity, which means that the X-ray photons only very slightly change their direction when scattered by the atoms, so the atomic scattering form factor f(q) should be taken at  $q \approx 0$ . Finally, we can write the X-ray index of refraction as

$$n = 1 - \frac{2\pi\rho_{at}r_e f(0)}{k^2} = 1 - \delta + i\beta, \qquad (2.11)$$

$$5 = \frac{2\pi r_e \rho_{at}}{k^2} \Re\{f(0)\}, \qquad (2.12)$$

$$\beta = -\frac{2\pi r_e \rho_{at}}{k^2} \Im \mathfrak{m}\{f(0)\}.$$
(2.13)

The form factor f(0) changes monotonically with the X-ray energy  $\hbar\omega$ , except of the region near the absorption edges, where the dispersion corrections to the atomic scattering form factor can not be neglected (see Eq. (1.31) and Fig. 1.14). However, away from the absorption edges, one can neglect the dispersion corrections and obtain the following estimate for the index of refraction:

$$n = 1 - \frac{2\pi\rho_{at}r_e f(0)}{k^2} = 1 - \delta,$$
(2.14)

with

$$\delta = \frac{2\pi r_e \rho_{at}}{k^2} = \frac{2\pi r_e \rho_e}{k^2},\tag{2.15}$$

where  $\rho_e = Z \cdot \rho_{at}$  is the total electron density of the material.

Since we consider only small changes in the direction of the X-rays (small scattering angles), the index of refraction is not sensitive to the structure of the material. The only quantity it depends on is the total electron density (as in Eq. (2.14)) or, more precisely, the type of atoms as in Eqs. (2.11-2.13), where the dispersion corrections are taken into account. Some typical values for  $\delta$  and  $\beta$  are given in Table 3.

#### 2.1.3 Neutron index of refraction for atoms

Since neutron scattering is very similar to X-ray scattering (the order of magnitude of the scattering cross sections is similar), the index of refraction for neutrons can be also written as  $n = 1 - \delta + i\beta$ . However, for neutrons

	E = 8.04  keV		
	$(\operatorname{Cu-}K_{lpha})$		
	δ	eta	
Be	$5.3 \cdot 10^{-6}$	$2.3\cdot 10^{-9}$	
C	$7.1 \cdot 10^{-6}$	$1.2\cdot 10^{-8}$	
$SiO_2$	$7.1 \cdot 10^{-6}$	$9.3\cdot 10^{-8}$	
Si	$7.6 \cdot 10^{-6}$	$1.7\cdot 10^{-7}$	
Cu	$2.4 \cdot 10^{-5}$	$5.5\cdot 10^{-7}$	
Au	$4.7 \cdot 10^{-5}$	$4.9\cdot 10^{-6}$	
	E = 1	16 keV	
	δ	eta	
Be	$1.3 \cdot 10^{-6}$	$2.7\cdot 10^{-10}$	
С	$1.8 \cdot 10^{-6}$	$7.9\cdot 10^{-10}$	
$SiO_2$	$1.7 \cdot 10^{-6}$	$6.1\cdot 10^{-9}$	
Si	$1.9 \cdot 10^{-6}$	$1.2\cdot 10^{-8}$	
Cu	$6.7 \cdot 10^{-6}$	$3.4\cdot 10^{-7}$	
Au	$1.2 \cdot 10^{-5}$	$1.6\cdot 10^{-6}$	

Table 3: X-ray index of refraction  $n = 1-\delta+i\beta$ for various materials. The electron density was calculated for most common crystal structure (e.g. graphite for carbon). Data are taken from [2].

	$\lambda = 1 \text{ Å}$		
	δ	eta	
Be	$1.5 \cdot 10^{-6}$	$1.6\cdot 10^{-12}$	
C	$1.2 \cdot 10^{-6}$	$1.7\cdot 10^{-13}$	
$SiO_2$	$2.5 \cdot 10^{-7}$	$2.4\cdot10^{-12}$	
Si	$3.3 \cdot 10^{-7}$	$4.0\cdot 10^{-12}$	
Cu	$1.0 \cdot 10^{-6}$	$1.8\cdot 10^{-10}$	
Au	$7.4 \cdot 10^{-7}$	$2.6\cdot 10^{-9}$	

Table 4: Neutron index of refraction  $n = 1 - \delta + i\beta$  for various materials with natural isotopic mixture. The neutron wavelength  $\lambda = 1$  Åcorresponds to the energy E = 81.8 meV (see Eq. (1.2)). Data are taken from [14, 20].

the corrections should expressed through the scattering cross sections and scattering length. To do this, let us use the result of Eq. (2.9) and rewrite the index of refraction for X-rays as following:

$$n = 1 - \delta + i\beta = 1 - \frac{\lambda^2}{2\pi} r_e \rho_{at} \Re \mathfrak{e}\{f(0)\} + i \frac{\lambda}{4\pi} \mu.$$
(2.16)

Now it is very easy to rewrite this result for neutrons, by replacing the X-ray scattering length  $r_e \Re \mathfrak{e} \{f(0)\}$  by the neutron scattering length  $b_{coh}$  and rewriting the linear absorption coefficients according to Eq. (1.10) as  $\mu = \rho_{at}(\sigma_{abs} + \sigma_{inc})$ . Here we took into account the fact that only coherently scattered neutrons can interfere and therefore contribute to the real part of the index of refraction. Incoherently scattered neutrons, as well as absorbed neutrons, are "lost" and therefore should be included in the imaginary part of the index of refraction [21]. Finally, the index of refraction for neutrons is

$$n = 1 - \delta + i\beta = 1 - \frac{\lambda^2}{2\pi}\rho_{at}b_{coh} + i\frac{\lambda}{4\pi}\rho_{at}(\sigma_{abs} + \sigma_{inc}).$$
(2.17)

Since the neutron and X-ray scattering cross-sections have the same order of magnitude, the correction to the neutron index of refraction  $\delta$  is also  $10^{-6} - 10^{-5}$  as for X-rays, as shown for some materials in Table 4.

#### 2.2 Scattering at an ideal interface

Let us consider an ideal flat interface between two materials with the refraction indices  $n_1$  and  $n_2$  (see Fig. 2.1). When the incident wave (X-rays or neutrons) with a wave vector  $k_0$  propagates through the first materials and hits the interface, part of it is reflected (reflected wave). From optics it is known, that the angle of reflection equals to the angle of incidence:

$$\alpha_1 = \alpha_0. \tag{2.18}$$

The part of the wave that continues to propagate through the second material (transmitted wave) slightly changes its direction due to the difference in refraction indices. According to Snell's law:

$$n_1 \cos \alpha_0 = n_2 \cos \alpha_2. \tag{2.19}$$

Note that here the angles are counted from the surface, not from the normal to it, as it is common in optics.

#### 2.2.1 Total external reflection

Let us consider the situation, when the incident wave propagates in vacuum  $(n_1 = 1)$ , and the second material has the refractive index slightly less than unity  $(n_2 = n = 1 - \delta + i\beta)$ , which is very typical for X-rays and neutrons. If the incident angle is too small, the whole incident wave is reflected, i.e. there is no transmitted wave. This effect is called total external reflection, in contrast to the total internal reflection for visible light in optics. The critical angle of incidence  $\alpha_c$  below which the total external reflection is observed, can be found from the condition

$$\cos \alpha_2 = \frac{n_1}{n_2} \cos \alpha_0 \le 1, \tag{2.20}$$

from which one finds using the Taylor series (and neglecting absorption)

$$\alpha_0 \ge \alpha_c = \sqrt{2\delta}.\tag{2.21}$$



Fig. 2.1: Incident, reflected and transmitted waves at an ideal interface between two materials with different refraction indices:  $n_1$  for z > 0 and  $n_2$  for z < 0.



Fig. 2.2: Magnitude of the electric field in the evanescent wave below the surface (z < 0).

For more shallow incidence angles  $\alpha_0 < \alpha_c$ , the wave vector of the transmitted wave becomes an imaginary number:

$$k_{2z} = \sqrt{k_2^2 - k_{2x}^2} = \sqrt{k_0^2 n^2 - k_0^2 \cos^2 \alpha_0} \approx i k_0 \sqrt{\alpha_c^2 - \alpha_0^2}.$$
 (2.22)

This means that the transmitted wave is evanescent:

$$E_2(z) = E_2 e^{-ik_{2z}z - i\omega t} = E_2 e^{k_0 z \sqrt{\alpha_c^2 - \alpha_0^2}} e^{-i\omega t},$$

and its intensity decays exponentially for z < 0 (below the surface):

$$I_2(z) \propto |E_2(z)|^2 = I_0 e^{2k_0 z} \sqrt{\alpha_c^2 - \alpha_0^2} = I_0 e^{z/\Lambda}.$$

This is illustrated by Fig. 2.2. The penetration depth of the evanescent wave into the material can be evaluated as

$$\Lambda = \frac{1}{2k_0\sqrt{\alpha_c^2 - \alpha_0^2}} \tag{2.23}$$

or, including absorption,

$$\Lambda = \frac{1}{2\Im\mathfrak{m}\{k_{2z}\}} = \frac{1}{k_0\sqrt{2}\sqrt{\alpha_c^2 - \alpha_0^2 + \sqrt{(\alpha_c^2 - \alpha_0^2)^2 + 4\beta^2}}}.$$
 (2.24)

In case of large incidence incidence angles, one cannot use the approximation  $\sin \alpha_0 \approx \alpha_0$  anymore, so everywhere in Eqs. (2.22-2.24), one has to replace  $\alpha_0$  with  $\sin \alpha_0$  back. It is easy to check, that for the normal incidence  $(\alpha_0 = \pi/2 \text{ and } \sin \alpha_0 = 1)$ , the result of Eq. (2.24) coincides with Eq. (2.9).

If the X-ray critical angle  $\alpha_c$  is known, one can estimate the difference of electron densities of two materials as

$$\Delta \rho_e = \rho_e^2 - \rho_e^1 = \frac{\pi}{r_e \lambda^2} \cdot \alpha_c^2.$$
(2.25)

## 2.2.2 Transmission and reflection at ideal interface (Fresnel coefficients)

Let us consider a wave function  $\psi = \psi_0 e^{i\mathbf{kr} - i\omega t}$  describing plane monochromatic wave of neutrons (Fig. 2.3). In this section we will evaluate the amplitude reflectivity r and transmittivity t of the interface that are defined as

$$r = \frac{\psi_1}{\psi_0}$$

$$t = \frac{\psi_2}{\psi_0},$$
(2.26)

where  $\psi_1$  is the reflected wave and  $\psi_2$  is the transmitted wave. The quantities r and t characterize not only how strongly the neutrons are reflected or transmitted by the interface, but also how the phase of the wave is changed.

In experiment, however, it is much more common to use the intensity reflectivity R and transmittivity T defined as

$$R = |r|^{2} = \left|\frac{\psi_{1}}{\psi_{0}}\right|^{2}$$
  

$$T = |t|^{2} = \left|\frac{\psi_{2}}{\psi_{0}}\right|^{2}.$$
(2.27)

Using the boundary conditions at the interface, namely, continuity of the wave function and its derivative across the interface,

$$\begin{split} \psi_0|_{z=0} + \psi_1|_{z=0} &= \psi_2|_{z=0} \\ \frac{\partial \psi_0}{\partial z}\Big|_{z=0} + \frac{\partial \psi_1}{\partial z}\Big|_{z=0} &= \frac{\partial \psi_2}{\partial z}\Big|_{z=0}, \end{split}$$



Fig. 2.3: Reflection and transmission of the unpolarized neutron wave with the wave function  $\psi = \psi_0 e^{i\mathbf{k}\mathbf{r}-i\omega t}$  at an ideal interface.



Fig. 2.4: Reflection and transmission of the X-ray wave at an ideal interface. So-called s-polarization is shown in panel (a) and p-polarization - in panel (b).

one obtains

$$r = \frac{n_1 \sin \alpha_0 - n_2 \sin \alpha_2}{n_1 \sin \alpha_0 + n_2 \sin \alpha_2} = \frac{k_z - k'_z}{k_z + k'_z},$$
(2.28)

$$t = \frac{2n_1 \sin \alpha_0}{n_1 \sin \alpha_0 + n_2 \sin \alpha_2} = \frac{2k_z}{k_z + k'_z},$$
(2.29)

where

$$k_z = k \cdot n_1 \cdot \sin \alpha_0 \approx k n_1 \alpha_0, k'_z = k \cdot n_2 \cdot \sin \alpha_2 \approx k n_2 \alpha_2$$
(2.30)

are the z-components of the wave vector in two materials at the interface  $(k = 2\pi/\lambda \text{ is the wave vector in vacuum})$ . The relations (2.28-2.29) are known as Fresnel equations and are very important in optics.

For X-rays, the result is identical for so-called s-polarization<sup>6</sup>, when the electric field **E** is parallel to the interface, i.e.  $\mathbf{E} \parallel y$ -axis (Fig. 2.4(a)):

$$r_{s} = \frac{n_{1} \sin \alpha_{0} - n_{2} \sin \alpha_{2}}{n_{1} \sin \alpha_{0} + n_{2} \sin \alpha_{2}} = \frac{k_{z} - k_{z}'}{k_{z} + k_{z}'},$$

$$t_{s} = \frac{2n_{1} \sin \alpha_{0}}{n_{1} \sin \alpha_{0} + n_{2} \sin \alpha_{2}} = \frac{2k_{z}}{k_{z} + k_{z}'}.$$
(2.32)

Let us now consider in more detail the case of the interface between vacuum  $(n_1 = 1)$  and some material with the index of refraction  $n_2 = 1 - \delta + i\beta \neq 1$  To get an idea of how the transmission and refraction coefficients depend on the incidence angle  $\alpha_0$ , it is instructive to express the value  $k'_z$  in Eq. (2.30) through  $\alpha_0$ :

$$k'_{z} = kn_{2}\sqrt{1 - \cos^{2}\alpha_{2}} = k\sqrt{n_{2}^{2} - n_{2}^{2}\cos^{2}\alpha_{2}} = k\sqrt{n_{2}^{2} - \cos^{2}\alpha_{0}}$$
  
$$\approx k\sqrt{(1 - \delta + i\beta)^{2} - (1 - \frac{1}{2}\alpha_{0}^{2})} \approx k\sqrt{\alpha_{0}^{2} - \alpha_{c}^{2} + 2i\beta}.$$
 (2.33)

Here we assumed the common situation when the critical angle exist, which is always true for X-ray scattering and for most of the isotopes for neutron scattering. Finally, the Fresnel equations (2.29-2.28) can be written as

$$r = \frac{\alpha_0 - \sqrt{\alpha_0^2 - \alpha_c^2 + 2i\beta}}{\alpha_0 + \sqrt{\alpha_0^2 - \alpha_c^2 + 2i\beta}}$$
  
$$t = \frac{2\alpha_0}{\alpha_0 + \sqrt{\alpha_0^2 - \alpha_c^2 + 2i\beta}}.$$
  
(2.34)

Now it is easy to consider three cases (especially for  $\beta = 0$ ):

•  $\alpha_0 \ll \alpha_c$ : for small incidence angles,  $r \to -1$  and  $t \propto \alpha_0 \approx 0$ . This means that there is no transmitted wave and the incidence wave is totally reflected from the interface. At the same time the phase of the reflected wave is shifted by  $\Delta \varphi_r \approx -\pi$  with respect to the incident wave.

<sup>6</sup>In case of so-called p-polarization, when the electric field **E** lies in the plane of scattering and the magnetic field **H** is parallel to the interface, i.e. **H**  $\parallel$  *y*-axis (Fig. 2.4(b)), the reflectivity and transmittivity are slightly different:

$$r_{p} = \frac{n_{2} \sin \alpha_{0} - n_{1} \sin \alpha_{2}}{n_{2} \sin \alpha_{0} + n_{1} \sin \alpha_{2}} = \frac{n_{2}^{2} k_{z} - n_{1}^{2} k_{z}'}{n_{2}^{2} k_{z} + n_{1}^{2} k_{z}'},$$

$$t_{p} = \frac{2n_{1} \sin \alpha_{0}}{n_{2} \sin \alpha_{0} + n_{1} \sin \alpha_{2}} = \frac{2n_{1} n_{2} k_{z}}{n_{2}^{2} k_{z} + n_{1}^{2} k_{z}'}.$$
(2.31)

However, for X-rays  $n_1 \approx n_2 \approx 1$  and  $\alpha_0, \alpha_2 \ll 1$ , and therefore the difference between sand p-polarization is very small and can be neglected (which is not true for visible light).



Fig. 2.5: Dependence of the intensity reflectivity R (a), intensity transmittivity T (b), penetration length  $\Lambda$  (in logarithmic scale) (c), phase shift of the reflected wave  $\Delta \varphi_r$  (d), and phase shift of the transmitted wave  $\Delta \varphi_t$  (e) on the incidence angle  $\alpha_0$ .

- $\alpha_0 = \alpha_c$ : at the critical angle,  $r \approx 1$  and  $t \approx 2\alpha_0/\alpha_0 = 2$ . This still corresponds to the total external reflection, however the phase of the reflected wave matches with the phase of the incident wave  $(\Delta \varphi_r \approx 0)$ . The value t = 2 means that the electric field near the surface is two times larger than in the incoming wave (and the intensity of the evanescent wave near the surface is four times larger than in the incident intensity).
- $\alpha_0 \gg \alpha_c$ : at large incident angles, the Taylor expansion of the nominator gives for the reflectivity:

$$r \approx \frac{\alpha_0 - \alpha_0 \left(1 - \frac{\alpha_c^2}{2\alpha_0^2} + \frac{i\beta}{\alpha_0^2}\right)}{2\alpha_0} \approx \frac{\alpha_c^2}{2\alpha_0^2} = \left(\frac{q_c}{2q_z}\right)^2, \qquad (2.35)$$

where

$$q_z = k_{1z} - k_{0z} = 2k \cdot \sin \alpha_0 \approx 2k\alpha_0 \tag{2.36}$$

is the scattering vector corresponding to the reflection from the interface, and

$$q_c = 2k \cdot \sin \alpha_c \approx 2k\alpha_c \tag{2.37}$$

is some critical value. Eq. (2.35) states that above the critical angle the intensity of the scattered wave decays very fast, namely, as  $\propto \alpha_0^{-4}$  or  $\propto q^{-4}$ . Accordingly to that, the transmittivity  $t \approx 1$  at large incidence angles.

The sketches of the intensity reflectivity  $R = |r|^2$ , intensity transmittivity  $T = |t|^2$ , the penetration depth  $\Lambda$ , and the phase shifts of the reflected and transmitted waves  $\Delta \varphi_r$  and  $\Delta \varphi_t$  are shown in Fig. 2.5.

#### 2.3 Scattering from a homogeneous thin film on a substrate

Let us evaluate the reflectivity of a homogeneous film of thickness d with a refractive index  $n_2$  between two media with refractive indices  $n_1$  and  $n_3$  as shown in Fig. 2.6. The lower media with the refractive index  $n_3$  is usually a substrate on which the film is grown, and the upper medium is air or vacuum in the simplest case. To calculate the reflectivity of a film, we need to take into account the effects of interference between waves scattered multiple times from two interfaces.

Some fraction of the incident wave will be reflected already at the upper interface between two materials with refraction indices  $n_0$  and  $n_1$ . We will denote this fraction by  $r_{01}$ . Depending on the nature of the incident wave  $r_{01}$ , can be evaluated using one of the Eqs. (2.29, 2.28, 2.32, or 2.31). In the case of neutrons, the amplitude of the incoming wave can be written as  $\psi_0$ , and then the amplitude of the wave reflected from the first interface is  $r_{01}\psi_0$ . Therefore, the first approximation of the reflectivity of a film is simply  $r_{01}$ .

However, part of the incoming wave  $(t_{01}\psi_0)$  will pass through the film and reflect from the lower interface between the film with the index of refraction  $n_1$  and the lower medium with the index of refraction  $n_2$ , and finally pass through the upper interface with the transmission coefficient  $t_{21}$ . This wave reflected from the lower interface travels two times through the thickness of the film (back and forth) and therefore exhibits an additional phase shift of  $p^2$ , which can be evaluated as

$$p^2 = e^{i\Delta\phi} = e^{iq_{2z}d},\tag{2.38}$$

where  $q_{2z} = k'_{2z} - k_{2z} = 2k_2 \sin \alpha_2$  is the z-projection of the scattering vector inside the film (see Fig. 2.7). Therefore, the amplitude of the wave



Fig. 2.6: Multiple scattering at the two interfaces created by a slab of thickness *d*. Different colors represent multiple scattering of the wave from the interfaces.



Fig. 2.7: Evaluation of the phase difference  $p^2 = e^{i\Delta\phi}$  between the wave reflected from the upper interface and the wave traveled to the lower interface and back. Using the conditions  $k_{1x} = k_{2x} = k'_{1x}$  and  $\mathbf{AC}_x = \mathbf{AB}_x + \mathbf{BC}_x$ , one can evaluate the phase  $\Delta\phi = k'_{2z}d + k_{2z}(-d) = q_{2z}d$ , where  $q_{2z} = k'_{2z} - k_{2z} = 2k'_2 \sin\alpha_2$  is the scattering vector at the lower interface.

scattered from the lower interface can be written as  $t_{12}r_{23}t_{21}p^2\psi_0$  (shown with red color in Fig. 2.6). Analogously, the wave reflected three times (from the lower interface, then from the upper interface, then again from the lower interface) and leaving the film can be written as  $t_{12}r_{23}r_{21}r_{23}t_{21}p^4\psi_0$  (note that it travels the thickness of the slab four times, therefore the phase shift is  $p^4$ ). This scattering path is outlined with blue color in Fig. 2.6.

Finally, summing up the results of all possible multiple reflections, we can evaluate the reflectivity of the film as

$$r_{film} = \frac{\psi_{refl}}{\psi_0} = r_{12} + t_{12}r_{23}t_{21}p^2 + t_{12}r_{23}r_{21}r_{23}t_{21}p^4 + t_{12}r_{23}r_{21}r_{23}r_{21}r_{23}t_{21}p^6 + \dots,$$
(2.39)

which can be evaluated as a sum of geometric progression:

$$r_{film} = r_{12} + t_{12}t_{21}r_{23}p^2 \sum_{m=0}^{\infty} (r_{23}r_{21}p^2)^m$$
  
=  $r_{12} + t_{12}t_{21}r_{23}p^2 \frac{1}{1 - r_{23}r_{21}p^2}.$  (2.40)

This result can be further simplified using the equalities  $r_{12} = -r_{21}$  and  $t_{12}t_{21} = 1 - r_{12}^2$  that directly follow from Eqs. (2.29,2.28):

$$r_{film} = \frac{r_{12} + r_{23}p^2}{1 + r_{21}r_{23}p^2} = \frac{r_{12} + r_{23}e^{iq_{2z}d}}{1 + r_{21}r_{23}e^{iq_{2z}d}}.$$
 (2.41)

A practically important case is when the materials above and below the film are identical, i.e.  $n_1 = n_3$  and therefore  $r_{23} = r_{21} = -r_{12}$ . This free-standing films is sometimes called a slab. For this case,

$$r_{slab} = \frac{r_{12}(1 - e^{iq_{2z}d})}{1 - r_{12}^2 e^{iq_{2z}d}},$$
(2.42)

where

$$q_{2z} = 2k_2 \sin \alpha_2. \tag{2.43}$$

Two limiting cases can be easily considered:

- $\alpha_0 \ll \alpha_c$ : for small scattering angles (assuming  $d \gg \Lambda$ ),  $r_{12} \approx -1$  (see the first limit case in section 2.2.2), so  $r_{slab} \approx r_{12}$  meaning that the reflectivity of the slab equals to the reflectivity of its upper interface, because the wave does not penetrate the slab.
- $\alpha_0 \gg \alpha_c$ : for larger scattering angles,  $r_{12} \ll 1$ , so  $r_{slab} \approx r_{12}(1 e^{iq_{2z}d})$  meaning that the reflectivity of the slab has so-called Kiessig oscillations, the period of which is  $\Delta \alpha_0 \sim \lambda/2d$  or in reciprocal space units  $\Delta q \sim 2\pi/d$ . Measuring these oscillations is a commonly used technique to experimentally determine the thickness of thin films.

The reflectivity of a slab in comparison with a reflectivity from an interface is shown in Fig. 2.8.

#### 2.4 Scattering from a multilayer

In various applications [22, 23, 24, 25], it is common to have a stack of thin layers of different materials - a so-called multilayer. A reflectivity curve from such a stack of layers allows one to characterize the structure of the layers (in case of neutrons, also the magnetic order of layers).



Fig. 2.8: Intensity reflectivity of an ideal interface  $R_{12} = |r_{12}|^2$  (blue dash line) and intensity reflectivity  $R_{slab} = |r_{slab}|^2$  homogeneous slab with the thickness d (red line). The so-called Kiessig oscillations of appear due to interference between the wave scattered from the upper and lower interfaces of the slab, and therefore their period  $\Delta \alpha$  is inversely proportional to the thickness of the slab d.



Fig. 2.9: A stack of N bilayers with period  $\Lambda$ .

#### 2.4.1 Kinematical approximation

Let us consider a specific case of a multilayer - a stack of N bilayers composed of two materials (A and B) with the indices of refraction  $n_A$  and  $n_B$ , correspondingly (Fig. 2.9). For large angles of incidence ( $\alpha_0 \gg \alpha_c$ ) we can can neglect multiple scattering between the bilayers. Therefore the total reflectivity of a multilayer will be a sum of N reflectivities of bilayers with corresponding phase factors (here we also neglect scattering from the upper and lower interfaces of the multilayer):

$$r_N = \sum_{m=0}^{N-1} r_1 \cdot (p^2 e^{-\beta})^m = r_1 \cdot \frac{1 - e^{iq_z \Lambda N} e^{-i\beta N}}{1 - e^{iq_z \Lambda} e^{-i\beta}}.$$
 (2.44)

Here  $r_1$  is reflection from a single bilayer,  $p^2 = e^{i\Lambda q_z}$  is a phase shift between two bilayers,  $\beta$  is absorption in a single bilayer.

The reflecticivity  $r_1$  of a single bilayer can be calculated as (see the case  $\alpha_0 \gg \alpha_c$  after Eq. (2.43) and the corresponding reflectivity in Eq. (2.35))

$$r_{1} = r_{AB} \left( 1 - e^{iq_{zB}\Gamma\Lambda} \right) = \left( \frac{q_{c}}{2q_{zB}} \right)^{2} \left( 1 - e^{iq_{zB}\Gamma\Lambda} \right)$$
$$= \frac{2k^{2}(n_{B} - n_{A})}{q_{zB}^{2}} \cdot e^{iq_{zB}\frac{\Gamma\Lambda}{2}} \underbrace{\left( e^{-iq_{zB}\frac{\Gamma\Lambda}{2}} - e^{iq_{zB}\frac{\Gamma\Lambda}{2}} \right)}_{-2i\sin\left(q_{zB}\frac{\Gamma\Lambda}{2}\right)}$$
$$(2.45)$$
$$= -i\frac{2k^{2}(n_{B} - n_{A})\Gamma\Lambda}{q_{zB}} \cdot \frac{\sin\left(\frac{q_{zB}\Gamma\Lambda}{2}\right)}{\left(\frac{q_{zB}\Gamma\Lambda}{2}\right)} \cdot e^{iq_{zB}\frac{\Gamma\Lambda}{2}}.$$

Absorption of a single bilayer can be evaluated as (see Fig 2.10)

$$\beta = 2\left[\frac{\mu_B}{2} \cdot \frac{\Gamma\Lambda}{\sin\alpha} + \frac{\mu_A}{2} \cdot \frac{(1-\Gamma)\Lambda}{\sin\alpha}\right] = \frac{\Lambda}{\sin\alpha} \Big[\mu_B\Gamma + \mu_A(1-\Gamma)\Big], \quad (2.46)$$

where the factor 2 in the beginning originates from the fact that each bilayer is passed two times (back and forth), and the absorption coefficient  $\mu/2$  for amplitude is twice smaller than the absorption coefficient for intensity  $\mu$ , introduced in Eqs. (1.11) and (2.9). Here we also neglected the refraction and considered that the incidence angle is  $\alpha$  in both materials.

Finally, from Eqs. (2.44-2.46) we obtain for the reflectivity of a multilayer the following expression (in kinematical approximation):

$$r_{N} = -i\frac{2k^{2}(n_{B} - n_{A})\Gamma\Lambda}{q_{zB}} \cdot \underbrace{\frac{\operatorname{at} q_{zB} = \frac{2\pi n}{\Gamma\Lambda}}{\operatorname{sin}\left(\frac{q_{zB}\Gamma\Lambda}{2}\right)}}_{\left(\frac{q_{zB}\Gamma\Lambda}{2}\right)} \cdot e^{iq_{zB}\frac{\Gamma\Lambda}{2}} \cdot \underbrace{\frac{\operatorname{at} q_{zB} = \frac{2\pi n}{N\Lambda}}{1 - e^{iq_{z}\Lambda N}e^{-i\beta N}}}_{\text{principal maxima}}$$

(2.47)

The intensity reflectivity  $R_N = |r_N|^2$  calculated with this equation in shown in Fig. 2.11. Due to constructive interference of the waves scattering from different bilayers, the resulting reflectivity approaches 100% for the first principal diffraction maxima. This effect allows one to create very effective mirrors for X-ray and neutrons that can reflect almost the incident wave almost completely even at high angles.



Fig. 2.10: Absorption in a single bilayer.



Fig. 2.11: Reflectivity  $R_N$  of a multilayer shown in Fig. 2.9 and calculated by Eq. (2.47) for the following parameters: N = 10,  $\Lambda =$ 50 Å,  $\Gamma = 0.2$ ,  $\lambda = 1$  Å,  $n_A = 1$ ,  $n_B =$  $1 - 5 \cdot 10^{-5} + i \cdot 10^{-6}$ . The reflectivity of a single bilayer (N = 1) is shown with blue dash line.

#### 2.4.2 Parratt's formalism (exact solution) for a multilayer

Since a multilayer has only a limited number of ideal interfaces, it is also possible to find the exact expression for reflectivity known as Parratt's formalism [26]. Let us consider a stack of N layers on a substrate, each layer has a thickness  $d_j$  and an index of refraction  $n_j = 1 - \delta_j + i\beta_j$  where  $j = 1, \ldots, N$ (Fig. 2.12). First of all, let us note that the tangential component of the wave vector  $k_x$  is the same for all the layers:  $k_{xj} = k_x$ . This follows from the translational symmetry of the system along the direction of x - axisor from the boundary conditions at the interface (the wave function has to be continuous across the interface). Since the magnitude of the wave vector depends on the index of refraction,  $k_j = n_j \cdot k$ , one can calculate the perpendicular component of the wave vector in each layer as

$$k_{zj} = \sqrt{n_{zj}^2 k^2 - k_{xj}^2} = \sqrt{(1 - 2\delta_j + 2i\beta_j)k^2 - k_x^2} = \sqrt{k_z^2 - 2\delta_j k^2 + 2i\beta k^2}.$$
(2.48)

With this result we can calculate the exact reflectivity at the interface between any two adjacent layers "j" and "j + 1" using Eq. (2.28) (Fresnel reflectivity)

$$r'_{j,j+1} = \frac{k_{zj} - k_{zj+1}}{k_{zj} + k_{zj+1}},$$
(2.49)

where the prime denotes absence of multiple scattering effects (there is no multiple scattering at a single interface).

In Parratt's approach, the reflectivity is calculated recursively starting from the lowest interface between the  $N^{\rm th}$  layer and the substrate (denoted by " $\infty$ ")

(interface) (reflectivity)  
"N"/"\overline": 
$$r'_{N,\infty} = \frac{k_{zN} - k_{z\infty}}{k_{zN} + k_{z\infty}}$$
  
"N - 1"/"N":  $r'_{N-1,N} = \frac{r'_{N-1,N} + r'_{N,\infty} \cdot p_N^2}{1 + r'_{N-1,N}r'_{N,\infty} \cdot p_N^2}$   
"N - 2"/"N - 1":  $r'_{N-2,N-1} = \frac{r'_{N-2,N-1} + r'_{N-1,N} \cdot p_{N-1}^2}{1 + r'_{N-2,N-1}r'_{N-1,N} \cdot p_{N-1}^2}$  (2.50)  
"N - 3"/"N - 2":  $r'_{N-3,N-2} = \frac{r'_{N-3,N-2} + r'_{N-2,N-1} \cdot p_{N-2}^2}{1 + r'_{N-3,N-2}r'_{N-2,N-1} \cdot p_{N-2}^2}$ 

Here the multiple scattering is taken into account by using the exact expression for the reflectivity of the film (Eq. (2.41)) with the phase factor  $p_j^2 = e^{iq_{zj}d_j} = e^{i\cdot 2k_{zj}\cdot d_j}$ .

#### 2.5 Scattering from a graded interface

In this section we consider scattering of a wave from a graded interface, i.e. from the interface between two media at which the index of refraction does not change abruptly (as it was in section 2.2.2), but can be described with a smooth function n(z), as it is shown in Fig. 2.13. Here we assume that the changes in the index of refraction occur in the vicinity of z = 0, and for convenience select the direction of z - axis along the incident wave.

To evaluate reflectivity at such interface, we can approximately it as a stack of 2N + 1 ideal homogeneous slabs with a thickness  $d_j$  and an index of refraction  $n_j$  (j = -N : N). Here we assume that the interface j = -N lies deep in the upper medium (z < 0) with the index of refraction  $n_1$ , and



Fig. 2.12: Illustration of a multilayer structure consisting of N layers with  $d_j$  and an index of refraction  $n_j = 1 - \delta_j + i\beta_j$ . The substrate is denoted as  $\infty$ .

the interface j = -N lies in the lower medium (z > 0) with the index of refraction  $n_2$ . Since the differences in index of refraction  $n_{j+1} - n_j$  at each interface is infinitesimally small, the corresponding critical angle is also infinitesimally small, so one can use Eq. (2.35) to calculate the reflectivity  $r_{j,j+1}$  at this interface:

$$r_{j,j+1} = \left(\frac{\alpha_c}{2\alpha_0}\right)^2 = \frac{2(n_{j+1} - n_j)}{(2\alpha_0)^2},\tag{2.51}$$

where we assumed that the incident waves always comes at the incidence angle  $\alpha_0$ .

Following the same arguments as in section 2.3, the amplitude of the reflected wave from the graded interface is a sum of the waves reflected at each interfaces taken with a phase shift  $e^{iq_z z_j}$  corresponding to the additional distance that the wave need to travel from the interface at  $z_j$  and back. Therefore, the total reflectivity r of the graded interface can be approximated with a sum

$$r = \sum_{j=-N}^{N} r_{j,j+1} e^{iq_z z_j} = \frac{1}{2\alpha_0^2} \sum_{j=-N}^{N} \frac{n_{j+1} - n_j}{d_j} e^{iq_z z_j} \cdot d_j,$$
(2.52)

which can be further evaluated as an integral

$$r = \frac{1}{2\alpha_0^2} \int_{-\infty}^{\infty} \frac{dn}{dz} e^{iq_z z} dz = \frac{\Delta n}{2\alpha_0^2} \cdot \frac{1}{\Delta n} \int_{-\infty}^{\infty} \frac{dn}{dz} e^{iq_z z} dz, \qquad (2.53)$$

where  $\Delta n = n(z = \infty) - n(z = -\infty) = n_2 - n_1$ . The first factor in Eq. (2.53) is simply the Fresnel reflectivity of an ideal interface from Eq. (2.35) with the same total change of the index of refraction. The second factor is the correction which takes into account smooth variation of the index of refraction across the interface.

Finally, the intensity reflectivity of a graded interface can be written as

$$R = R_F \cdot \left| \frac{1}{\Delta n} \int_{-\infty}^{\infty} \frac{dn}{dz} e^{iq_z z} dz \right|^2,$$
(2.54)

where  $R_F$  is the Fresnel reflectivity of an ideal interface:

$$R_F = \left(\frac{q_c}{2q}\right)^4 = \left(\frac{\alpha_c}{2\alpha}\right)^4 = \left(\frac{\Delta n}{2\alpha}\right)^2.$$
(2.55)

In practice, a smooth change of the index of refraction across the interface can be modeled by the error function:

$$n(z) = n_1 + \Delta n \cdot \operatorname{erf}\left(\frac{-z}{\sqrt{2}\sigma}\right), \qquad (2.56)$$

where  $\sigma$  describes the width of the interface. In this case, the integral in Eq. (2.54) can be evaluated to yield the final answer

$$R = R_F \cdot e^{-\sigma^2 q^2}.\tag{2.57}$$

The reflectivity of a slab with one graded interface is shown in Fig. 2.14.

#### 2.6 Scattering from a rough surface

In this section we will consider the sharp interface between two media, but in this case the border between them is no longer a flat surface. As it is evident from Fig. 2.15, in this case one can observe not only specular reflection, but



Fig. 2.13: Scattering from a graded interface centered around z = 0, at which the index of refraction n(z) is a smooth function.



Fig. 2.14: Intensity reflectivity of a slab with graded upper interface (shown in the upper panel) in comparison with intensity reflectivity from an ideal slab with two sharp interfaces. The Kiessig oscillations become less pronounced at higher scattering angles for the slab with a graded interface.

also non-specular scattering, at which the scattering angle is different from the incidence angle.

Here, we will follow the description published in [27] and consider the X-ray scattering cross section in the form (see the corresponding illustration in Fig. 2.16)

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \left|-r_e \int e^{-i\mathbf{q}\mathbf{r}} \rho_e(\mathbf{r}) d\mathbf{r}\right|^2 = r_e^2 \rho_e^2 \iint_V e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}'.$$
(2.58)

Here we assumed that the upper part of the space is vacuum, and the lower part (volume V) has the electron density  $\rho_e$ . In the case of neutrons, the X-ray scattering length  $-r_e\rho_e$  should be replaced with a neutron scattering length b. Now the scattering vector **q** is not parallel to the z-axis, but all its three components are non-zero.

The volume integral in Eq. (2.58) can be re-written as an integral over the surface between the two media using the Ostrogradsky-Gauss theorem (see Appendix C):

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = r_e^2 \rho_e^2 \oint_S \oint_{S'} \frac{e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{(\mathbf{q}\cdot\mathbf{A})^2} (\mathbf{A}d\mathbf{S})(\mathbf{A}d\mathbf{S}'), \tag{2.59}$$

where **A** is an arbitrary vector, and **S** is a normal to the surface. Choosing  $\mathbf{A} = \hat{\mathbf{z}}$  as a unit vector normal to the average interface (in our case,  $\hat{\mathbf{z}}$  is a unit vector of z-axis), we can use  $\mathbf{q} \cdot \hat{\mathbf{z}} = q_z$  (projection of the scattering vector) and  $\hat{\mathbf{z}} \cdot d\mathbf{S} = dxdy$  (projection of the area of the rough surface onto the xy-plane), we can further simplify the scattering cross section:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{r_e^2\rho_e^2}{q_z^2} \iint dxdy \iint dx'dy' e^{-iq_z[h(x,y)-h(x',y')]} e^{-iq_y(y-y')} e^{-iq_x(x-x')}.$$
(2.60)

Here h(x, y) is the height variation of the rough surface.

We can approximate the first exponential factor in the Eq. (2.60) with its average value and evaluate it, assuming that the height difference is small:

$$\exp\left(-iq_{z}[h(x,y)-h(x',y')]\right) \approx \left\langle \exp\left(-iq_{z}[h(x,y)-h(x',y')]\right) \right\rangle$$
$$\approx \exp\left(-\frac{q_{z}^{2}}{2} \left\langle [h(x,y)-h(x',y')]^{2} \right\rangle \right).$$
(2.61)

The approximation is exact if h(x, y) is a Gaussian variable (the Baker-Hausdorff theorem). Let us also assume that  $\langle [h(x, y) - h(x', y')]^2 \rangle$  depend only on difference between positions (x, y) and (x', y'), and therefore introduce the height difference correlation function:

$$g(x - x', y - y') = \left\langle [h(x, y) - h(x', y')]^2 \right\rangle.$$
(2.62)

Thus, Eq. (2.60) can be further simplified:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{r_e^2\rho_e^2}{q_z^2}L_xL_y \iint \exp\left[-\frac{q_z^2}{2}g(x,y)\right]\exp(-iq_yy)\exp(-iq_xx)dxdy,$$
(2.63)

where  $L_x \cdot L_y = \iint dxdy$  is the area of the projection of the surface onto xy-plane.

While different types of surfaces produce different functions g(x, y), in many cases the surface can be described with  $g(x, y) \propto (x^2 + y^2)^{\alpha}$  for the small values of argument (see Fig. 2.17). For large distances, the height



Fig. 2.15: Origin of non-specular scattering from a rough surface.



Fig. 2.16: Illustration to application of the Ostrogradsky-Gauss theorem to Eq. (2.58).



Fig. 2.17: The height difference correlation function g(x, y) for smooth and jagged surfaces with the same mean square surface fluctuations  $\sigma^2$ .

difference correlation function of a flat surface should saturate:

$$g(x,y) = \left\langle [h(x,y) - h(0,0)]^2 \right\rangle = \underbrace{\left\langle h^2(x,y) \right\rangle}_{\sigma^2} - 2\underbrace{\left\langle h(x,y) \cdot h(0,0) \right\rangle}_{C(x,y)} + \underbrace{\left\langle h^2(0,0) \right\rangle}_{\sigma^2}$$
$$= 2\sigma^2 - 2C(x,y), \tag{2.64}$$

where  $\langle h^2 \rangle = \sigma^2$  is the mean square surface fluctuations and  $\langle h(x, y) \cdot h(0, 0) \rangle = C(x, y)$  is the height-height correlation function., which approaches zero at the distances much larger than a characteristic size  $\xi$ . Finally, for many surfaces we can use the following model:

$$g(x,y) = 2\sigma^2 \left( 1 - \exp\left[ -\frac{(x^2 + y^2)^{\alpha}}{\xi^{2\alpha}} \right] \right),$$
  

$$C(x,y) = \sigma^2 \exp\left[ -\frac{(x^2 + y^2)^{\alpha}}{\xi^{2\alpha}} \right].$$
(2.65)

Substituting Eq. (2.64) into Eq. (2.63), we obtain for the scattering cross section:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{r_e^2 \rho_e^2}{q_z^2} L_x L_y \iint e^{-q_z^2 \sigma^2} e^{q_z^2 C(x,y)} e^{-iq_y y} e^{-iq_x x} dx dy.$$
(2.66)

Since for large distances  $C(x, y) \to 0$  and  $\exp(q_z^2 C(x, y) \to 1)$ , the integral in Eq. (2.66) does not converge. It help to explicitly separate the diverging part ( $\delta$ -function-like specular reflection) by subtracting and adding unity:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \frac{r_e^2\rho_e^2}{q_z^2}L_xL_ye^{-q_z^2\sigma^2} \iiint \left[\underbrace{e^{q_z^2C(x,y)}-1}_{\text{diffuse}}\underbrace{+1}_{\text{specular}}\right]e^{-iq_yy}e^{-iq_xx}dxdy.$$
(2.67)

Thus the scattering cross section can be split into two parts: the specular reflection from the average surface which occurs only when the scattering angle matches the incidence angle, and the diffuse scattering from the roughness:

$$\left(\frac{\partial\sigma}{\partial\Omega}\right) = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{spec}} + \left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}},\tag{2.68}$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\rm spec} = \frac{r_e^2 \rho_e^2}{q_z^2} L_x L_y e^{-q_z^2 \sigma^2} (2\pi)^2 \delta(q_x) \delta(q_y), \qquad (2.69)$$

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}} = \frac{r_e^2 \rho_e^2}{q_z^2} L_x L_y e^{-q_z^2 \sigma^2} \iint \left[e^{q_z^2 C(x,y)} - 1\right] e^{-iq_y y} e^{-iq_x x} dx dy,$$
(2.70)

where  $\delta(q)$  denotes the Dirac delta function. For small scattering angles  $(q_z^2 \sigma^2 \ll 1)$ , one can expand the exponential in Eq. (2.70) in the Taylor series, to show that the expression in the brackets approximately equals to  $q_z^2 \cdot C(x, y)$ , leading to

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}} \approx r_e^2 \rho_e^2 L_x L_y e^{-q_z^2 \sigma^2} \iint C(x,y) e^{-iq_y y} e^{-iq_x x} dx dy.$$
(2.71)

Therefore, the diffuse scattering is proportional to the Fourier transform of the height-height correlation function.

In Fig. 2.18 the scattering profile  $I(q_y)$  is shown for a typical rough surface, for which the model Eqs. (2.65) can be applied. It is also not uncommon that the hills and valleys of a rough surface have approximately the same size, so the correlation function C(x, y) is oscillating and decaying. In this case, the diffuse scattering will exhibit characteristic wings, as shown in Fig. 2.19.



Fig. 2.18: Smooth surface h(y) (a), the corresponding height-height correlation function C(y) (b) and the scattered intensity  $I(q_y)$  (c).



Fig. 2.19: Smooth surface h(y) with a characteristic period a (a), the corresponding heightheight correlation function C(y) with a characteristic correlation length  $\xi$  (b) and the scattered intensity  $I(q_y)$  with diffuse scattering wings (c).

#### 2.7 Distorted wave Born approximation (DWBA)

The above results (Section 2.6) were obtained using the first Born approximation, which means that we considered only single scattering events and neglected the possibility that an X-ray photon or neutron can interact with several atoms and be scattered multiple times. This approximation is justified by weak interaction of X-ray photons and matter, but it fails to describe the surface scattering close to the critical angle, when the whole incoming beam is reflected and therefore the interaction can not be considered weak. One of the ways to describe the surface scattering close to the critical angle is to consider the multiple scattering processes in the perturbation theory.

#### 2.7.1 The Helmholtz equation for neutrons and X-rays

Let us consider a plane monochromatic wave of neutrons with energy  $E = \hbar^2 k^2/2m$ , elastically scattered by some potential  $V(\mathbf{r})$ . The stationary Schrödinger equation is

$$\nabla^2 \psi(\mathbf{r}) + \frac{2m_n}{\hbar^2} (E - V(\mathbf{r}))\psi(\mathbf{r}) = 0, \qquad (2.72)$$

where  $\nabla^2 = \nabla \cdot \nabla = \text{grad} \operatorname{div} = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$  is the Laplace operator.

The case of a scattering from a single nucleus,  $V(\mathbf{r}) = \hat{V}_N(\mathbf{r})$  was already considered in Section 1.2.1. Here we will consider scattering from an extended object, for example, an interface between some material and vacuum. In this case,  $V(\mathbf{r}) = 0$  in vacuum, and in the medium one can take into account the density of the atoms and calculate the averaged potential:

$$V(\mathbf{r}) = \left\langle \sum_{\mathbf{R}} \hat{V}_N(\mathbf{r} - \mathbf{R}) \right\rangle = \frac{1}{v} \int_v \sum_{\mathbf{R}} \hat{V}_N(\mathbf{r} - \mathbf{R}) d\mathbf{r}$$
  
=  $\rho_{at}(\mathbf{r}) \cdot \int \hat{V}_N(\mathbf{r}) d\mathbf{r} = \rho_{at}(\mathbf{r}) \cdot \frac{2\pi\hbar^2}{m_n} b_{coh},$  (2.73)

where angular brackets denote coarse-grain averaging over a small volume v around the position  $\mathbf{r}$ , b is the neutron scattering length introduced in Eq. (1.42),  $\mathbf{R}$  is the positions of the nuclei inside the volume v, and  $\rho_{at}(\mathbf{r})$  is the density of atoms (nuclei) inside the volume v.

This allows us to rewrite the Schrödinger equation (2.72) using the index of refraction  $n(\mathbf{r})$  [21]:

$$\nabla^2 \psi(\mathbf{r}) + k^2 \underbrace{\left(1 - \frac{V(\mathbf{r})}{E}\right)}_{n^2(\mathbf{r})} \psi(\mathbf{r}) = 0, \qquad (2.74)$$

because from Eqs. (2.17) and (2.73) it follows that

$$n^{2} = \left(1 - \frac{\lambda^{2}}{2\pi}\rho_{at}b_{coh}\right)^{2} \approx 1 - 2 \cdot \frac{2\pi}{k^{2}}\rho_{at}b_{coh} = 1 - \frac{4\pi}{k^{2}}\frac{m_{n}}{2\pi\hbar^{2}}V(\mathbf{r}).$$
 (2.75)

Therefore to describe the scattering of neutrons from the object (i.e. surface) described with the index of refraction  $n(\mathbf{r})$ , one has to solve the Helmholtz equation:

$$\nabla^2 \psi(\mathbf{r}) + k^2 n^2(\mathbf{r}) \psi(\mathbf{r}) = 0.$$
(2.76)

This equation describes propagation of monochromatic wave (therefore the wave vector  $k = 2\pi/\lambda$  is constant) through an homogeneous medium with the index of refraction  $n(\mathbf{r})$ .

A similar equation can be derived for the electric field of X-rays from Maxwell's equations (see Appendix D):

$$\nabla^2 \mathbf{E}(\mathbf{r}) + k^2 n^2(\mathbf{r}) \mathbf{E}(\mathbf{r}) = 0.$$
(2.77)

In the following, we will consider only neutrons described by a scalar wave function  $\psi(\mathbf{r})$  and will be solving Eq. (2.76).

#### 2.7.2 Born approximation (BA)

In this section, we will be solving the Helmholtz equation (2.74) written as:

$$\nabla^2 \psi(\mathbf{r}) + k^2 \psi(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r}), \qquad (2.78)$$

with the potential  $V(\mathbf{r}) = k^2 [1 - n^2(\mathbf{r})]$ . The solution of this equation in vacuum  $(V(\mathbf{r}) = 0)$  is known: it is a plane monochromatic wave  $\psi_0 \sim e^{i\mathbf{k}_1\mathbf{r}}$ . If the potential  $V(\mathbf{r})$  decays fast at large distances (faster than  $\sim 1/r$ ), the solution  $\psi(\mathbf{r})$  of Eq. (2.78) should have an asymptotic behavior [28]:

$$\psi_{\mathbf{k}_1}(\mathbf{r}) \xrightarrow[r \to \infty]{} e^{i\mathbf{k}_1\mathbf{r}} + f(\mathbf{k}_1, \mathbf{k}_2) \frac{e^{ikr}}{r},$$
 (2.79)

where  $f(\mathbf{k}_1, \mathbf{k}_2)$  is the scattering amplitude (i.e.  $|f(\mathbf{k}_1, \mathbf{k}_2)|^2$  i the probability to detect a particle with momentum  $\mathbf{k}_2$  far away from the scattering center).

In vacuum, we also know the Green function

$$G(\mathbf{r}, \mathbf{r}') = -\frac{1}{4\pi} \cdot \frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|},\tag{2.80}$$

which satisfies the equation

$$\nabla^2 G(\mathbf{r}, \mathbf{r}') + k^2 G(\mathbf{r}, \mathbf{r}') = (\nabla^2 + k^2) G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}').$$
(2.81)

This allows us to write the solution of the inhomogeneous equation

$$(\nabla^2 + k^2)\psi(\mathbf{r}) = F(\mathbf{r}) \tag{2.82}$$

as a sum of a vacuum solution  $\psi_0(\mathbf{r})$  and an integral term:

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') F(\mathbf{r}') d\mathbf{r}'.$$
(2.83)

Using Eqs. (2.82-2.83), we can assume  $F(\mathbf{r}) = V(\mathbf{r})\psi(\mathbf{r})$  and write the solution of Eq. (2.78) as

$$\psi(\mathbf{r}) = \psi_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') V(\mathbf{r}') \psi(\mathbf{r}') d\mathbf{r}', \qquad (2.84)$$

which is essentially an integral equation equivalent to the initial Helmholtz equation (2.78).

Assuming that the scattering potential  $V(\mathbf{r})$  is weak, we can treat the integral term in Eq. (2.84) as a small perturbation, which allows us to solve it iteratively:

$$\psi_{\mathbf{k}_{1}}^{(0)}(\mathbf{r}) = e^{i\mathbf{k}_{1}\mathbf{r}},$$

$$\psi_{\mathbf{k}_{1}}^{(1)}(\mathbf{r}) = e^{i\mathbf{k}_{1}\mathbf{r}} + \int G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}_{1}}^{(0)}(\mathbf{r}')d\mathbf{r}',$$

$$\psi_{\mathbf{k}_{1}}^{(2)}(\mathbf{r}) = e^{i\mathbf{k}_{1}\mathbf{r}} + \int G(\mathbf{r},\mathbf{r}')V(\mathbf{r}')\psi_{\mathbf{k}_{1}}^{(1)}(\mathbf{r}')d\mathbf{r}'$$

$$\dots$$
(2.85)



Fig. 2.20: Illustration of the asymptotic behavior of the wave function given in Eq. (2.79).

This series is known the Born series. The multiple scattering effects are taken into account in different orders of this series.

to calculate the scattering amplitude  $f(\mathbf{k}_1, \mathbf{k}_2)$  defined in Eq. (2.79) we need to consider the asymptotic behavior of the exact solution (2.84), i.e. for  $|\mathbf{r}| \gg |\mathbf{r}'|$ , where  $|\mathbf{r}'|$  is the characteristic length scale of the scattering potential  $V(\mathbf{r}')$ . In this limit, using the approximation

$$|\mathbf{r} - \mathbf{r}'| = \sqrt{(\mathbf{r} - \mathbf{r}')^2} \approx r\left(1 - \frac{\mathbf{r}\mathbf{r}'}{r^2}\right) = r - \mathbf{r}'\frac{\mathbf{r}}{r} = r - \frac{\mathbf{r}'\mathbf{k}_2}{k}$$
(2.86)

and calculate the asymptotic behavior of the Green function (2.80):

$$G(\mathbf{r}, \mathbf{r}') \xrightarrow[|\mathbf{r}| \gg |\mathbf{r}'|]{} - \frac{1}{4\pi} \cdot \frac{e^{ikr} e^{-i\mathbf{k}_2 \mathbf{r}'}}{k}.$$
 (2.87)

Substituting this approximation into Eq. (2.78) we obtain

$$\psi_{\mathbf{k}_1}(\mathbf{r}) \xrightarrow[r \to \infty]{} e^{i\mathbf{k}_1\mathbf{r}} - \frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \int e^{-i\mathbf{k}_2\mathbf{r}'} V(\mathbf{r}')\psi_{\mathbf{k}_1}(\mathbf{r}')d\mathbf{r}', \qquad (2.88)$$

which immediately gives for the scattering amplitude (compare with Eq. (2.79))

$$f(\mathbf{k}_1, \mathbf{k}_2) = -\frac{1}{4\pi} \int e^{-i\mathbf{k}_2 \mathbf{r}} V(\mathbf{r}) \psi_{\mathbf{k}_1}(\mathbf{r}) d\mathbf{r} = -\frac{1}{4\pi} \left\langle e^{i\mathbf{k}_2 \mathbf{r}} | V | \psi_{\mathbf{k}_1}(\mathbf{r}) \right\rangle. \quad (2.89)$$

This result is exact, and in order to calculate the scattering amplitude  $f(\mathbf{k}_1, \mathbf{k}_2)$  one needs to know the exact wave function  $\psi_{\mathbf{k}_1}(\mathbf{r})$ . But using this equation, the scattering amplitude  $f(\mathbf{k}_1, \mathbf{k}_2)$  can be calculated with any given precision by substituting the exact wave function  $\psi_{\mathbf{k}_1}(\mathbf{r})$  with one of the approximations from the Born series (2.85). For example, the so-called first Born approximation (BA), can be obtained by using the zeroth-order approximation  $\psi_{\mathbf{k}_1}^{(0)}(\mathbf{r}) = e^{i\mathbf{k}_1\mathbf{r}}$  from Eq. (2.85):

$$f(\mathbf{k}_1, \mathbf{k}_2) \approx -\frac{1}{4\pi} \langle e^{i\mathbf{k}_2 \mathbf{r}} | V | e^{i\mathbf{k}_1 \mathbf{r}} \rangle = -\frac{1}{4\pi} \int V(\mathbf{r}) e^{-i(\mathbf{k}_2 - \mathbf{k}_1) \mathbf{r}} d\mathbf{r}, \qquad (2.90)$$

which we already used in Eq. (1.42). This result for the scattering amplitude is equivalent to calculating the first-order approximation  $\psi_{\mathbf{k}_1}^{(1)}(\mathbf{r})$  using the Born series (2.85).

#### 2.7.3 The essence of the distorted wave Born approximation (DWBA)

Sometimes the potential  $V(\mathbf{r})$  is too large, so the Born series does not converge well. The situation can be improved by choosing the basis functions more accurately. Let us assume that the potential  $V(\mathbf{r})$  in the Helmholtz equation (2.78) can be represented as a sum

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r}), \qquad (2.91)$$

where  $\Delta V(\mathbf{r})$  is a small perturbation of the potential  $V_0(\mathbf{r})$  (Fig. 2.21). Let us also assume, that for the undisturbed potential  $V_0(\mathbf{r})$  we know the correponding Green function  $G_{\mathbf{k}_1}^{V_0}(\mathbf{r}, \mathbf{r}')$  which satisfies the identity

$$\left[\nabla^2 + k^2 - V_0(\mathbf{r})\right] G_{\mathbf{k}_1}^{V_0}(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}'), \qquad (2.92)$$

and we also know the solution  $\psi_{\mathbf{k}_1}(\mathbf{r})$  of the Helmholtz equation:

$$\left[\nabla^2 + k^2 - V_0(\mathbf{r})\right]\psi_{\mathbf{k}_1}(\mathbf{r}) = 0.$$
(2.93)



Fig. 2.21: Illustration of scattering by the potential  $V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r})$ .

Analogously to how it was done in section 2.7.2, the solution  $\phi_{\mathbf{k}_1}(\mathbf{r})$  of the Helmholtz equation with the disturbed potential (2.91),

$$\left[\nabla^2 + k^2 - V_0(\mathbf{r})\right]\phi_{\mathbf{k}_1}(\mathbf{r}) = \Delta V(\mathbf{r})\phi_{\mathbf{k}_1}(\mathbf{r}), \qquad (2.94)$$

can be written as (compare to Eq. (2.84))

$$\phi_{\mathbf{k}_{1}}(\mathbf{r}) = \underbrace{\psi_{\mathbf{k}_{1}}(\mathbf{r})}_{\text{exact solution}} + \underbrace{\int G_{\mathbf{k}_{1}}^{V_{0}}(\mathbf{r}, \mathbf{r}') \Delta V(\mathbf{r}') d\mathbf{r}'}_{\text{perturbation from } \Delta V(\mathbf{r})}$$
(2.95)

To calculate the scattering amplitude  $f(\mathbf{k}_1, \mathbf{k}_2)$ , we should consider the asymptotic behavior of the exact solution  $\phi_{\mathbf{k}_1}(\mathbf{r})$  and write it as

$$\phi_{\mathbf{k}_1}(\mathbf{r}) \xrightarrow[r \to \infty]{} e^{i\mathbf{k}_1\mathbf{r}} + f(\mathbf{k}_1, \mathbf{k}_2) \frac{e^{ikr}}{r}.$$
 (2.96)

This can be done in a similar way as in section 2.7.2, by considering the asymptotic behavior of the Green function  $G_{\mathbf{k}_1}^{V_0}(\mathbf{r}, \mathbf{r}')$ . Although the exact form of this function is unknown, it can be shown [29], that the Green function  $G_{\mathbf{k}_1}^{V_0}(\mathbf{r}, \mathbf{r}')$  has the following asymptotics (compare with Eq. (2.87)):

$$G_{\mathbf{k}_{1}}^{V_{0}}(\mathbf{r},\mathbf{r}') \xrightarrow[|\mathbf{r}|\gg|\mathbf{r}'|]{} \rightarrow -\frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \cdot \psi_{-\mathbf{k}_{2}}(\mathbf{r}').$$
(2.97)

Substituting (2.97) into (2.95), we obtain

$$\phi_{\mathbf{k}_{1}}(\mathbf{r}) \xrightarrow[r \to \infty]{} \psi_{\mathbf{k}_{1}}(\mathbf{r}) - \frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \cdot \underbrace{\int \psi_{-\mathbf{k}_{2}}(\mathbf{r}')\Delta V(\mathbf{r}')\psi_{\mathbf{k}_{1}}(\mathbf{r}')d\mathbf{r}'}_{\langle\psi_{-\mathbf{k}_{2}}^{*}|\Delta V|\phi_{\mathbf{k}_{1}}\rangle}$$

$$\approx e^{i\mathbf{k}_{1}\mathbf{r}} - \frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \langle e^{i\mathbf{k}_{2}\mathbf{r}}|V_{0}|\psi_{\mathbf{k}_{1}}\rangle - \frac{1}{4\pi} \cdot \frac{e^{ikr}}{r} \cdot \langle\psi_{-\mathbf{k}_{2}}^{*}|\Delta V|\phi_{\mathbf{k}_{1}}\rangle,$$

$$(2.98)$$

where we used the asymptotics (2.88) for the exact solution  $\phi_{\mathbf{k}_1}(\mathbf{r})$  of the undistorted Helmholtz equation. Comparing Eqs. (2.98) and (2.96) immediately gives the exact identity for the scattering amplitude

$$f(\mathbf{k}_{1},\mathbf{k}_{2}) = -\frac{1}{4\pi} \left\langle e^{i\mathbf{k}_{2}\mathbf{r}} | V_{0} | \psi_{\mathbf{k}_{1}} \right\rangle - \frac{1}{4\pi} \left\langle \psi_{-\mathbf{k}_{2}}^{*} | \Delta V | \phi_{\mathbf{k}_{1}} \right\rangle.$$
(2.99)

Using the scattering reversibility (see Appendix E), the scattering amplitude can be written as

$$f(\mathbf{k}_{1},\mathbf{k}_{2}) = -\frac{1}{4\pi} \langle \psi_{-\mathbf{k}_{2}}^{*} | V_{0} | e^{i\mathbf{k}_{1}\mathbf{r}} \rangle - \frac{1}{4\pi} \langle \psi_{-\mathbf{k}_{2}}^{*} | \Delta V | \phi_{\mathbf{k}_{1}} \rangle.$$
(2.100)

Now we can we continue in the spirit of the first Born approximation and replace the exact wave function  $\phi_{\mathbf{k}_1}$  in the distorted potential  $V_0 + \Delta V$  by the wave function in the undistorted potential  $V_0$ , assuming that the distortion  $\Delta V$  is small. Thus, we obtain the following equation for the scattering amplitude in the distorted wave Born approximation (DWBA)

$$f(\mathbf{k}_{1},\mathbf{k}_{2}) = -\frac{1}{4\pi} \langle \psi_{-\mathbf{k}_{2}}^{*} | V_{0} | e^{i\mathbf{k}_{1}\mathbf{r}} \rangle - \frac{1}{4\pi} \langle \psi_{-\mathbf{k}_{2}}^{*} | \Delta V | \psi_{\mathbf{k}_{1}} \rangle.$$
(2.101)

The first term in Eq. (2.101) describes the exact solution (multiple scattering) for the undistorted potential  $V_0(\mathbf{r})$ , and the second term correspond to a single scattering of the distorted wave  $\psi(\mathbf{r})$  by the perturbation  $\Delta V(\mathbf{r})$ .

#### 2.7.4 Application of DWBA to scattering from a rough surface

In this section we will follow the work [27] and apply the DWBA equation (2.101) to the X-ray and neutron scattering from a rough surface. In this approach we will treat the roughness as a small perturbation of an ideal interface, since the exact solution for the ideal are known (see Fresnel equations in section 2.2.2).

Let us start with explicitly writing the undistorted potential  $V_0(\mathbf{r})$  and the corresponding exact wave functions,  $\psi_{\mathbf{k}_1}$  and  $\psi^*_{-\mathbf{k}_2}$ . Assuming an ideal interface at z = 0 between the vacuum at z > 0 and the medium at z < 0, we can write

$$V_0 = \begin{cases} 0, & \text{for } z > 0, \\ k^2(1 - n^2), & \text{for } z < 0. \end{cases}$$
(2.102)

The wave function  $\psi_{\mathbf{k}_1}$  is an exact solution of the scattering problem when the incident wave has a wave vector  $\mathbf{k}_1$  (Fig. 2.22). Therefore, using the results of section 2.2.2, we can write

$$\psi_{\mathbf{k}_{1}} = \begin{cases} e^{i\mathbf{k}_{1}\mathbf{r}} + r(\mathbf{k}_{1})e^{i\mathbf{k}_{1}^{T}\mathbf{r}}, & \text{for } z > 0, \\ t(\mathbf{k}_{1})e^{i\mathbf{k}_{1}^{t}\mathbf{r}}, & \text{for } z < 0, \end{cases}$$
(2.103)

where  $\mathbf{k}_1^r$  and  $\mathbf{k}_1^t$  are the wave vectors of the reflected and transmitted waves correspondingly, and the reflectivity  $r(\mathbf{k}_1)$  and transmittivity  $t(\mathbf{k}_1)$ are defined by the Fresnel equations (see section 2.2.2).

Analogously, the wave function  $\psi^*_{-\mathbf{k}_2}$  can be seen as a solution of the scattering problem when the reflected wave has a wave vector  $\mathbf{k}_2$  (Fig. 2.23):

$$\psi_{-\mathbf{k}_{2}}^{*} = \begin{cases} r^{*}(\mathbf{k}_{2})e^{i\mathbf{k}_{2}^{t}\mathbf{r}} + e^{i\mathbf{k}_{2}\mathbf{r}}, & \text{for } z > 0, \\ t^{*}(\mathbf{k}_{2})e^{i\mathbf{k}_{2}^{t}\mathbf{r}}, & \text{for } z < 0. \end{cases}$$
(2.104)

Now let us define the distortion potential  $\Delta V$  in such a way, that the total potential  $V = V_0 + \Delta V = 0$  above the surface h(x, y), and  $V = V_0 + \Delta V = k^2(1 - n^2) > 0$  below the surface h(x, y) (h(x, y) is the height variation of the rough surface introduced in section 2.6). This can be done assuming (Fig. 2.24)

$$\Delta V = \begin{cases} k^2(1-n^2) , & \text{for } 0 < z < h(x,y) , & \text{if } h(x,y) > 0, \\ -k^2(1-n^2) , & \text{for } h(x,y) < z < 0 , & \text{if } h(x,y) < 0, \\ 0 , & \text{elsewhere.} \end{cases}$$
(2.105)

Substituting  $V = V_0 + \Delta V$  from Eqs. (2.102) and (2.105) into Eq. (2.90) leads to the following cross section of the diffuse scattering in the first Born approximation (it is identical to Eq. (2.70)):

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}} = |f(\mathbf{k}_1, \mathbf{k}_2)|^2$$

$$= \frac{|k^2(1-n^2)|^2}{16\pi^2} L_x L_y e^{-q_z^2 \sigma^2} \iint \left[e^{q_z^2 C(x,y)} - 1\right] e^{-iq_y y} e^{-iq_x x} dx dy.$$
(2.106)

The DWBA result can be obtained [27] substituting Eqs. (2.102)-(2.105) into Eq. (2.101):

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}} = \frac{\left|k^2(1-n^2)\right|^2}{16\pi^2} L_x L_y |t(\mathbf{k}_1)|^2 |t(\mathbf{k}_2)|^2 \cdot \frac{\exp\left[-\frac{\sigma^2}{2}(q_z^t)^2 - \frac{\sigma^2}{2}(q_z^{t*})^2\right]}{|\mathbf{q}_2^t|^2} \times \\ \times \iint \left[e^{|q_z^t|^2 C(x,y)} - 1\right] e^{-iq_y y} e^{-iq_x x} dx dy.$$
(2.107)



Fig. 2.22: Illustration to Eq. (2.103) describing the exact wave function  $\psi_{\mathbf{k}_1}$  at an ideal interface.



Fig. 2.23: Illustration to Eq. (2.104) describing the exact wave function  $\psi^*_{-\mathbf{k}_2}$  at an ideal interface. Note that the function  $\psi^*_{-\mathbf{k}_2}$  is a time inversion of the function  $\psi_{\mathbf{k}_2}$ , which is the solution, when the incident wave has a wave vector  $\mathbf{k}_2$ .



Fig. 2.24: Illustration to Eq. (2.105) describing the distortion potential  $\Delta V(\mathbf{r})$  corresponding to the surface roughness. Red regions correspond to the "hills" on the surface where  $\Delta V > 0$ , and blue regions correspond to the "valleys" on the surface where  $\Delta V < 0$ . In all other regions  $\Delta V = 0$ .

In Eqs. (2.106)-(2.107),  $\sigma^2 = \langle h^2 \rangle$  are the mean square surface fluctuations, t is transmittivity (see section 2.2.2),  $\mathbf{q} = \mathbf{k}_2 - \mathbf{k}_1$  is the scattering vector, and  $\mathbf{q}_z^t = \mathbf{k}_{2z}^t - \mathbf{k}_{1z}^t$  is the z-component of the scattering vector in the media.

While the DWBA solution (2.107) looks much more complicated than the BA solution (2.106), they actually match for high incident and reflected angles  $\alpha_1, \alpha_2 \gg \alpha_c$ , because for high angles the transmittivity approaches unity,  $t(\mathbf{k}_1) = t(\mathbf{k}_2) = 1$  and  $q_z^t = q_z$  becomes a real-value. However, when the incident angle or the angle of reflection is close to the critical angle of the material, the DWBA solution significantly differs from the BA. A particularly known effect is a dramatic increasing of the transmittivity  $|t|^2 =$ 4 at the critical angle, i.e.  $\alpha_1 \approx \alpha_c$  or  $\alpha_2 \approx \alpha_c$  (see Fig. 2.5b). It leads to a dramatic increase of the diffuse scattering intensity - so-called Yoneda wings, since the diffuse scattering is proportional tp the transmittivity (Fig. 2.25).

## 2.7.5 Application of DWBA to scattering from a nanoparticle on a surface

Another instructive and rather common example of DWBA is scattering from a single nanoparticle on a flat surface. As in the previous section, the undistorted potential  $V_0$  corresponds to a flat interface between vacuum and a material with the index of refraction n, and therefore it is defined by Eq. (2.102). The nanoparticle with the index of refraction  $n_{NP}$  is described by a distortion potential

$$\Delta V = \begin{cases} k^2 (1 - n_{NP}^2), & \text{inside the nanoparticle,} \\ 0, & \text{outside the nanoparticle.} \end{cases}$$
(2.108)

The diffusion scattering from such a nanoparticle on a surface can be written as

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{\text{diff}} = \frac{\left|k^2(1-n_{NP}^2)\right|^2}{16\pi^2} \cdot |F|^2, \qquad (2.109)$$

in both approximations (BA and DWBA). In the first Born approximation, the form factor F represents single scattering of a plane wave by a nanoparticle:

$$F^{\mathrm{BA}} = \int_{NP} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} = \int_{NP} e^{-iq_x x} e^{-iq_y y} e^{-iq_z z} dx dy dz, \qquad (2.110)$$

where the integral is taken over the volume of the nanoparticle. In the distorted wave Born approximation, the form factor F represents a single scattering of the distorted wave by the nanoparticle. It means, that it contains all possible multiple scattering from the flat surface and single scattering by the nanoparticle, therefore F can be represented as a sum of four terms [30]:

$$F^{\text{DWBA}} = \int_{NP} e^{-iq_x x} e^{-iq_y y} e^{-i(k_{2z} - k_{1z})z} dx dy dz + r(\alpha_1) \int_{NP} e^{-iq_x x} e^{-iq_y y} e^{-i(k_{2z} + k_{1z})z} dx dy dz + r(\alpha_2) \int_{NP} e^{-iq_x x} e^{-iq_y y} e^{i(k_{2z} + k_{1z})z} dx dy dz$$
(2.111)  
$$r(\alpha_1) r(\alpha_2) \int_{NP} e^{-iq_x x} e^{-iq_y y} e^{i(k_{2z} - k_{1z})z} dx dy dz.$$

The origin of these four terms is illustrated in Fig. 2.26. The first term matches with the BA (Eq. (2.110)), while the other terms which include multiple scattering from the surface are only taken into account within DWBA.

+



Fig. 2.25: Scheme for measuring a so-called rocking curve: the incident and reflection angles are set to  $\theta$ , and then the sample is rocked by an angle  $\omega$ . In the bottom part the resulting reflected intensity is shown: it has a strong specular peak at  $\omega = 0$  and diffuse scattering around this point, i.e. when the incident angle matches the angle of reflection,  $\alpha_1 \approx \alpha_2 \approx \theta$ . The Yoneda wings appear when either the incident angle  $\alpha_1$  or the angle of reflection  $\alpha_2$  matches with the critical angle  $\alpha_c$ .



Fig. 2.26: The four scattering channels taken into account by DWBA in Eq. (2.111). Only the first channel is taken into account by BA in Eq. (2.110).

### 3 Scattering from non-crystalline materials

In this section, we will consider small angle scattering from an individual nanoparticle and investigate how its shape influences the scattering. Later we will consider an ensemble of nanoparticles, e.g. solution of nanoparticles, and discuss when the solution can be considered as diluted, and when the interaction between the nanoparticles have to be taken into account.

By nanoparticle we mean any nanoobject, be it an inorganic nanoparticle itself or a micelle of a liquid crystalline phase, or a large organic molecule [31], for example, a polymer or protein.

For the simplicity, we will consider only X-ray scattering, and we will not include the polarization effects (see the polarization factor  $P^2$  in Eq. (1.17)). However the obtained results can be easily converted to the neutron scattering by replacing the classical radius of electron  $r_e$  (Eq. (1.16) with the neutron scattering length b (Eq. (1.42)) and the electron density  $\rho_e$  with the atomic density  $\rho_{at}$  (similarly to how it was done with the index of refraction in section 2.1.3). Strictly speaking, in the following sections we will consider the scattering cross-section  $\left(\frac{\partial\sigma}{\partial\Omega}\right)$  defined in Eq. (1.18) which does not depend on the distance R between the scatterer and the detector. However, to be closer to the real experiment, where the intensity I of the scattered intensity. To summarize, we will omit the factor  $(-r_e \cdot P/R)^2$  in all equations for intensity and write them using proportionality.

#### 3.1 Small angle scattering from a single nanoparticle

#### 3.1.1 Scattering form factor

Let us consider small angle X-ray scattering from an individual nanoparticle positioned at  $\mathbf{R}_{NP}$  with electron density  $\rho_{NP}(\mathbf{r})$  in a solvent with electron density  $\rho_{sol}$  (Fig. 3.1). The magnitude of the scattered wave is a sum of the photons scattered by the nanoparticle and by the solvent:

$$E \propto \int \rho_{el} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} = \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} + \int [\rho_{NP}(\mathbf{r} - \mathbf{R}_{NP})] e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
$$= \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} + e^{-i\mathbf{q}\mathbf{R}_{NP}} \int \underbrace{[\rho_{NP}(\mathbf{r}) - \rho_{sol}]}_{\Delta\rho(\mathbf{r})} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}.$$
(3.1)

If the nanoparticle is floating in the solvent, its position  $\mathbf{R}_{NP}$  is not fixed, so the average value of the phasor  $\langle e^{-i\mathbf{q}\mathbf{R}_{NP}}\rangle = 0$  is zero. Therefore, the total scatted intensity  $I_{tot} \propto \langle |E|^2 \rangle$  does not contain the cross-term, which is proportional to  $\langle e^{-i\mathbf{q}\mathbf{R}_{NP}} \rangle$ :

$$I_{tot} \propto \langle |E|^2 \rangle \propto \underbrace{\left| \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2}_{I_{sol}} + \underbrace{\left| \int \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2}_{I_{NP}}.$$
 (3.2)

Thus, the total scattered intensity has two contributions: scattering from the nanoparticle  $I_{NP}$  and scattering from the solvent  $I_{sol}$ . In an experiment, the term  $I_{sol}$  can contain all scattering signal which does not come from the nanoparticle, for example, scattering from the parts of the experimental setup (glass capillary with the solvent), scattering from air etc. This scattering signal  $I_{sol}$  can be treated as a background and measured separately in an identical scattering experiment which has everything except of the nanoparticle. The scattering signal from the nanoparticle  $I_{NP}$  can be



$$\begin{aligned} |\vec{k}_{in}| &= |\vec{k}_{out}| = k = \frac{2\pi}{\lambda} \\ \vec{q} &= \vec{k}_{out} - \vec{k}_{in} \\ |\vec{q}| &= \frac{4\pi}{\lambda} \sin\theta \end{aligned}$$

Fig. 3.1: Illustration of elastic X-ray scattering by a single nanoparticle in solution.

then calculated as a difference between the total scattering signal and the scattering from the solvent (background):

$$I_{NP}(\mathbf{q}) = I_{tot} - I_{sol} = \left| \int \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2.$$
(3.3)

Obviously, if the nanoparticle has the same electron density as the solvent, i.e.  $\Delta \rho \equiv 0$ , there will be no scattering from the nanoparticle, because there will be no interface between the nanoparticle and solvent at which the refraction of X-rays could happen. There is an important technique (especially for neutron scattering) called contrast variation [32], where the scattering of the solvent matches the scattering from a certain region of a nanoparticle, making this region "invisible" in the scattering experiment.

In the case of N non-interacting nanoparticles floating in the solvent, the magnitude of the scattered wave can be written similarly to Eq. (3.1):

$$E \propto \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} + \sum_{i=1}^{N} e^{-i\mathbf{q}\mathbf{R}_{NP}^{i}} \int \Delta \rho_{i}(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}.$$
 (3.4)

Since the nanoparticles do not interact with each other (for example, in the case of a very diluted solution),  $\langle e^{-i\mathbf{q}(\mathbf{R}_{NP}^{i}-\mathbf{R}_{NP}^{j})} \rangle = 0$  for  $i \neq j$ , meaning that there will be no interference between the X-rays scattered from different nanoparticles. Therefore,

$$I_{NP}(\mathbf{q}) = I_{tot} - I_{sol} = \sum_{i=1}^{N} \left| \int \Delta \rho_i(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2, \tag{3.5}$$

or in the case of identical nanoparticles

$$I_{NP}(\mathbf{q}) = I_{tot} - I_{sol} = N \cdot \left| \int \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2.$$
(3.6)

Here we see that the scattered intensity is proportional to the number of scatterers N (and not  $N^2$ , as it would be if the positions of nanoparticles would be correlated).

For rigid nanoparticles with a constant electron density inside its volume

$$\Delta \rho(\mathbf{r}) = \begin{cases} \Delta \rho , & \text{inside} \\ 0 , & \text{outside.} \end{cases}$$
(3.7)

we can write

$$I_{NP}(\mathbf{q}) = I_{tot} - I_{sol} = N \cdot \Delta \rho^2 \cdot V_{NP}^2 |F(\mathbf{q})|^2, \qquad (3.8)$$

where  $V_{NP}$  is the volume of individual nanoparticle, and  $F(\mathbf{q})$  is the scattering form factor of individual nanoparticle<sup>7</sup>

$$F(\mathbf{q}) = \frac{1}{V_{NP}} \int_{V_{NP}} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}.$$
(3.9)

The scattering form factor defined in Eq. (3.9) is analogous to the atomic scattering form factor introduced in Eq. (1.29).

For a nanoparticle, which electron density is not a constant, the form factor can be calculated in a similar way as

$$F(\mathbf{q}) = \frac{\int \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}}{\int \Delta \rho(\mathbf{r}) d\mathbf{r}}.$$
(3.10)

<sup>&</sup>lt;sup>7</sup>Sometimes, instead of the form factor,  $F(\mathbf{q})$ , a so-called shape factor  $P(\mathbf{q}) = |F(\mathbf{q})|^2$  is used.
The form factor  $F(\mathbf{q})$  depends on the shape of the nanoparticle, therefore measuring the small angle scattering from the solution of nanoparticles can revel information about the shape of the nanoparticles, which is especially important in the case when the nanoparticles only exist in solution and can not be observed *ex situ* by AFM or another imaging techniques. For example, this is the case for liquid crystal micelles or large protein molecules or another molecular agglomerates which can only exist in a solution.

# **3.1.2** Absolute intensity at q = 0

From the definition of the scattering form factor (Eq. (3.9)), it is clear that F(q = 0) = 1. Therefore, the scattered intensity (Eq. (3.8)) in the forward direction  $(q \rightarrow 0)$  depends on the electron density  $\Delta \rho$  and the volume of the nanoparticle  $V_{NP}$ . In an experiment, one can measure the scattered intensity I(q) (in photons/sec), normalized by the scattering volume V (the volume of the solution) and the flux of an incident beam  $\Phi_0$  (in photons/sec/cm<sup>2</sup>). In result, using definition (1.6), one obtains the differential scattering cross-section normalized per volume of the sample:

$$\frac{I_{tot}(q) - I_{sol}(q)}{V\Phi_0} = \frac{1}{V} \left(\frac{\partial\sigma}{\partial\Omega}\right) \xrightarrow[q \to 0]{} r_e^2 \frac{N}{V} \Delta \rho^2 V_{NP}^2. \tag{3.11}$$

Since we want to work with absolute values, it is important to explicitly write the classical radius of the electron in this equation. The combination on the left hand side has units of inverse length (by convention,  $\text{cm}^{-1}$ ). It is common in SAXS experiment, that this combination is denoted simply as I(0), and only from the units it is clear that the measured intensity was normalized, as shown above. Such normalization is usually called "absolute scale".

Now, Eq (3.11) can be used to determine the molecular weight of a single nanoparticle. For example, this is one of the techniques which allows one to determine the molecular weight of large protein molecules with an accuracy of  $\sim 10\%$  by measuring the intensity of the X-ray scattered in the forward direction.

To do this, let us write the mass concentration of the nanoparticles c (in mg/ml) via a specific volume of nanoparticles  $\nu$  (inverse mass density of nanoparticle material, in ml/mg):

$$c = \frac{N}{V} \cdot \frac{V_{NP}}{\nu}.$$
(3.12)

Here the first term is the concentration of nanoparticles, and the second term - mass of a single nanoparticle. Then, the molecular weight of a nanoparticle  $M_w$ , i.e. weight of one mole of nanoparticles (in g/mole) can be calculated via the weight of a single nanoparticle as

$$M_w = \frac{V_{NP}}{\nu} \cdot N_A, \qquad (3.13)$$

where  $N_A \approx 6.022 \cdot 10^{23} \text{ mol}^{-1}$  is Avogadro's number. Combining Eqs. (3.11-3.13), we obtain

$$\frac{I_{tot}(q) - I_{sol}(q)}{V\Phi_0} \xrightarrow[q \to 0]{} c \frac{\nu}{V_{NP}} \cdot r_e^2 \Delta \rho^2 V_{NP}^2 = c \cdot \nu r_e^2 \Delta \rho^2 \cdot \frac{M_w \nu}{N_A} = \frac{c \nu^2 M_w}{N_A} r_e^2 \Delta \rho^2$$
(3.14)

Here we should note, that one cannot directly measure the scattered intensity at q = 0, because at this point the intensity is dominated by the direct beam, i.e. the photons which passed through the sample without scattering. Instead, one has to measure the scattered intensity at small values of the scattering vector q and then approximate it to  $q \rightarrow 0$ . How exactly to do this approximation, will be discussed in section 3.1.4.



Fig. 3.2: Intensity scattered from a spherical nanoparticle. Red curve shows the asymptotic behavior at  $qR \ll 1$  (see Eq. (3.17)); blue line indicates the envelope for  $qR \gg 1$  (see Eq. (3.18)).



Fig. 3.3: Intensity scattered from an ensemble of spherical particles of different sizes with the same mean radius R. The radii of the spheres are distributed normally with  $\sigma = 0.01R$ , 0.05R and 0.1R.

### 3.1.3 Example: scattering form factor of a solid sphere

As an example, let us calculate the scattering form factor of a solid sphere with radius R and constant electron density  $\Delta \rho$  inside the sphere. In this case, we need to evaluate the integral in Eq. (3.9), which can be done using spherical system of coordinates:

$$F(\mathbf{q}) = \frac{1}{V_{NP}} \int_{V_{NP}} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
  
=  $\frac{1}{\frac{4}{3}\pi R^3} \int_0^R r^2 dr \int_0^\pi \sin\theta d\theta \underbrace{\int_0^{2\pi} d\varphi}_{2\pi} e^{-iqr\cos\theta}$   
=  $\frac{1}{\frac{2}{3}R^3} \int_0^R r^2 dr \int_0^\pi e^{-iqr\cos\theta} \sin\theta d\theta = \frac{3}{2R^3} \int_0^R r^2 dr \int_{-1}^1 e^{-iqr\cdot t} dt.$   
(3.15)

The inner integral can be easily evaluated

$$\int_{-1}^{1} e^{-iqr \cdot t} dt = \frac{e^{-iqr} - e^{iqr}}{-iqr} = 2\frac{\sin(qr)}{qr}.$$

The outer integral in Eq. (3.15) can be evaluated using partial integration:

$$\int_{0}^{R} \frac{2r}{q} \sin(qr) dr = \frac{2}{q^{3}} \int_{0}^{R} \underbrace{qr}_{qr} \sin(qr) \frac{dt}{d(qr)} = -\frac{2}{q^{3}} \int_{0}^{qR} t \, d\cos t$$
$$= -\frac{2}{q^{3}} \cdot t \cos t \Big|_{0}^{qR} + \frac{2}{q^{3}} \int_{0}^{qR} \cos t dt = -\frac{2}{q^{3}} qR \cos(qR) + \frac{2}{q^{3}} \cdot \sin(qR).$$

Substituting this result in Eq. (3.15), we obtain

$$F(q) = 3 \cdot \frac{\sin(qR) - qR\cos(qR)}{(qR)^3}.$$
 (3.16)

The intensity  $I(q) \propto |F(q)|^2$  scattered by a sphere is shown in Fig. 3.2.

In a real experiment, one has to take into account polydispersity of the nanoparticles. It means, that different nanoparticles can have different sizes, which would lead to the smearing of the strong oscillations of the scattering structure factor (Fig. 3.3). Moreover, since the scattered intensity is proportional to the square of the nanoparticle's valume (see Eq. (3.8)), the larger particles dominate in the scattering curve I(q).

When  $qR = \tan(qR)$ , the scattered intensity drops to zero (this happens for  $qR \approx 4.49$ , 7.73, 10.90, ...). For the small scattering angles ( $qR \ll 1$ ), one can use Taylor expansion to calculate the asymptotic behavior:

$$F(q \to 0) = \frac{3}{(qR)^3} \left( \underbrace{qR - \frac{(qR)^3}{3!} + \frac{(qR)^5}{5!} - \dots}_{\sin(qR)} \underbrace{-qR + \frac{(qR)^3}{2!} - \frac{(qR)^5}{4!} + \dots}_{-qR\cos(qR)} \right)$$
$$\approx \frac{3}{(qR)^3} \left( \frac{(qR)^3}{3} - \frac{(qR)^5}{30} \right) = 1 - \frac{(qR)^2}{10} \approx e^{-\frac{(qR)^2}{10}}.$$
(3.17)

Such a quadratic decay of intensity at small q is a general result, which will be discussed in section 3.1.4.



Fig. 3.4: Radius of gyration for (a) solid sphere with radius R, (b) solid ellipsoid with semiaxes a, b and c, (c) solid cylinder with diameter D and height L, (d) flat disc with diameter D, (e) thin rod with length L.

In another limiting case,  $qR \ge 1$ , one can neglect the sine function in the nominator of Eq. (3.16), and obtain the asymptotic behavior

$$F(q) \xrightarrow{qR \ge 1} 3 \cdot \frac{\cos(qR)}{(qR)^2}.$$
 (3.18)

The decay of the scattered intensity as  $I \propto |F(q)|^2 \propto q^{-4}$  is also a general result (see sections 2.2.2 and 3.1.5).

#### **3.1.4** Guinier analysis at $q \rightarrow 0$

Let us investigate the dependence of the scattering form factor at  $q \rightarrow 0$  for a nanoparticle with an arbitrary shape. To consider a general case (not only hard-core nanoparticles as in Eq. (3.9)), we will use the scattering form factor written as

$$F(\mathbf{q}) = \frac{1}{V_{NP}} \int_{V_{NP}} \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}.$$
 (3.19)

This will allow us to consider the variation of the electron density  $\Delta \rho(\mathbf{r})$  within the nanoparticle. We will consider such small values of the scattering vector q that  $\mathbf{qr} \ll 1$  for any  $\mathbf{r}$  inside the nanoparticle. This allows us to use the Taylor expansion for the exponential,  $\exp(-i\mathbf{qr}) \approx 1 - i(\mathbf{qr}) - \frac{(\mathbf{qr})^2}{2}$ :

$$F(\mathbf{q} \to 0) = \frac{1}{V_{NP}} \int \Delta \rho(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
  

$$\approx \frac{1}{V_{NP}} \int \Delta \rho(\mathbf{r}) d\mathbf{r} - \frac{i}{V_{NP}} \mathbf{q} \underbrace{\int \mathbf{r} \Delta \rho(\mathbf{r}) d\mathbf{r}}_{\mathbf{r}_c} - \frac{1}{2V_{NP}} \int (\mathbf{q}\mathbf{r})^2 \Delta \rho(\mathbf{r}) d\mathbf{r}.$$
(3.20)

Here the first term is related to the total electron density of a nanoparticle, and it can be denoted as F(0). The integral in the second term, denoted as  $\mathbf{r}_c$ , defines the position of the "center of scattering density". Let us assume that the particle is placed in the origin of the coordinates, so that  $\mathbf{r}_c = 0$ . After all, the translation of the particle by a vector  $\Delta \mathbf{R}_{NP}$  will introduce a phase  $e^{-i\mathbf{q}\Delta \mathbf{R}_{NP}}$  to the form factor (see Eq. (3.19)), which doesn't influence the scattered intensity, because  $I_{NP} \propto |F|^2$ . Therefore, we can write for  $\mathbf{qr} \ll 1$ 

$$F(\mathbf{q}) \xrightarrow[q \to 0]{} F(0) - \frac{1}{2V_{NP}} \int (\mathbf{qr})^2 \Delta \rho(\mathbf{r}) d\mathbf{r}.$$
(3.21)

Usually the orientation of the particle is not fixed, so one has to average  $F(\mathbf{q})$  over all possible orientations of a nanoparticle. The same result will be obtained if one averages over all possible orientations of the scattering vector  $\mathbf{q}$ . Therefore, we need to calculate  $\langle (\mathbf{qr})^2 \rangle$ , where averaging is taken over all possible orientations of q. The easiest way to do this is to use spherical coordinates:

$$\langle (\mathbf{qr})^2 \rangle = \frac{\int_0^{\pi} (qr \cos \theta)^2 \cdot \sin \theta d\theta}{\int_0^{\pi} \cdot \sin \theta d\theta} \int_0^{2\pi} d\phi}{\int_0^{\pi} \cdot \sin \theta d\theta} \int_0^{2\pi} d\phi} = \frac{q^2 r^2 \int_{-1}^1 t^2 dt \cdot 2\pi}{4\pi} = \frac{q^2 r^2}{3}.$$
(3.22)

Therefore,

$$F(q) \xrightarrow[q \to 0]{} = \underbrace{\frac{1}{V_{NP}} \int \Delta\rho(\mathbf{r})d\mathbf{r}}_{F(q=0)} - \frac{1}{2V_{NP}} \cdot \frac{q^2}{3} \int r^2 \Delta\rho(\mathbf{r})d\mathbf{r}}_{(3.23)}$$
$$= F(q=0) \left(1 - \frac{q^2 R_g^2}{6}\right),$$



Fig. 3.5: Dependence of the scattered intensity I(q) vs.  $q^2$  for a nanoparticle (in logarithmic scale). The slope of the intensity at  $q \approx 0$  depends on the radius of gyration  $R_g$ . For this illustration, intensity scattered by a solid sphere was used (as in Fig. 3.2).

where we introduced radius of gyration  $R_q$  defines as

$$R_g^2 = \frac{\int r^2 \Delta \rho(\mathbf{r}) d\mathbf{r}}{\int \Delta \rho(\mathbf{r}) d\mathbf{r}}.$$
(3.24)

Radius of gyration  $R_g$  is a mean square distance from the center of scattering density. It it an important parameter which characterizes the size and the shape of the nanoparticle. Mathematically, it is related to the moment of inertia in mechanics with the difference that the gyration radius is related to the distribution of the scattering density, and moment of inertia is related to the distribution of mass density. The gyration radius for some simple geometrical shapes is shown in Fig. 3.4.

The scattered intensity for  $q \to 0$  is then

$$I(q) \propto |F(q)|^2 \propto I(0) \cdot \left(1 - 2 \cdot \frac{q^2 R_g^2}{6}\right).$$
 (3.25)

Therefore, the experimental determination of the radius of gyration is possible by calculating the slope of I(q) vs  $q^2$  in logarithmic scale, as shown in Fig. 3.5.

# **3.1.5** Porod analysis at $q \to \infty$

For a solid sphere, we can use the result of Eq. (3.18) and write the scattered intensity in Eq. (3.6) for  $qR \ge 1$  as

$$I(q) = N \cdot \Delta \rho^2 \cdot V_{NP}^2 \cdot |F(q)|^2 \xrightarrow{qR \ge 1} N \cdot \Delta \rho^2 \cdot \left(\frac{4}{3}\pi R^3\right)^2 \cdot 9 \cdot \frac{\cos^2(qR)}{(qR)^4}.$$
 (3.26)

Introducing the area of the nanoparticle's surface  $S_{NP} = 4\pi R^2$  and taking the average of the oscillating form factor,  $\langle \cos^2(qR) \rangle = \frac{1}{2}$ , we can rewrite Eq. (3.26) as

$$I(q) \xrightarrow{qR \ge 1} \frac{2\pi N \Delta \rho^2 \cdot S_{NP}}{q^4} \propto \frac{S_{NP}}{q^4}.$$
 (3.27)

This asymptotic result is general for all 3D nanoparticles with a sharp interface [33]; and the exponent of the algebraic decay of the scattered intensity is called Porod's exponent. A similar dependence,  $I \propto q^{-4}$  was also obtained for the scattering from a sharp interface in section 2.2.2, however we did not do angular averaging there.

For a 3D nanoparticle with a rough interface (which can be described by a fractal dimensionality 2 < d < 3), the dependence is slightly different:

$$I(q) \propto \frac{1}{q^{6-d}}.\tag{3.28}$$

It can be shown, that the Porod exponent also depends on the dimensionality of the nanoparticle;  $I \propto q^{-2}$  for 2D nanoparticles and  $I \propto q^{-1}$  for 1D nanoparticles. For example [34],

• 2D disk with diameter D:

$$F(q)|^{2} = \frac{8}{q^{2}D^{2}} \left[ 1 - 2\frac{J_{1}(qD)}{qD} \right] \propto \frac{1}{q^{2}},$$
(3.29)

where  $J_1(x)$  is the first-order Bessel function.

• 1D rod with length L:

$$|F(q)|^2 = \frac{2}{qL} \left[ Si(qL) - \frac{1 - \cos(qL)}{qL} \right] \propto \frac{1}{q}, \qquad (3.30)$$

where  $Si(x) = \int_0^x \frac{\sin t}{t} dt$  is sine integral function.



Fig. 3.6: Squared scattering form factor  $|F(q)|^2$  for two cylinders with different aspect ratios: (a) D/H = 20 (disc-like), (b) D/H = 0.02 (rod-like). For  $qR_g \leq 1$  the form factor can be well approximated with Guinier law (see Eq. (3.25) and Fig. 3.4). For  $qR_g \gg 1$  the form factor decays as  $\propto q^{-4}$  according to Eq. (??). For the intermediate values, the disc-like cylinder exhibits  $\propto q^{-2}$  dependence, typical for 2D objects, and the rod-like cylinder exhibits  $\propto q^{-1}$  dependence, typical for 1D objects. The figure is plotted in double logarithmic scale.

Any real nanoparticle is of course a 3D object, which means that at sufficiently high q-values (which corresponds to a very small length scale in real space), any 3D nanoparticle scatters as  $\propto q^{-4}$ . However, at some intermediate q-values  $(q \sim R_g^{-1})$ , we can expect some deviations from the law  $I \propto q^{-4}$ , which are related to the dimensionality. This is illustrated in Fig 3.6, where the scattered intensity is calculated for two cylinder with different aspect ratios (disk-like and rod-like).

#### 3.2 Scattering from an ensemble of nanoparticles

#### 3.2.1 Structure factor

Let us consider X-ray scattering from a solution of nanoparticles, similarly to what was done in section 3.1.1. However, now we will not assume that the positions of the individual nanoparticles are completely independent from each other, and therefore we will not be able to neglect the interference between the X-ray photons, scattered from different nanoparticles.

Let us consider N nanoparticles with ositioned at  $r_j$  (j = 1, 2, ..., N). The electron density of each nanoparticle is  $\rho_j(\mathbf{r})$ , and the electron density of the solution is  $\rho_{sol}$ . The magnitude of the scattered wave is a sum of the photons scattered by the nanoparticles and by the solvent:

$$E \propto \int \rho_{el} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} = \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} + \sum_{j=1}^{N} \int [\rho_j(\mathbf{r} - \mathbf{r}_j)] e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
$$= \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} + \sum_{j=1}^{N} e^{-i\mathbf{q}\mathbf{r}_j} \underbrace{\int \left[\rho_j(\mathbf{r}) - \rho_{sol}\right] e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}}_{\propto F_j(\mathbf{q})},$$
(3.31)

analogously to how it was done in Eq. (3.1). The Fourier transform of the electron density of each nanoparticle is proportional to the scattering structure factor  $F_i(\mathbf{q})$ , which was considered before (see Eqs. (3.9-3.10))<sup>8</sup>.

The total scattered intensity  $I_{tot} \propto \langle |E|^2 \rangle$  contains the squares of each term in Eq. (3.31) as well as the cross-products. However, the average value of the cross-products are proportinal to  $\langle e^{-i\mathbf{qr}_j} \rangle = 0$ , which equals to zero, since the position of the nanoparticles is not fixed (similar to Eq. (3.2)). Therefore the total scattered intensity can be written as

$$I_{tot} \propto \langle |E|^2 \rangle \propto \underbrace{\left| \int \rho_{sol} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \right|^2}_{I_{sol}} + \underbrace{\left\langle \left| \sum_{j=1}^N e^{-i\mathbf{q}\mathbf{r}_j} \cdot F_j(\mathbf{q}) \right|^2 \right\rangle}_{I_{NP}}.$$
 (3.32)

Here the averaging is taken over all possible positions of the nanoparticles, i.e. ensemble averaging.

Similarly to how it was done in section 3.1.1, we can treat  $I_{sol}$  as background and include in there all scattered photons which come not from the nanoparticles. The scattering signal from the nanoparticles (which we will



Fig. 3.7: Illustration of elastic X-ray scattering by an ensemble of N nanoparticles in solution.

<sup>&</sup>lt;sup>8</sup>For a solid nanoparticle with a constant electron density, the integral in Eq. (3.31) equals to  $\Delta \rho_j \cdot F_j(\mathbf{q})$ . In the following consideration, we will not explicitly write it the electron density, but rather include it into the form factor

simply denote as  $I(\mathbf{q})$  can be written as

$$I(\mathbf{q}) \equiv I_{NP}(\mathbf{q}) = I_{tot} - I_{sol} = \left\langle \left| \sum_{j=1}^{N} F_j(\mathbf{q}) \cdot e^{-i\mathbf{q}\mathbf{r}_j} \right|^2 \right\rangle$$
$$= \left\langle \sum_{j=1}^{N} F_j(\mathbf{q}) e^{-i\mathbf{q}\mathbf{r}_j} \cdot \sum_{i=1}^{N} F_i^*(\mathbf{q}) e^{i\mathbf{q}\mathbf{r}_i} \right\rangle$$
$$= \left\langle \sum_{i,j=1}^{N} F_i^*(\mathbf{q}) F_j(\mathbf{q}) \cdot e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle,$$
(3.33)

where asterisk denotes complex conjugation. We can separate the terms with i = j from the double sum in Eq. (3.33):

$$I(\mathbf{q}) = \sum_{i=1}^{N} \left\langle |F_i(\mathbf{q})|^2 \right\rangle + \sum_{\substack{i,j=1\\i\neq j}}^{N} \left\langle F_i^*(\mathbf{q})F_j(\mathbf{q}) \cdot e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle$$

$$= N \left\langle |F(\mathbf{q})|^2 \right\rangle + \sum_{\substack{i,j=1\\i\neq j}}^{N} \left\langle F_i^*(\mathbf{q})F_j(\mathbf{q}) \cdot e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle.$$
(3.34)

Here the first term is proportional to the number of particles N and it corresponds to the sum of the scattering intensities from each individual nanoparticle (we have already obtained this term in Eq. (3.8)).

To evaluate the second term in Eq. (3.34), we will use so-called decoupling approximation. Specifically, we will assume that the position of the nanoparticle  $\mathbf{r}_j$  does not depend on its size, shape or orientation, i.e. its form factor  $F_j(\mathbf{q})$ . This allows us to write

$$\left\langle F_{i}^{*}(\mathbf{q})F_{j}(\mathbf{q})\cdot e^{-i\mathbf{q}(\mathbf{r}_{j}-\mathbf{r}_{i})}\right\rangle = \left\langle F_{i}^{*}(\mathbf{q})\right\rangle\cdot\left\langle F_{j}(\mathbf{q})\right\rangle\cdot\left\langle e^{-i\mathbf{q}(\mathbf{r}_{j}-\mathbf{r}_{i})}\right\rangle$$

$$= \left|\left\langle F(\mathbf{q})\right\rangle\right|^{2}\cdot\left\langle e^{-i\mathbf{q}(\mathbf{r}_{j}-\mathbf{r}_{i})}\right\rangle.$$

$$(3.35)$$

The decoupling approximation works well in the diluted systems, however when the distance between the individual nanoparticles becomes comparable to the size of the nanoparticles, one cannot simply assume that the orientation of the nanoparticles is independent on their position. An example of such system can be liquid crystal phases, where strongly anisotropic molecules have preferred orientation [35, 36].

Now the scattered intensity can be written as

$$I(\mathbf{q}) = N \left\langle |F(\mathbf{q})|^2 \right\rangle + \left| \left\langle F(\mathbf{q}) \right\rangle \right|^2 \cdot \left\langle \sum_{\substack{i,j=1\\i \neq j}}^N e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle, \tag{3.36}$$

which does not depend on absolute positions of the nanoparticles, but only on their relative positions  $(\mathbf{r}_j - \mathbf{r}_i)$ . This allows us to define the structure factor as

$$S(\mathbf{q}) = \left\langle \frac{1}{N} \sum_{i,j=1}^{N} e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle = 1 + \frac{1}{N} \left\langle \sum_{\substack{i,j=1\\i \neq j}}^{N} e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle,$$
(3.37)

where the N terms for which i = j can be include in the double sum, or evaluated separately which gives the unity. The structure factor  $S(\mathbf{q})$  is the ensemble-averaged Fourier transform of the positions of the nanoparticles, as it will be clear from the upcoming sections. It contains information on the relative position of the nanoparticles, but it does not depend on the size or shape of the individual nanoparticle (this information is "hidden" in the scattering form factors).

Finally, the scattered intensity (Eq. (3.36)) can be written using the structure factor  $S(\mathbf{q})$  as

$$I(\mathbf{q}) = N \left\langle |F(\mathbf{q})|^2 \right\rangle \cdot \left( 1 + \frac{\left| \langle F(\mathbf{q}) \rangle \right|^2}{\left\langle |F(\mathbf{q})|^2 \right\rangle} \cdot \underbrace{\frac{1}{N} \left\langle \sum_{\substack{i,j=1\\i \neq j}}^N e^{-i\mathbf{q}(\mathbf{r}_j - \mathbf{r}_i)} \right\rangle}_{S(\mathbf{q}) - 1} \right)$$
(3.38)

$$= N \Big\langle |F(\mathbf{q})|^2 \Big\rangle \cdot \left( 1 + \frac{\left| \langle F(\mathbf{q}) \rangle \right|^2}{\left\langle |F(\mathbf{q})|^2 \right\rangle} \cdot \left[ S(\mathbf{q}) - 1 \right] \right).$$

Often the system consists of identical nanoparticles (with the same size, shape and orientation), or at least can be approximated by such a model. In this case, the fraction in Eq. (3.38) approximately equals to unity

$$\frac{\left|\langle F(\mathbf{q})\rangle\right|^2}{\left\langle|F(\mathbf{q})|^2\right\rangle} = \beta(q) \approx 1, \tag{3.39}$$

and the scattered intensity can be written as a simple product of three factors:<sup>9</sup>

$$I(\mathbf{q}) = N \cdot \left\langle |F(\mathbf{q})|^2 \right\rangle \cdot S(\mathbf{q}).$$
(3.40)

Thus, the scattered intensity is proportional to the number of particles N, to the average shape factor of the nanoparticles  $P(q) = \langle |F(\mathbf{q})|^2 \rangle$ , which determines the scattering from individual nanoparticle, and to the structure factor  $S(\mathbf{q})$ , which is defined by the relative position of the nanoparticles.

When the polydispersity of the nanoparticles has to be taken into account, one can keep the beta function introduced in Eq. (3.39) (so-called beta-decoupling approximation) and evaluate the scattered intensity as

$$I(\mathbf{q}) = N \cdot \left\langle |F(\mathbf{q})|^2 \right\rangle \cdot \left(1 + \beta(q) \left[S(\mathbf{q}) - 1\right]\right), \tag{3.41}$$

where  $\beta(q)$  is defined in Eq. (3.39).

# 3.2.2 Pair distribution function (PDF)

In this section we will establish a connection between the structure factor  $S(\mathbf{q})$  and the relative positions of the nanoparticles in real space. In order to do this, let us first define a number density function  $n(\mathbf{r})$  which determines a probability to find a nanoparticle at the position  $\mathbf{r}$ :

$$n(\mathbf{r}) = \sum_{j=1}^{N} \delta(\mathbf{r} - \mathbf{r}_j), \qquad (3.42)$$

where  $\delta(\mathbf{r})$  is the Dirac delta-function, and the sum runs over all nanoparticles in the system. According this definition, the amount of nanoparticles

<sup>&</sup>lt;sup>9</sup>Remember, that the form factor  $F(\mathbf{q})$  is proportional to the electron density difference  $\Delta \rho$ . Therefore, the larger is the difference between the electron densities of the nanoparticles and the solution, the stronger is the scattered intensity.

within a volume V is  $N = \int_V n(\mathbf{r}) d\mathbf{r}$ . Therefore, the physical meaning of  $n(\mathbf{r})$  is the concentration of the nanoparticles (number of nanoparticles per volume) at the position  $\mathbf{r}$ . For a solution, the ensemble-averaged value  $\langle n(\mathbf{r}) \rangle = \langle n \rangle$  is just an average concentration of nanoparticles, which does not depend on the position.

We have already seen that in the scattering problem, only the relative position of the nanoparticles,  $\mathbf{r}_j - \mathbf{r}_i$ , is important. Moreover, in real space the translation of the system as a whole over some vector  $\Delta \mathbf{R}$  should not change any physical processes in the system (translation invariance or translation symmetry). Therefore, only relative positions of the nanoparticles are essential to describe the system. This leads us to the necessity to introduce a density-density correlation function in real space:

$$G(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{N} \langle n(\mathbf{r}_1) n(\mathbf{r}_2) \rangle = \frac{1}{N} \Big\langle \sum_{i,j=1}^N \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \Big\rangle.$$
(3.43)

Here  $\langle \ldots \rangle$  denotes ensemble averaging, which means averaging over all microscopy realizations of a macroscopic system at the given thermodynamic parameters (temperature, concentration, pressure etc.)

If the system is translationally invariant, as suggested above, the correlation function  $G(\mathbf{r}_1, \mathbf{r}_2)$  only depends on the difference  $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ , so one can explicitly integrate the correlation function over  $\mathbf{r}_1$  (averaging over all other microscopic parameters is kept):

$$G(\mathbf{r}) = \int G(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 = \int \frac{1}{N} \langle n(\mathbf{r}_1) n(\mathbf{r}_1 + \mathbf{r}) \rangle d\mathbf{r}_1$$
  
$$= \frac{1}{N} \int \Big\langle \sum_{i,j=1}^N \underbrace{\delta(\mathbf{r}_1 - \mathbf{r}_i)}_{\mathbf{r}_1 = \mathbf{r}_i} \delta(\mathbf{r}_1 + \mathbf{r} - \mathbf{r}_j) \Big\rangle d\mathbf{r}_1$$
  
$$= \frac{1}{N} \Big\langle \sum_{i,j=1}^N \delta(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i)) \Big\rangle.$$
 (3.44)

The obtained density-density correlation function  $G(\mathbf{r})$  is proportional to the probability to find a pair of particles separated by the vector  $\mathbf{r}$ . This function also includes self-correlations at  $\mathbf{r} = 0$ , which are always present for any system. To exclude these self-correlations, the pair distribution function  $g(\mathbf{r})$  (PDF) is introduced and used even more often than the density-density correlation function. The PDF is obtained by explicit separation of the terms with i = j from the double sum in Eq. (3.44):

$$G(\mathbf{r}) = \frac{1}{N} \left\langle \sum_{\substack{i,j=1\\i=j}}^{N} \delta(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i)) + \sum_{\substack{i,j=1\\i\neq j}\\N \cdot \sum_{j=2}^{N} \delta(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_i))} \right\rangle$$
(3.45)

$$= \frac{N}{N}\delta(\mathbf{r}) + \frac{N}{N} \Big\langle \sum_{j=2}^{N} \delta(\mathbf{r} - (\mathbf{r}_j - \mathbf{r}_1)) \Big\rangle$$
$$= \delta(\mathbf{r}) + \langle n \rangle \cdot g(\mathbf{r}).$$

Here we evaluated the terms with  $i \neq j$  assuming that on average, the separations between any given  $i^{\text{th}}$  particle are the same, so we instead of calculating the sum over i for every particle, we can calculate this sum just once (for i = 1), and then multiply this result by N.



Fig. 3.8: (a) System of N particles. Each particle is a hard-core disc with radius R. The separation between the particle j = 1 and some other particle for evaluation of the correlation functions is shown. The average amount of particles within the volume  $d\mathbf{r}$  (marked with red rectangle) at the separation  $\mathbf{r}$  from any given particle is  $\langle n \rangle g(\mathbf{r}) d\mathbf{r}$ . (b) Calculated density-density correlation function  $G(\mathbf{r})$ with self-correlations. (c) Calculated pair distribution function  $g(\mathbf{r})$  with excluded selfcorrelations is shown with blue solid line. The peaks of the correlation functions (the most prominent one around 2R) correspond to the highest probability of finding the particles at this separation in a dense system.

From Eq. (3.45) one can obtain the mathematical definition of the PDF  $g(\mathbf{r})$ :

$$g(\mathbf{r}) = \frac{1}{\langle n \rangle} \Big\langle \sum_{j \neq 1}^{N} \delta \big( \mathbf{r} - (\mathbf{r}_{j} - \mathbf{r}_{1}) \big) \Big\rangle.$$
(3.46)

A clear physical meaning has the combination  $\langle n \rangle g(\mathbf{r}) d\mathbf{r}$ , which is an average amount of particles that can be found in the vicinity  $d\mathbf{r}$  at the separation  $\mathbf{r}$  from a given particle excluding self-correlations. The exclusion of selfcorrelation means that  $g(\mathbf{r} \to 0) \to 0$ . At the limit of large distances r, one can expect that the probability to find the particle should not depend on the distance and just be equal to the average concentration of the particles  $\langle n \rangle$ , so  $g(\mathbf{r} \to \infty) \to 1$ . The sketch of the PDF for a liquid is shown in Fig. 3.8.

Let us find now the relation between the structure factor defined in Eq. (3.37) and the density-density correlation function given by Eq. (3.43). In order to do this, let us rewrite the structure factor via integral over delta functions and then change the order of the integration and summation:

$$S(\mathbf{q}) = \left\langle \frac{1}{N} \sum_{i,j=1}^{N} e^{-i\mathbf{q}(\mathbf{r}_{j}-\mathbf{r}_{i})} \right\rangle$$

$$= \left\langle \frac{1}{N} \sum_{i,j=1}^{N} \underbrace{\int e^{-i\mathbf{q}(\mathbf{r}_{1}-\mathbf{r}_{2})} \delta(\mathbf{r}_{1}-\mathbf{r}_{i}) \delta(\mathbf{r}_{2}-\mathbf{r}_{j}) d\mathbf{r}_{1} d\mathbf{r}_{2}}_{e^{-i\mathbf{q}(\mathbf{r}_{j}-\mathbf{r}_{i})}} \right\rangle$$

$$= \int e^{-i\mathbf{q}(\mathbf{r}_{1}-\mathbf{r}_{2})} \underbrace{\left\langle \frac{1}{N} \sum_{i,j=1}^{N} \delta(\mathbf{r}_{1}-\mathbf{r}_{i}) \delta(\mathbf{r}_{2}-\mathbf{r}_{j}) \right\rangle}_{G(\mathbf{r}_{1},\mathbf{r}_{2})} d\mathbf{r}_{1} d\mathbf{r}_{2}$$

$$= \int e^{-i\mathbf{q}(\mathbf{r}_{1}-\mathbf{r}_{2})} G(\mathbf{r}_{1},\mathbf{r}_{2}) d\mathbf{r}_{1} d\mathbf{r}_{2}.$$
(3.47)

This means that the structure factor is just a Fourier transform of the density-density correlation function, as it was claimed in section 3.2.1. For a translationally invariant system (as described by Eq. (3.44)), one should keep the Fourier transform over the difference  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$  and perform the integration over absolute position  $\mathbf{r}_1$ :

$$S(\mathbf{q}) = \int e^{-i\mathbf{q}} \underbrace{\left(\mathbf{r}_{1} - \mathbf{r}_{2}\right)}_{G(\mathbf{r}_{1}, \mathbf{r}_{2})} d\mathbf{r}_{1} d\mathbf{r}_{2}$$
$$= \int e^{-i\mathbf{q}\mathbf{r}} \underbrace{G(\mathbf{r}_{1}, \mathbf{r}_{2})}_{G(\mathbf{r})} d\mathbf{r} \qquad (3.48)$$
$$= \int e^{-i\mathbf{q}\mathbf{r}} G(\mathbf{r}) d\mathbf{r}.$$

Finally, we can write the relation between the structure factor and the number density, which is also broadly used [35]:

$$S(\mathbf{q}) = \frac{1}{N} \langle n(\mathbf{q})n(-\mathbf{q}) \rangle, \text{ where } n(\mathbf{q}) = \int e^{-i\mathbf{q}\mathbf{r}} n(\mathbf{r}) d\mathbf{r}.$$
(3.49)

Substituting Eq. (3.45) into Eq. (3.48), we can obtain the relation between the structure factor  $S(\mathbf{q})$  and the pair distribution function  $g(\mathbf{r})$ :

$$S(\mathbf{q}) = \int e^{-i\mathbf{q}\mathbf{r}} G(\mathbf{r}) d\mathbf{r} = \int e^{-i\mathbf{q}\mathbf{r}} \left(\delta(\mathbf{r}) + \langle n \rangle \cdot g(\mathbf{r})\right) d\mathbf{r} = 1 + \langle n \rangle \int e^{-i\mathbf{q}\mathbf{r}} g(\mathbf{r}) d\mathbf{r}.$$
(3.50)



Fig. 3.9: Calculation of the pair distribution function g(r) (Eq. (3.46)) and the corresponding structure factor S(q) (Eq. (3.51)) for a model 1D system [37]. The system consists of a hard-core discs with the average radius Rdistributed normally with a standard deviation  $\sigma$ . The values of the standard deviation are (a)  $\sigma = 15\%$ , (b)  $\sigma = 25\%$  and (c)  $\sigma = 35\%$ . The PDF q(r) shown with a blue line exhibits peaks at  $r = 2R, 4R, 6R, \ldots$ , and the structure factor S(q) shown with a red line has peaks at  $q = 2\pi/2R, 4\pi/2R, 6\pi/2R, \ldots$  The horizontal dash line indicates the asymptotic behavior  $g(r \to \infty) = 1$  and  $S(q \to \infty) = 1$ . The stronger polydiversity of the discs results in less pronounced peaks of the PDF and the corresponding structure factor.

Although Eq. (3.50) is exact, it is not very useful for numeric computations. The reason for this is the asymptotic behavior of the PDF at large distances,  $g(\mathbf{r}) \rightarrow 1$ , which makes the Fourier integral in Eq. (3.50) to converge very slowly. One can avoid this problem by subtracting and adding unity from the PDF, and therefore ensure the fast convergence of the integral:

$$S(\mathbf{q}) = 1 + \langle n \rangle \int e^{-i\mathbf{q}\mathbf{r}} [g(\mathbf{r}) - 1 + 1] d\mathbf{r}$$
  
= 1 + \langle n \langle \int e^{-i\mathbf{q}\mathbf{r}} [g(\mathbf{r}) - 1] d\mathbf{r} + \langle n \rangle \int e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}  
= 1 + \langle n \langle \int e^{-i\mathbf{q}\mathbf{r}} [g(\mathbf{r}) - 1] d\mathbf{r} + \langle n \langle (2\pi)^3 \delta(\mathbf{q}),  
often neglected (3.51)

where we used  $\int e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} = (2\pi)^3 \delta(\mathbf{q})$ . The first term here (unity) comes from the self-correlation of the particles; the second term (integral of the PDF) arises from the correlation between different particles; and the third term (delta function) comes from the uncorrelated particles. In practice, the last term is sometimes omitted, because it is non-zero only for  $\mathbf{q} = 0$ , which is experimentally is challenging to measure because of the direct beam.

Omitting this term also leads to the symmetry between  $S(\mathbf{q}) - 1$  and  $g(\mathbf{r}) - 1$ , which are now just related via the Fourier transform. In order to show this, one has to multiplying both sides of Eq. (3.51) by  $e^{i\mathbf{qr}'}$  and integrate it over  $\mathbf{q}$ , which leads to

$$g(\mathbf{r}) = 1 + \frac{1}{(2\pi)^3 \langle n \rangle} \int [S(\mathbf{q}) - 1] e^{i\mathbf{q}\mathbf{r}} d\mathbf{q}.$$
 (3.52)

# 3.2.3 Radial distribution function (RDF)

For an isotropic system, the pair distribution function  $g(\mathbf{r})$  (PDF) and the structure factor  $S(\mathbf{q})$  are independent on the direction of vectors  $\mathbf{r}$  and  $\mathbf{q}$ , correspondingly. Therefore, one can introduce the radial distribution function  $g(\mathbf{r})$  (RDF), where the integration over directions of vector  $\mathbf{r}$  is already performed. In spherical coordinates:

$$S(q) = \int S(\mathbf{q}) \sin \theta d\theta d\phi,$$
  

$$g(r) = \int g(\mathbf{r}) \sin \theta d\theta d\phi.$$
(3.53)

The radial distribution function shows the probability of finding a particle at a distance r from any given particle. In other words,  $\langle n \rangle \cdot g(r) \cdot 4\pi r^2 dr$  is the average amount of particles at the distances from r to r + dr separated from any given particle (see Fig. 3.10)

Let us now establish the connection between S(q) and g(r) by explicit calculating of the Fourier integral, for example, in Eq. (3.51), where the term



Fig. 3.10: Definition of the radial distribution function g(r). The combination  $\langle n \rangle \cdot g(r) \cdot 4\pi r^2 dr$  the average amount of particles within the distance [r, r+dr] from any given particle.

proportional to  $\delta(\mathbf{q})$  was omitted:

^

$$S(q) = 1 + \langle n \rangle \int e^{-i\mathbf{q}\mathbf{r}} [g(\mathbf{r}) - 1] d\mathbf{r}$$

$$= 1 + \langle n \rangle \int_{0}^{+\infty} r^{2} dr \int_{0}^{\pi} \underbrace{\sin\theta d\theta}_{2\pi} \int_{0}^{2\pi} d\phi e^{-iqr \cos\theta} [g(r) - 1]$$

$$= 1 + 2\pi \langle n \rangle \int_{0}^{+\infty} [g(r) - 1] r^{2} dr \underbrace{\int_{-1}^{1} e^{-iqr \cdot t} dt}_{2 \cdot \frac{\sin(qr)}{qr}}$$

$$= 1 + \frac{4\pi \langle n \rangle}{q} \int_{0}^{+\infty} [g(r) - 1] \sin(qr) r dr.$$
(3.54)

Performing the same procedure with Eq. (3.52) leads to

$$g(r) = 1 + \frac{1}{2\pi^2 \langle n \rangle r} \int_0^{+\infty} [S(q) - 1] \sin(qr) q dq.$$
(3.55)

# **3.2.4** The structure factor S(q) at $q \rightarrow 0$ (isothermal compressibility)

Let us discuss the asymptotic behavior of the structure factor S(q) at small values of the scattering vector q [38]. We will start the definition of the structure factor given in Eq. (3.49), and assume that the local concentration of the particles  $n(\mathbf{r})$  at any point can be represented as a sum of the average concentration n plus the local fluctiation  $\Delta n(\mathbf{r})$ . Therefore, the structure factor can be written as

$$S(\mathbf{q}) = \frac{1}{N} \langle n(\mathbf{q})n(-\mathbf{q}) \rangle = \frac{1}{N} \int e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \langle n(\mathbf{r}_1)n(\mathbf{r}_2) \rangle d\mathbf{r}_1 d\mathbf{r}_2$$
  

$$= \frac{1}{N} \int e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \langle (n + \Delta n(\mathbf{r}_1))(n + \Delta n(\mathbf{r}_2)) \rangle d\mathbf{r}_1 d\mathbf{r}_2$$
  

$$= \frac{1}{N} \langle n \rangle^2 \underbrace{\int e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2}_{(2\pi)^6 \delta(\mathbf{q})}$$
  

$$+ \frac{1}{N} \langle n \rangle \int e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \left( \underbrace{\langle \Delta n(\mathbf{r}_1) \rangle}_{0} + \underbrace{\langle \Delta n(\mathbf{r}_1) \rangle}_{0} \right) d\mathbf{r}_1 d\mathbf{r}_2$$
  

$$+ \frac{1}{N} \int e^{-i\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2)} \langle \Delta n(\mathbf{r}_1) \Delta n(\mathbf{r}_2) \rangle d\mathbf{r}_1 d\mathbf{r}_2.$$
(3.56)

As it was already done before, we will neglect the first term proportional to  $\delta(\mathbf{q})$  (see section 3.2.2). Furthermore, the cross-terms equal to zero, because the average value of the fluctuation is zero,  $\langle \Delta n \rangle = 0$ . Therefore, leaving only the last term in Eq. (3.56) and assuming that  $\mathbf{q}(\mathbf{r}_1 - \mathbf{r}_2) \to 0$  we obtain

$$S(\mathbf{q} \to 0) = \frac{1}{N} \int \langle \Delta n(\mathbf{r}_1) \Delta n(\mathbf{r}_2) \rangle d\mathbf{r}_1 d\mathbf{r}_2$$
  
=  $\frac{1}{N} \langle \int \Delta n(\mathbf{r}_1) d\mathbf{r}_1 \cdot \int \Delta n(\mathbf{r}_2) d\mathbf{r}_2 \rangle = \frac{\langle \Delta N^2 \rangle}{N},$  (3.57)

where  $\Delta N$  is the total fluctuation of the number of the particles in the system.

For a system with a fixed number of particles, the fluctuation of the total number of particles is zero. However, if we consider only a part of such a system (in a diffraction experiment, we can illuminate only some part of the solution with nanoparticles), the amount of the nanoparticles within the considered volume can be fluctuating. If we assume that the average concentration n = N/V is constant, to a first approximation we can write that the fluctuations of the number of particles is proportional to the fluctuations of the volume:

$$\frac{\Delta N}{N} = \frac{\Delta V}{V},$$

and from that

$$\langle \Delta V^2 \rangle = \frac{V^2}{N^2} \cdot \langle \Delta N^2 \rangle = \frac{\langle \Delta N^2 \rangle}{n^2}.$$
 (3.58)

Using the fact that the average square fluctuations of the volume are proportional to the isothermal compressibility,  $\langle \Delta V^2 \rangle = k_B T \chi_T V$  (see Appendix F), we can write now for the structure factor

$$S(q \to 0) = \frac{n^2 \langle \Delta V^2 \rangle}{N} = \frac{n^2}{N} \cdot k_B T \chi_T V = n \cdot k_B T \cdot \chi_T.$$
(3.59)

Therefore, the structure factor and hence the scattered intensity in the limit of  $q \to 0$  is determined by a thermodynamic parameter, namely, isothermal compressibility  $\chi_T$ . This explains the effect of critical opalescence, when the close to the critical point of the liquid  $\chi_T$  increases leading to stronger scattering at small q (which is small even for large angles for visible light).

It is easy to see, that for non-interacting particles (an ideal gas of particles, for which  $PV = Nk_BT$  and  $\chi_T = 1/P$ ), the structure factor at small values of q approaches unity,  $S(q \to 0) \to 1$ . Including interaction, for example via the Van der Waals equation of state, leads to the fact that  $S(q \to 0) < 1$ . This happens because the interactions between the particles modify their pair distribution function  $g(\mathbf{r})$ , which according to Eq. (3.51) leads to the changes in the structure factor. The connection between the inter-particle interaction and the correlation function will be considered in more details in the next section.

#### 3.2.5 Virial coefficients and Mayer *f*-function

In an ideal gas, the particles do not interact with each other. It means, that the probability to find another particle at any separation  $\mathbf{r}$  from a given one is constant and equal to the average density of the particles in the system  $\langle n \rangle$ . In other words,  $g(\mathbf{r}) \equiv 1$  for an ideal gas. From Eq. (3.51), it immediately follows, that the structure factor of an ideal gas is  $S(\mathbf{q}) \equiv 1$  everywhere outside of the point q = 0. If one could slowly "turn on" the interactions between the particles, one could see how the PDF  $g(\mathbf{r})$  would start to deviate from unity, and accordingly, the structure factor  $S(\mathbf{q})$  would also deviate from unity. The goal of this section is to show, how weak interactions between the particles result in deviations from the ideal gas model, and how these interactions can be experimentally measured in a scattering experiment via considering  $S(q \to 0)$ .

Let us start with a diluted gas (or solution) of weakly interacting particles. The total energy of such a system can be written as a sum of kinetic energy of all particles plus the potential energy of their interactions:

$$E = E_{\rm kin} + U = \sum_{j=1}^{N} \frac{\mathbf{p}_j^2}{2m} + U(\mathbf{r}_1, ..., \mathbf{r}_N), \qquad (3.60)$$

where  $\mathbf{r}_j$  and  $\mathbf{p}_j$  is the position and momentum of  $j^{\text{th}}$  particle. Eventually, we want to calculate the Helmholtz free energy F and pressure P of this system [39]. To do this, let us first evaluate the partition function Z(Zustandssumme):

$$Z = \frac{1}{(2\pi\hbar)^{3N}N!} \int \dots \int d\mathbf{p}_1 \dots d\mathbf{p}_N d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left[-\frac{E}{k_B T}\right].$$
 (3.61)

Here the integration is performed over all coordinates and momenta of the particles in the system.

Using the fact, that the total energy of the system is a sum of kinetic and potential energies, we can represent the partition function as a product of two factors: the first includes integration over momenta and the second over coordinates:

$$Z = \frac{1}{(2\pi\hbar)^{3N}N!} \cdot V^N \cdot \int d\mathbf{p}_1 \dots d\mathbf{p}_N \prod_{j=1}^N \exp\left[-\frac{\mathbf{p}_j^2}{2mk_BT}\right] \cdot \frac{1}{V^N} \cdot \int d\mathbf{r}_1 \dots d\mathbf{r}_N \exp\left[-\frac{U(\mathbf{r}_1, \dots \mathbf{r}_N)}{k_BT}\right].$$
(3.62)

In the case of ideal gas (U = 0), the second multiplier equals to unity. This means, that the first multiplier corresponds to the case of the ideal gas. This term can be easily evaluated, taking into account that it is just a product of 3N Gaussian integrals<sup>10</sup>. Therefore, the second multiplier describes the deviation of the gas from being ideal, which is not a huge surprise, since the potential energy of the interaction between the particles only enters the second factor.

Finally, we can write the partition function of a non-ideal gas as a product

$$Z = Z_{\rm id} \cdot Q, \tag{3.63}$$

where the partition function of an ideal gas  $Z_{id}$  equals to

$$Z_{\rm id} = \frac{V^N}{N!} \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{\frac{3N}{2}},$$
 (3.64)

and the configuration integral Q is

$$Q = \frac{1}{V^N} \cdot \int d\mathbf{r}_1 \dots d\mathbf{r}_N \left[ e^{-\frac{U(\mathbf{r}_1,\dots,\mathbf{r}_N)}{k_B T}} - 1 \right] + 1.$$
(3.65)

Here we subtracted and added unity from the exponential under the integral<sup>11</sup>. This is done to explicitly indicate that the value of the configuration integral Q is unity for an ideal gas (U = 0) and only slightly deviates from unity if the interactions between the particles are weak  $(U \approx 0)$ .

Let us now estimate, how a weak interaction potential between the particles would affect the value of the configuration integral. First, let us assume that only pair interactions exist in the system, i.e.  $U(\mathbf{r}_1, ... \mathbf{r}_N) =$ 

$$\int_{-\infty}^{+\infty} \exp\left[\frac{-p^2}{2mk_BT}\right] dp = \sqrt{\pi \cdot 2mk_BT}$$

 $^{11}\mathrm{Note}$  that

$$\frac{1}{V^N} \cdot \int d\mathbf{r}_1 ... d\mathbf{r}_N = \frac{V^N}{V^N} = 1$$

<sup>&</sup>lt;sup>10</sup>Note that

 $\sum_{i>j}^{N} u(\mathbf{r}_i, \mathbf{r}_j)$ , where  $u(\mathbf{r}_i, \mathbf{r}_j)$  describes the pair interaction between the  $i^{\text{th}}$  and  $j^{\text{th}}$  particles. Even under this assumption, the computation of the integral (3.65) is an extremely complex problem which includes consideration of non-direct interactions between the particles [39, 40, 41] (also see section 3.2.7 for a short summary of the Ornstein-Zernike theory).

We will make another assumption and consider a diluted system, in which the probability of three particles to be close enough to interact with each other (pairwise) is negligible. To introduce this assumption mathematically, it is convenient to introduce so-called Mayer f-function as

$$f_{ij} = e^{-\frac{u(\mathbf{r}_i, \mathbf{r}_j)}{k_B T}} - 1.$$
(3.66)

The Mayer f-function  $f_{ij}$  is non-zero only if the  $i^{\text{th}}$  and  $j^{\text{th}}$  particles are close enough, so the interaction potential between them is zero. If the particles are far apart from each other, the interaction potential is zero  $u(\mathbf{r}_i, \mathbf{r}_j) = 0$ , and consequently the Mayer f-function is also zero  $f_{ij} = 0$ .

Now we can split the total potential energy of the system into pair interactions of  $N(N-1)/2 \approx N^2/2$  pairs of particles and write

$$\exp\left[-\frac{U(\mathbf{r}_1,...,\mathbf{r}_N)}{k_BT}\right] = \exp\left[-\frac{1}{k_BT}\sum_{i>j}^N u(\mathbf{r}_i,\mathbf{r}_j)\right]$$

$$=\prod_{i>j}^N \exp\left[-\frac{u(\mathbf{r}_i,\mathbf{r}_j)}{k_BT}\right] = \prod_{i>j}^N (1+f_{ij}).$$
(3.67)

In this product, it is sufficient to take into account only linear terms. Indeed, for example, the quadratic term  $f_{12}f_{13}$  will be non-zero only if the particle "1" is surrounded by two other particles "2" and "3", so that  $f_{12} \neq 0$  and  $f_{13} \neq 0$ . But we have already assumed that the system is so diluted, that three particles can not be simultaneously so close to each other. Therefore, for a diluted system we can assume

$$\exp\left[-\frac{U(\mathbf{r}_1,...,\mathbf{r}_N)}{k_BT}\right] = \prod_{i>j}^N (1+f_{ij}) = 1 + \sum_{i>j}^N f_{ij}.$$
 (3.68)

The number of terms in the sum (3.68) equals to the number of pairs in the system,  $N^2/2$ . Since we are going to integrate over all possible positions of the particles in Eq. (3.65), the integral over each pair will be the same. Therefore, we can evaluate this integral for any selected two particles (for example, "1" and "2") and then multiply the result by total amount of pairs  $N^2/2$ :

$$\int d\mathbf{r}_{1}...d\mathbf{r}_{N} \left[ e^{-\frac{U(\mathbf{r}_{1},...\mathbf{r}_{N})}{k_{B}T}} - 1 \right] \approx \int d\mathbf{r}_{1}...d\mathbf{r}_{N} \left[ 1 + \frac{N^{2}}{2} f_{12} - 1 \right]$$

$$= \frac{N^{2}}{2} \cdot V^{N-2} \int f_{12} d\mathbf{r}_{1} d\mathbf{r}_{2}.$$
(3.69)

If we now assume that the interaction potential  $u(\mathbf{r}_1, \mathbf{r}_2)$  depends only on separation between two particles  $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$ , we can also evaluate one more integral in Eq. (3.69) which will give the volume of the system V. Finally, we can write

$$\int d\mathbf{r}_1 \dots d\mathbf{r}_N \left[ e^{-\frac{U(\mathbf{r}_1,\dots\mathbf{r}_N)}{k_B T}} - 1 \right] \approx \frac{N^2}{2} \cdot V^{N-1} \int f(\mathbf{r}) d\mathbf{r} = -N^2 \cdot V^{N-1} \cdot B_2(T),$$
(3.70)

where we introduced so-called second virial coefficient  $B_2(T)$  (note the sign convention)

$$B_2(T) = -\frac{1}{2} \int f(\mathbf{r}) d\mathbf{r} = \frac{1}{2} \int \left[ 1 - e^{-\frac{u(\mathbf{r})}{k_B T}} \right] d\mathbf{r}.$$
 (3.71)

This temperature-dependent coefficient is non-zero when the direct pair interaction between two particles  $u(\mathbf{r})$  is non-zero.

The non-zero value of the second virial coefficient  $B_2(T)$  is our first approximation to which the interaction between the particles can be considered. It is instructive to evaluate the second virial coefficient  $B_2(T)$  for some simple systems, which will be done in the section 3.2.6.

Now we can finally return back to the configuration integral given by Eq. (3.65) and write

$$Q = \frac{1}{V^N} \cdot -N^2 V^{N-1} B_2(T) + 1 = 1 - \frac{N^2}{V} B_2(T).$$
(3.72)

Using the Taylor expansion  $\ln(1-x) \approx -x$  for  $x \ll 1$ , we can evaluate the Helmholtz energy of the system of weakly interacting particles:

$$F = -k_B T \ln Z = \underbrace{-k_B T \ln Z_{id}}_{F_{id}} - k_B T \ln Q = F_{id} + \frac{N^2}{V} k_B T B_2(T), \quad (3.73)$$

where  $F_{id}$  is the Helmholtz energy of the ideal gas. The pressure can be now easily evaluated as

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T} = -\left(\frac{\partial F_{\rm id}}{\partial V}\right)_{T} - Nk_{B}T \cdot \frac{-N}{V^{2}}B_{2}(T)$$
$$= \frac{Nk_{B}T}{V} + nk_{B}T \cdot \frac{N}{V}B_{2}(T)$$
$$= \frac{Nk_{B}T}{V}(1 + nB_{2}(T)), \qquad (3.74)$$

where we used the pressure of the ideal gas  $P_{\rm id} = -\left(\frac{\partial F_{\rm id}}{\partial V}\right)_T = \frac{Nk_BT}{V}$ .

Here we see that the correction term to pressure that we have just evaluated is proportional to the density n. The same applies to the correction to the free energy in Eq. (3.73). In principle, it is possible to evaluate the next correction terms and write the pressure of a non-ideal gas as a power series of density n:

$$P = \frac{Nk_BT}{V} \sum_{m=1}^{+\infty} B_m(T) n^{m-1}.$$
 (3.75)

This series is called the virial expansion and the coefficients  $B_m$  - the virial coefficients. The first term of this series corresponds to the ideal gas (no interactions), so  $B_1 = 1$ . The second term with the second virial coefficient  $B_2(T)$  defined in Eq. (3.71) we just have evaluated. In practice, the third term is sometimes also included.

Knowing the virial coefficients is important, because they describe the deviation of a system from ideal gas and they depend on pair interactions between the particles. The virial coefficients, and particularly  $B_2(T)$  can be experimentally measured in a scattering experiment by considering the scattering form factor  $S(q \to 0)$ .

In section 3.2.4, we have shown that  $S(q \to 0) = n \cdot k_B T \cdot \chi_T$ . Let us now explicitly evaluate the isothermal compressibility  $\chi_T$  using the virial expansion (3.75). First,

$$\left(\frac{\partial P}{\partial V}\right)_T = k_B T \sum_{m=1}^{+\infty} B_m(T) \frac{\partial}{\partial V} \left(\frac{N^m}{V^m}\right) = -\frac{k_B T}{V} \sum_{m=1}^{+\infty} B_m(T) m \frac{N^m}{V^m}.$$
 (3.76)

Then, using the definition of the isothermal compressibility,

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T = -\frac{1}{V} \cdot \frac{1}{\left(\frac{\partial P}{\partial V}\right)_T} = \frac{1}{k_B T (B_1 n + 2B_2 n^2 + 3B_3 n^3 + ...)}$$
$$\approx \frac{1}{n k_B T} \cdot \frac{1}{1 + 2n B_2(T)},$$
(3.77)

where we kept only the second virial coefficient. This immediately gives us the asymptotic behavior of the structure factor (see Eq. (3.59))

$$S(q \to 0) = n \cdot k_B T \cdot \chi_T = \frac{1}{1 + 2nB_2(T)}.$$
(3.78)

In practice, one would measure the scattered intensity  $I(q \to 0) \propto n/(1 + 2nB_2(T))$  for different concentrations n of particles in the solution. By fitting this dependence, one can obtain the value of the second virial coefficient  $B_2(T)$ .

#### **3.2.6** Model inter-particle interaction potential u(r)

Partition functions and pair distribution function provide us two alternative approaches for the statistical description of the systems [39]. While the partition function formalism is founded on a solid theoretical basis and therefore is used to describe simple systems, this approach becomes too complicated in the case of a real dense system of strongly interacting particles. Contrary to that, the pair distribution function allow one to consider dense systems with reasonable accuracy. For example, the total average potential energy of N nanoparticles interacting with each other via potential  $u(\mathbf{r})$  will be

$$\langle U \rangle = \frac{1}{2} \Big\langle \sum_{\substack{i,j=1\\i \neq j}}^{N} u(\mathbf{r}_i - \mathbf{r}_j) \Big\rangle$$

$$= \frac{1}{2} \int u(\mathbf{r}_i - \mathbf{r}_j) \Big\langle \sum_{\substack{i,j=1\\i \neq j}}^{N} \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \Big\rangle d\mathbf{r}_1 d\mathbf{r}_2$$

$$= \frac{N \langle n \rangle}{2} \int u(\mathbf{r}) g(\mathbf{r}) d\mathbf{r},$$

$$(3.79)$$

where we used the definition of the PDF  $g(\mathbf{r})$  from Eq. (3.45).

Moreover, pair distribution functions can be measured experimentally by elastic scattering as we have seen in this chapter. Finally, the formalism of correlation functions (such as PDF) works even for the non-equilibrium systems, for which the partition function Z can not be defined.

In order to fully connect the microscopic interactions between the individual nanoparticles and the resulting pair distribution function, let us first consider the case of a dilute system, so only the pair interactions need to be taken into account. In this case, the distance between particles is distributed according to the Boltzmann statistics, which would lead to the following approximation for the PDF:

$$g(\mathbf{r}) \approx \exp\left[-\frac{u(\mathbf{r})}{k_B T}\right].$$
 (3.80)

One can use different models for the potential u(r), and below we will list a few most common ones (Fig. 3.11):

• Hard spheres of diameter D

$$u(r) = \begin{cases} \infty , & \text{for } r \le D, \\ 0 , & \text{for } r > D. \end{cases}$$
(3.81)

• Sticky hard spheres

$$u(r) = \begin{cases} \infty , & \text{for } r \le D, \\ -U_0 , & \text{for } D < r \le D + \Delta, \\ 0 , & \text{for } r > D. \end{cases}$$
(3.82)

• Hard spheres with weak attraction

$$u(r) = \begin{cases} \infty, & \text{for } r \leq D, \\ -U_0 \left(\frac{D}{r}\right)^m, & \text{for } r > D. \end{cases}$$
(3.83)

• Hard spheres with screened Coulomb interaction

$$u(r) = \begin{cases} \infty , & \text{for } r \leq D, \\ \frac{Z^2 e^2}{\epsilon \left(1 + \frac{\kappa_D D}{2}\right)^2} \cdot \frac{\exp[-\kappa_D (r-D)]}{r} , & \text{for } r > D. \end{cases}$$
(3.84)

• Lennard-Jones potential

$$u(r) = 4U_0 \left[ \left(\frac{D}{r}\right)^{12} - \left(\frac{D}{r}\right)^6 \right]$$
(3.85)

The corresponding PDFs g(r) calculated using Eq. (3.80) are shown in Fig. 3.12.

Finally, let us calculate the second virial coefficient  $B_2$  for some interaction potentials using the definitions in Eqs. (3.71-3.66). Thus, for the hard spheres, the Mayer f-function is

$$f(r) = \exp\left[-\frac{u(r)}{k_B T}\right] - 1 = \begin{cases} -1 , & \text{for } r \le D, \\ 0 , & \text{for } r > D. \end{cases}$$
(3.86)

Therefore, the second virial coefficient  $B_2^{HS}$  is

$$B_2^{HS} = -\frac{1}{2} \int f(r) d\mathbf{r} = \frac{4\pi}{2} \int_0^D r^2 dr = 4 \cdot \frac{4\pi}{3} \left(\frac{D}{2}\right)^3, \qquad (3.87)$$

meaning that the second virial coefficient is simply four times the volume of the sphere. Its positive value is a characteristic feature of any repulsive potential. In the particular case of hard spheres, the second virial coefficient does not depend on temperature.



Fig. 3.11: Potentials u(r) of interaction between two particles for different models given by Eqs. (3.81-3.85): (a) hard spheres, (b) sticky hard spheres. (c) hard spheres with weak attraction, (d) hard spheres with screened Coulomb interaction, (e) Lennard-Jones potential.



Fig. 3.12: The model pair distribution function g(r) calculated with Eq. (3.80) for the potentials given by Eqs. (3.81-3.85).

One can also analytically calculate  $B_2(T)$  for the Lennard-Jones potential. Omitting the evaluation, we will just write the result:

$$B_2^{LJ}(T) = \frac{2\pi}{3} D^3 \left[ \left( \frac{4U_0}{k_B T} \right)^{\frac{1}{4}} \Gamma\left( \frac{3}{4} \right) - \left( \frac{4U_0}{k_B T} \right)^{\frac{1}{2}} \Gamma\left( \frac{1}{2} \right) \right], \qquad (3.88)$$

where  $\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$  is Euler's gamma-function. In this case, the second virial coefficient  $B_2(T)$  depends on temperature (Fig. 3.13). Moreover, it is negative for low temperatures and positive for high temperatures.

This means that at low temperatures, the attraction between the particles is dominating. At high temperatures, the kinetic energy of particles is so high that the weak attraction potential at large distances does not play a role, and the particles behave similar to the hard spheres. The temperature, at which the second virial coefficient  $B_2(T)$  changes its sign is called the Boyle temperature.

# 3.2.7 Ornstein-Zernike equation

In a dense system, each particle is influenced by many neighbors. Therefore, the correlation function is determined by the potential of mean force w(r), which includes indirect interactions between several particles:

$$g(\mathbf{r}) = \exp\left[-\frac{w(\mathbf{r})}{k_B T}\right].$$
(3.89)

But the mean force potential w(r), in turn, depends on distribution of particles, i.e. the pair distribution function  $g(\mathbf{r})$ . It is possible to construct an integral equation for the pair distribution function, known as Ornstein-Zernike equation [40]. To write down this equation, let us introduce two new correlation functions:

- h(r) = g(r) 1 total correlation function, which is determined by the potential of mean force, and therefore describes the real correlation in the system;
- $c(\mathbf{r})$  direct correlation function, which is determined exclusively by pair interactions  $u(\mathbf{r})$  between two particles.

Then, the Ornstein-Zernike equation can be written (without derivation)

$$h(\mathbf{r}_{12}) = c(\mathbf{r}_{12}) + \langle n \rangle \int c(\mathbf{r}_{13}) h(\mathbf{r}_{23}) d\mathbf{r}_3.$$
(3.90)

Here  $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$  denotes the relative position of two particles. The Ornstein-Zernike equation states that the correlation between two particles are determined by the direct correlations between these two particles plus indirect correlations via a third particle (Fig. 3.14). In the case of a dilute system  $\langle n \rangle \rightarrow 0$ ,  $h(\mathbf{r}_{12}) = c(\mathbf{r}_{12})$ , i.e. the correlations between particles are determined only by direct pair interactions between them.

If the direct correlation function  $c(\mathbf{r})$  is known, the Ornstein-Zernike equation can be solved recursively:

$$h(\mathbf{r}_{12}) = \underbrace{c(\mathbf{r}_{12})}_{\text{direct interaction}} + \underbrace{\langle n \rangle \int d\mathbf{r}_3 c(\mathbf{r}_{13}) c(\mathbf{r}_{23})}_{\text{inderect interaction via an intermediate particle}}$$
(3.91)  
$$+ \langle n \rangle^2 \int \int c(\mathbf{r}_{13}) d\mathbf{r}_3 \int d\mathbf{r}_4 c(\mathbf{r}_{24}) c(\mathbf{r}_{34}) + \dots,$$

inderect interaction via two intermediate particles



Fig. 3.13: Sketch of the temperature dependence of the second virial coefficient  $B_2^{LJ}(T)$  for the Lennard-Jonnes potential given by Eq. (3.88).



Fig. 3.14: Illustration to the Ornstein-Zernike equation (3.90). The correlation between two particles are determined by direct interaction between these two particles and the indirect interactions via a third particle.



Fig. 3.15: Graphical illustration for the recursive terms in Eq. (3.91).

as illustrated by Fig. 3.15.

Another approach to the Ornstein-Zernike equation is to consider it in reciprocal space. To do this, let us rewrite Eq. (3.90):

$$h(\mathbf{r}_{12}) = c(\mathbf{r}_{12}) + \langle n \rangle \int c(\mathbf{r}_{13})h(\mathbf{r}_{23})d\underbrace{(\mathbf{r}_3 - \mathbf{r}_2)}_{-\mathbf{r}_{23}}$$
$$= c(\mathbf{r}_{12}) + \langle n \rangle \int c(\mathbf{r}_{12} + \mathbf{r}_{23})h(\mathbf{r}_{23})d(-\mathbf{r}_{23}).$$

Now, denoting  $\mathbf{r}_{12} = \mathbf{r}$ ,  $-\mathbf{r}_{23} = \mathbf{r}'$ , and using  $h(-\mathbf{r}') = h(\mathbf{r}')$ , we can write the Ornstein-Zernike equation as a convolution:

$$h(\mathbf{r}) = c(\mathbf{r}) + \langle n \rangle \int c(\mathbf{r} - \mathbf{r}')h(\mathbf{r}')d\mathbf{r}'.$$
(3.92)

Using the convolution theorem, the Fourier transforms  $h(\mathbf{q})$  and  $c(\mathbf{q})$  of the correlation functions  $h(\mathbf{r})$  and  $c(\mathbf{r})$  are related to each other in a much less complicated way:

$$h(\mathbf{q}) = c(\mathbf{q}) + \langle n \rangle \cdot c(\mathbf{q}) \cdot h(\mathbf{q}).$$
(3.93)

Since  $S(\mathbf{q}) = 1 + \langle n \rangle h(\mathbf{q})$  (Eq. (3.51)), the structure factor  $S(\mathbf{q})$  is determined by the Fourier transform of the direct correlation function:

$$S(\mathbf{q}) = \frac{1}{1 - \langle n \rangle \cdot c(\mathbf{q})}.$$
(3.94)

This allows us to estimate the shape of the structure factor peak. Indeed, if the system has some periodicity (or characteristic distance), the Fourier transform of a direct correlation function c(q) will have a peak at some value  $q_0$ . In the vicinity of this maximum, we can approximate c(q) with the Taylor series,  $c(q) \approx c(q_0) + c'(q_0) \cdot \frac{1}{2}(q-q_0)^2$ . This will lead to the Lorentzian shape of the structure factor:

$$S(q \sim q_0) \propto \frac{1}{\xi^{-2} + (q - q_0)^2},$$
 (3.95)

where  $\xi$  is the correlation length. This can be illustrated by Fig. 3.9, where the peak of the structure factor has Lorentzian shape, and its width is inversely proportional to the correlation length in the system.

# 3.2.8 Closure relations

The Ornstein-Zernike equation (3.90) is exact, but it can not be solved because it contains two unknown functions, the direct correlation function  $c(\mathbf{r})$  and the total correlation function  $h(\mathbf{r}) = g(\mathbf{r}) - 1$ . To be able to find the correlation functions, one needs to have another equation, which would be a reasonable assumption about  $c(\mathbf{r})$  or a connection between  $h(\mathbf{r})$  and  $c(\mathbf{r})$ . These additional relations are called closure relations, and there are many different forms of closure relations. Here we will give just two examples:

• Mean-spherical approximation (MSA)

At low densities of the particles, we can assume that  $c(r) \approx h(r) = g(r) - 1 = \exp[-u(r)/k_BT] - 1$ . For  $r \to \infty$ , the pair interactions between the particles go to zero,  $u(r) \to 0$ , so we can use Taylor expansion

$$c(r) \approx -\frac{1}{k_B T} \cdot u(r). \tag{3.96}$$

In the MSA approximation, this behavior extends to all distances.

• Percus-Yevick approximation (PY)

Let us rewrite Eq. (3.92) using the PDF g(r):

$$g(r) - 1 = c(r) + \langle n \rangle \int c(r') [g(|\mathbf{r} - \mathbf{r}'|) - 1] d\mathbf{r}',$$
  
$$c(r) = g(r) - \underbrace{\left\{ 1 + \langle n \rangle \int c(r') [g(|\mathbf{r} - \mathbf{r}'|) - 1] d\mathbf{r}' \right\}}_{g_{ind}(r)} = g(r) - g_{ind}(r).$$

Here we introduced the indirect part of the pair correlation function. Since  $g(r) = \exp\left[-w(r)/k_BT\right]$  (Eq. (3.89)), we can assume that the indirect part of the correlation function has the same form, the potential of mean force w(r) should be replaced by the difference w(r) - u(r):  $g_{ind}(r) \approx \exp\left[-(w(r) - u(r))/k_BT\right]$ . Using this approximation, the direct correlation can be calculated as

$$c(r) = g(r) - g_{ind}(r) \approx \exp\left[-\frac{w(r)}{k_B T}\right] - \exp\left[-\frac{w(r) - u(r)}{k_B T}\right]$$
$$= \exp\left[-\frac{w(r)}{k_B T}\right] \cdot \left(1 - \exp\left[\frac{u(r)}{k_B T}\right]\right)$$
$$= g(r) \cdot \left(1 - \exp\left[\frac{u(r)}{k_B T}\right]\right).$$
(3.97)

This is the PY closure equation, which works quite well for the short-ranged potentials.

# 4 Inelastic neutron scattering

In this section, we will continue discussing the scattering from an ensemble of atoms or nanoparticles (see section 3.2.1). Now we will consider inelastic scattering, which will naturally lead us to the generalized time-dependent van Hove correlation function (time-independent correlation functions relevant for elastic scattering were considered in sections ?? and 3.2.3).

Inelastic scattering means that the particle (X-ray photon or neutron) exchanges energy with the system which scatters the wave. This means, that the systems changes its state and the obtain or loose some energy  $\Delta E$ , which is transferred to the X-ray photon or neutron. In condensed matter, this energy  $\Delta E$  is usually related to a certain excitation, such as phonon or magnon, and its magnitude is rarely exceeding a few eVs (a characteristic energy at room temperature is actually much smaller,  $k_B T \approx 0.025$  eV). Such a small energy change can be neglected in many cases when we consider X-ray scattering of the photons with the initial energy  $E \sim 10$  keV ( $\Delta E/E \sim 10^{-6}$ ). It is quite difficult to measure such a small change in the X-ray photon energy, so the inelastic X-ray scattering is a challenging technique, which requires extremely good energy resolution. In contrast, the energy of a neutron with a wavelength  $\lambda \sim 1$  Å is of the order of  $10^{-1}$  eV (Eq. 1.2), which means that  $\Delta E/E \sim 0.3$ . This is already a significant change of the neutron's energy which can be relatively easy detected. Therefore, inelastic scattering is much more common effect when neutron scattering is considered.

For the sake of simplicity, in the following text, we will consider inelastic scattering of neutrons on a systems consisting of N nuclei. The obtained results can be transferred to inelastic neutron scattering on other systems (molecules, nanoparticles etc.) or to the inelastic X-ray scattering.

#### 4.1 Nuclear neutron scattering by an ensemble of atoms

Let us consider a system of N atoms which scatter the incident plane monochromatic wave of neutrons. The positions of the atoms are given by radius vectors  $\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N$ , which we will simply denote as  $\mathbf{R}$ . The positions of the atoms are not fixed, and the probability to find the atoms at certain positions  $\mathbf{R}$  is determined by the wave function of the system  $\chi(\mathbf{R}_1, \mathbf{R}_2, \ldots, \mathbf{R}_N) = \chi(\mathbf{R})$ . Since we only consider scattering by nuclei with a very short-range nuclear potential (see section 1.2.1), the interaction between the neutrons and the atoms can be written as

$$\hat{V}(\mathbf{R},\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} \sum_{n=1}^N b_j \delta(\mathbf{R}_n - \mathbf{r}), \qquad (4.1)$$

where  $m_n$  is the neutron mass,  $b_n$  is the neutron scattering length (see Eq. (1.42 and the text before it), and **r** is the position of the neutron.

The wave function of the incident neutrons can be written as a plane monochromatic wave with a wave vector  $\mathbf{k}_{in}$ :

$$\psi_{in}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_{in}\mathbf{r}}.$$
(4.2)

Here we used so-called "box normalization" and consider only some space with the volume  $V \to \infty$  around the system of atoms. This will make calculations easier, and the result will be independent of V.

The neutrons will be scattered in all directions (see Eq. (1.40)), but we will only consider those with a wave vector  $\mathbf{k}_{out}$ , i.e. described by the wave function:

$$\psi_{out}(\mathbf{r}) = \frac{1}{\sqrt{V}} e^{i\mathbf{k}_{out}\mathbf{r}}.$$
(4.3)



Fig. 4.1: Inelastic neutron scattering by an ensemble of N atoms.

In other words, we consider the scattering problem in the first Born approximation (see sections 2.7.1 and 2.7.2). Note, that here the energy of a neutron is not conserved, so  $|\mathbf{k}_{in}| \neq |\mathbf{k}_{out}|$ . The scheme of the scattering problem is shown in Fig. 4.1.

#### 4.1.1 Double-differential scattering cross-section

Similar to Eq. (1.6), we will define double-differential cross-section

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{I_{sc}}{\Phi_0 \cdot d\Omega dE'},\tag{4.4}$$

where  $I_{sc}$  is a flux of the photons (photons per second) scattered into a solid angle  $d\Omega$  with the energy within the range from E' to E' + dE and  $\Phi_0$  is the density of the incoming flux (photons per second per square meter). In a real experiment, one would directly measure  $I_{sc}$ , and the defined doubledifferential cross-section is just a normalized value of it.

Using Eq. (4.2), we can immediately calculate the incoming flux as a product of neutron velocity and their density:

$$\Phi_0 = \frac{\hbar k_{in}}{m_n} \cdot |\psi_{in}|^2 = \frac{\hbar k_{in}}{m_n V}.$$
(4.5)

Another step, which we will need in the next section, is to calculate the number of neutron states  $dN_k$ , for which the wave vector lies in a solid angle  $d\Omega$  and has an absolute value between  $k_{out}$  and  $k_{out} + dk$  (corresponding to the energy range from E' to E' + dE). It is known [42], that a single neutron state occupies the volume  $V_k = \frac{(2\pi)^3}{V}$  in reciprocal space. Therefore, the number of neutron states will be just the volume of the cylinder shown in Fig. 4.2, divided by  $V_k$ :

$$dN_k = \rho_k \cdot dk = \frac{k_{out}^2 d\Omega dk}{V_k} = \frac{V}{(2\pi)^3} \cdot k_{out}^2 d\Omega dk,$$
(4.6)

where  $\rho_k$  is the density of states in reciprocal space. The range dk can be found from the neutron dispersion  $E = \frac{\hbar^2 k^2}{2m_n}$  as

$$dk = \frac{m_n}{\hbar^2 k_{out}} dE'. \tag{4.7}$$

Combining Eqs. (4.6) and (4.7) gives

$$dN_k = \frac{V}{(2\pi)^3} \cdot \frac{m_n k_{out}}{\hbar^2} \cdot d\Omega dE'.$$
(4.8)

# 4.1.2 Fermi's golden rule

Fermi's golden rule allows one to calculate the transition probability per unit of time for a system to change its state from  $|i\rangle$  to  $|f\rangle$  as a result of some small perturbation  $\hat{V}$ :

$$\Gamma_{i \to f} = \frac{2\pi}{\hbar} \left| \left\langle f \right| \hat{V} \left| i \right\rangle \right|^2 \rho(E_f), \tag{4.9}$$

where  $\rho(E_f)$  is the density of final states.

In our case, we can use Fermi's golden rule to evaluate  $I_{sc}$  in Eq. (4.4). Let us assume that the neutron interacts with the system via interaction potential  $\hat{V}$  (Eq. 4.1), so it changes its wave vector from  $\mathbf{k}_{in}$  to  $\mathbf{k}_{out}$ , and the system changes its state from  $|\nu\rangle$  to  $|\nu'\rangle$ . In this case,

$$I_{sc} = \frac{2\pi}{\hbar} \left| M_{\nu\nu'} \right|^2 dN_k, \qquad (4.10)$$



Fig. 4.2: Definition of the double-differential scattering cross-section

where the corresponding matrix element is

$$M_{\nu\nu'} = \int \chi^*_{\nu'}(\mathbf{R}) \psi^*_{out}(\mathbf{r}) \cdot \hat{V}(\mathbf{R}, \mathbf{r}) \cdot \psi_{in}(\mathbf{r}) \chi_{\nu}(\mathbf{R}) d\mathbf{R} d\mathbf{r}.$$
 (4.11)

Using Eqs. (4.1-4.3), this matrix element can be further simplified

$$M_{\nu\nu\nu'} = \frac{1}{V} \frac{2\pi\hbar^2}{m_n} \sum_{n=1}^N b_n \int \chi^*_{\nu'}(\mathbf{R}) e^{-i\mathbf{k}_{out}\mathbf{r}} \cdot \delta(\mathbf{R}_j - \mathbf{r}) \cdot e^{i\mathbf{k}_{in}\mathbf{r}} \chi_{\nu}(\mathbf{R}) d\mathbf{R} d\mathbf{r}$$
$$= \frac{1}{V} \frac{2\pi\hbar^2}{m_n} \sum_{n=1}^N b_n \int \chi^*_{\nu'}(\mathbf{R}) \cdot e^{-i\mathbf{q}\mathbf{R}_n} \cdot \chi_{\nu}(\mathbf{R}) d\mathbf{R}.$$
(4.12)

Finally, combining Eqs. (4.4), (4.5), (4.8), (4.10), and (4.12), we obtain the following double-differential scattering cross-section

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\nu\nu'} = \frac{k_{out}}{k_{in}} \cdot \left|\sum_{n=1}^N b_n \int \chi_{\nu'}^*(\mathbf{R}) \cdot e^{-i\mathbf{q}\mathbf{R}_n} \cdot \chi_{\nu}(\mathbf{R}) d\mathbf{R}\right|^2 = \frac{k_{out}}{k_{in}} \cdot \left|\sum_{n=1}^N b_n \left\langle \nu' \right| e^{-i\mathbf{q}\mathbf{R}_n} \left|\nu\right\rangle\right|^2.$$
(4.13)

Here the prefactor  $k_{out}/k_{in}$  is a result of the normalization of neutron flux. The matrix element  $\langle \nu' | e^{-i\mathbf{q}\mathbf{R}_n} | \nu \rangle$  corresponds to the wave function of the neutrons scattered by the  $n^{\mathrm{th}}$  nucleus. Therefore the whole equation describes the interference of neutrons scattered by different nuclei.

So far we have calculated the probability of a transition from  $|\nu\rangle$  to  $|\nu'\rangle$ , but we have not discussed if this transition is possible at all. In the case of neutron scattering, the total energy of the system and the neutron should be conserved

$$E_{\nu} + E = E_{\nu'} + E', \qquad (4.14)$$

where  $E_{\nu}$  is the energy of the system in the initial state  $|\nu\rangle$ ,  $E_{\nu'}$  is the energy of the system in the final state  $|\nu'\rangle$ ,  $E = \hbar^2 k_{in}^2/2m_n$  is the energy of the incident neutron and  $E' = \hbar^2 k_{out}^2/2m_n$  is the energy of the scattered neutron. If the condition given by Eq. (4.14) is not fulfilled, the corresponding double-differential cross-section should be zero.

Mathematically, this can be written by multiplying the probability of the transition by the Dirac delta function, for example, already in Fermi's golden rule (4.9). We will do this now, so the final expression for the doubledifferential scattering cross-section is

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\nu\nu'} = \frac{k_{out}}{k_{in}} \cdot \left|\sum_{n=1}^N b_n \left\langle \nu' \right| e^{-i\mathbf{q}\mathbf{R}_n} \left|\nu\right\rangle \right|^2 \delta(E_\nu - E_{\nu'} + E - E').$$
(4.15)

In this way, we can formally consider any possible transitions of the system between any possible states  $|\nu\rangle$  and  $|\nu'\rangle$  while the wave vector of neutron is changed from  $\mathbf{k}_{in}$  to  $\mathbf{k}_{out}$ . But if the total energy in such a transition is not conserved, the corresponding double-differential cross section (4.15) will be zero, because of the delta function.

Finally, denoting  $\hbar\omega = E' - E$  as the change in the neutron energy, we can use the integral representation of delta function (see Appendix A) and write<sup>12</sup>

$$\delta(E_{\nu} - E_{\nu'} + \underbrace{E - E'}_{-\hbar\omega}) = \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} e^{-\frac{i}{\hbar}(E_{\nu'} - E_{\nu})t} e^{i\omega t} dt.$$
(4.16)

<sup>&</sup>lt;sup>12</sup>Here we used the property  $\delta(\alpha x) = |\alpha|^{-1} \delta(x)$ 

This trick, which might look artificial here, will play an important role in the following text, where we will establish a connection between the neutron energy gain  $\hbar\omega$  and the evolution of the system in time.

Substituting Eq. (4.16) into Eq. (4.15) and writing the modulus squared as a double sum, we obtain<sup>13</sup>

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\nu\nu'} = \frac{k_{out}}{k_{in}} \sum_{m,n=1}^N b_m^* b_n \left\langle \nu \right| e^{i\mathbf{q}\mathbf{R}_m} \left|\nu'\right\rangle \left\langle \nu'\right| e^{-i\mathbf{q}\mathbf{R}_n} \left|\nu\right\rangle \times \\ \times \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} e^{-\frac{i}{\hbar}(E_{\nu'} - E_{\nu})t} e^{i\omega t} dt.$$
(4.17)

Changing the order of summation and integration

$$\left(\frac{\partial^{2}\sigma}{\partial\Omega\partial E'}\right)_{\nu\nu'} = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \sum_{m,n=1}^{N} b_{m}^{*} b_{n} \left\langle\nu\right| e^{i\mathbf{q}\mathbf{R}_{m}} \left|\nu\right\rangle \times \\ \times \underbrace{e^{\frac{i}{\hbar}E_{\nu'}t} \left\langle\nu'\right| e^{-i\mathbf{q}\mathbf{R}_{n}} \left|\nu\right\rangle e^{-\frac{i}{\hbar}E_{\nu}t}}_{\left\langle\nu'\right| e^{\frac{i}{\hbar}\hat{H}t} e^{-i\mathbf{q}\mathbf{R}_{n}} e^{-\frac{i}{\hbar}\hat{H}t} \left|\nu\right\rangle} \cdot e^{i\omega t} dt,$$

$$(4.18)$$

where we used the result

$$e^{\frac{i}{\hbar}E_{\nu'}t}\left\langle\nu'\right|e^{-i\mathbf{q}\mathbf{R}_{n}}\left|\nu\right\rangle e^{-\frac{i}{\hbar}E_{\nu}t} = \left\langle\nu'\right|e^{\frac{i}{\hbar}\hat{H}t}e^{-i\mathbf{q}\mathbf{R}_{n}}e^{-\frac{i}{\hbar}\hat{H}t}\left|\nu\right\rangle$$
(4.19)

from Appendix G.

Now it can be seen, that in Eq. (4.19) we have obtained Heisenberg representation of the operator  $e^{-i\mathbf{q} \cdot \mathbf{R}_n}$  (see details in Appendix H):

$$e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} = e^{\frac{i}{\hbar}\hat{H}t}e^{-i\mathbf{q}\mathbf{R}_n}e^{-\frac{i}{\hbar}\hat{H}t}.$$
(4.20)

Analogously, the operator  $e^{i\mathbf{q}\mathbf{R}_m}$  in the first matrix element in Eq. (4.18) can be seen as a corresponding Heisenberg operator at time t = 0:

$$e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} = e^{i\mathbf{q}\mathbf{R}_m}.$$
(4.21)

Here we remind that in Heisenberg picture, the operator  $\hat{\mathbf{R}}_n(t)$  returns the position  $\mathbf{R}_n$  of the  $n^{\text{th}}$  nucleus at the moment t.

Rewriting Eq. (4.18) with time-dependent Heisenberg operators, we obtain

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\nu\nu\nu'} = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \sum_{m,n=1}^{N} b_m^* b_n \left\langle \nu \right| e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} \left|\nu\right\rangle \times \times \left\langle \nu'\right| e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} \left|\nu\right\rangle \cdot e^{i\omega t} dt.$$
(4.22)

#### 4.1.3 Ensemble averaging

In a neutron scattering experiment, the parameters of the incident beam (energy and wave vector) are known and the parameters of the scattered beam are directly measured. However, usually nothing is known about the scattering system, i.e. the initial state  $|\nu\rangle$  and the final state  $|\nu'\rangle$  are generally unknown. Therefore, to obtain the experimentally measured double-differential scattering cross section, we have to average Eq. (4.22) over all possible initial and final states. This is done in two steps:

$$\langle \nu' | e^{-i\mathbf{q}\mathbf{R}_m} | \nu \rangle^* = \langle \nu | e^{i\mathbf{q}\mathbf{R}_m} | \nu' \rangle$$

 $<sup>^{13}\</sup>mathrm{Here}$  we used the following property of the conjugated matrix elements

• averaging over all possible initial states  $|\nu\rangle$ . Here we will assume that the probability of the system to be in the initial state  $|\nu\rangle$  with energy  $E_{\nu}$  is given by  $\rho_{\nu}$ . In the case of Boltzmann statistics, this probability if given by

$$\rho_{\nu} = \frac{1}{Z} e^{-\frac{E_{\nu}}{k_B T}} = \frac{e^{-\frac{E_{\nu}}{k_B T}}}{\sum_{\nu} e^{-\frac{E_{\nu}}{k_B T}}},$$
(4.23)

where Z is partition function.

• summing over all possible final states  $|\nu'\rangle$ . Because of the delta function introduced in Eq. (4.15), the contribution of the final states, for which the energy conservation is violated, will be zero.

Thus, the experimentally measured double-differential scattering crosssection is

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \sum_{\nu} \rho_{\nu} \sum_{\nu'} \left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)_{\nu\nu'}.$$
(4.24)

When Eq. (4.22) is inserted into Eq. (4.24), it is possible to perform summation over all possible final states  $\nu'$  using the closure relation (see footnote 3 on page 8):

$$\sum_{\nu'} \langle \nu | e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} | \nu' \rangle \langle \nu' | e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} | \nu \rangle = \langle \nu | e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} \cdot e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} | \nu \rangle. \quad (4.25)$$

Note that operators  $\hat{\mathbf{R}}_m(0)$  and  $\hat{\mathbf{R}}_n(t)$  do not commute, so one cannot change the order of exponentials in Eq. (4.25).

Finally, the double-differential scattering cross-section is

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \sum_{\nu} \rho_{\nu} \sum_{m,n=1}^{N} b_{j'}^* b_j \int_{-\infty}^{+\infty} \langle \nu | e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} \cdot e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} | \nu \rangle \cdot e^{i\omega t} dt.$$
(4.26)

This expression is quite complex, and the proper calculation of the matrix elements is possible for only limited amount of systems (e.g. ideal gas of non-interacting free atoms, or atoms in a crystal which oscillate due to phonons). In many practical applications, especially, in soft matter systems, it is impossible to evaluate the double-differential scattering cross-section using exact formula 4.26. However, one can use a classical approximation, where the operators  $\hat{\mathbf{R}}_m(0)$  and  $\hat{\mathbf{R}}_n(t)$  are treated simply as numbers, i.e. it is assumed that they commute. In the following we will use the classical approximation

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right)^{cl} = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \sum_{\nu} \rho_{\nu} \sum_{m,n=1}^{N} b_m^* b_n \int_{-\infty}^{+\infty} \langle \nu | e^{-i\mathbf{q} \left[\mathbf{R}_n(t) - \mathbf{R}_m(0)\right]} |\nu\rangle \cdot e^{i\omega t} dt,$$
(4.27)

and for the sake of simplicity we will omit the superscript  $"\mathit{cl}"$  in the following text.

The last simplification can be made, if we use the definition of the ensemble average of a value A with a corresponding operator  $\hat{A}$ :

$$\langle A \rangle = \sum_{\nu} \rho_{\nu} \langle \nu | \hat{A} | \nu \rangle .$$
(4.28)

Here we first calculate the average value of the operator  $\hat{A}$  for the state of the system  $|\nu\rangle$  and then average over all possible states  $|\nu\rangle$ . Thus, the

double-differential neutron scattering cross-section can be written as

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \sum_{m,n=1}^{N} b_m^* b_n \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q} \left[\mathbf{R}_n(t) - \mathbf{R}_m(0)\right]} \right\rangle \cdot e^{i\omega t} dt,$$
(4.29)

where  $\langle \ldots \rangle$  denote ensemble averaging.

We should note, that although a specific moment of time t = 0 naturally appears in Eqs. (4.20-4.22) the choice of the "time zero" is arbitrary. As it is shown in Appendix H (specifically, Eq. (H.10)), the matrix elements in Eqs. (4.25-4.26) only depend on time difference between two moments of time. Therefore, the value of the scattering cross-section will not change if one calculates the operators for times t' and t' + t instead of 0 and t.

# 4.1.4 Example: scattering from free nuclei

As an example of using Eq. (4.26), let us consider inelastic neutron scattering from a single free nucleus. Let us assume that the initial wavevector of a nucleus is **K**. It means that its wavefunction normalized to the volume V is

$$|\mathbf{K}\rangle = \frac{1}{\sqrt{V}}e^{i\mathbf{KR}}.$$
(4.30)

Since the initial state of the nuclei is defined, there is no need to perform the averaging over all possible initial states. Also the double sum over all nuclei is now consisting of a single term (m = n = 1) proportional to  $\langle b^2 \rangle$ (incoherent scattering). Therefore Eq. (4.26) can be simplified to

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{k_{out}}{k_{in}} \langle b^2 \rangle \underbrace{\frac{1}{2\pi\hbar} \int_{-\infty}^{+\infty} \langle \mathbf{K} | e^{i\mathbf{q}\hat{\mathbf{R}}(0)} \cdot e^{-i\mathbf{q}\hat{\mathbf{R}}(t)} | \mathbf{K} \rangle \cdot e^{i\omega t} dt}_{S_{inc}(\mathbf{q},\omega)}.$$
 (4.31)

Now we should evaluate the matrix element in Eq. (4.31), using Heisenberg picture (see Eqs. (4.20-4.21) and Appendix H):

$$\langle \mathbf{K} | e^{i\mathbf{q}\hat{\mathbf{R}}(0)} \cdot e^{-i\mathbf{q}\hat{\mathbf{R}}(t)} | \mathbf{K} \rangle = \langle \mathbf{K} | e^{i\mathbf{q}\mathbf{R}} \cdot e^{\frac{i}{\hbar}\hat{H}t} e^{-i\mathbf{q}\mathbf{R}} e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{K} \rangle.$$
(4.32)

Since the nucleus is free, its Hamiltonian is  $\hat{H} = -\frac{\hbar^2}{2M}\nabla^2$ , where the differential operator is calculated over the position of a nucleus **R** and *M* is the mass of the nucleus. The wavefunction given by Eq. (4.30) is, obviously, an eigenfunction of this Hamiltonian, i.e.

$$\hat{H} \left| \mathbf{K} \right\rangle = \frac{\hbar^2 \mathbf{K}^2}{2M} \left| \mathbf{K} \right\rangle. \tag{4.33}$$

Using the exponential of a Hamilton operator (see Appendix G), we can step-by-step calculate the matrix element in Eq. (4.32) by applying the operators to the nuclei wavefunction  $|\mathbf{K}\rangle$ :

$$\begin{split} e^{-\frac{i}{\hbar}\hat{H}t}\left|\mathbf{K}\right\rangle &= e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\left|\mathbf{K}\right\rangle,\\ e^{-i\mathbf{q}\mathbf{R}}e^{-\frac{i}{\hbar}\hat{H}t}\left|\mathbf{K}\right\rangle &= e^{-i\mathbf{q}\mathbf{R}}\cdot e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\cdot\frac{1}{\sqrt{V}}e^{i\mathbf{K}\mathbf{R}} = e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\left|\mathbf{K}-\mathbf{q}\right\rangle,\\ e^{\frac{i}{\hbar}\hat{H}t}e^{-i\mathbf{q}\mathbf{R}}e^{-\frac{i}{\hbar}\hat{H}t}\left|\mathbf{K}\right\rangle &= e^{\frac{i}{\hbar}\hat{H}t}\cdot e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\left|\mathbf{K}-\mathbf{q}\right\rangle = e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\cdot e^{\frac{it}{\hbar}\cdot\frac{\hbar^{2}(\mathbf{K}-\mathbf{q})^{2}}{2M}}\left|\mathbf{K}-\mathbf{q}\right\rangle,\\ e^{i\mathbf{q}\mathbf{R}}\cdot e^{\frac{i}{\hbar}\hat{H}t}e^{-i\mathbf{q}\mathbf{R}}e^{-\frac{i}{\hbar}\hat{H}t}\left|\mathbf{K}\right\rangle &= e^{i\mathbf{q}\mathbf{R}}e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\cdot e^{\frac{it}{\hbar}\cdot\frac{\hbar^{2}(\mathbf{K}-\mathbf{q})^{2}}{2M}}\cdot \frac{1}{\sqrt{V}}e^{i(\mathbf{K}-\mathbf{q})\mathbf{R}} = e^{-\frac{it}{\hbar}\cdot\frac{\hbar^{2}K^{2}}{2M}}\cdot e^{\frac{it}{\hbar}\cdot\frac{\hbar^{2}(\mathbf{K}-\mathbf{q})^{2}}{2M}}\left|\mathbf{K}\right\rangle. \end{split}$$

Finally,

$$\langle \mathbf{K} | e^{i\mathbf{q}\mathbf{R}} \cdot e^{\frac{i}{\hbar}\hat{H}t} e^{-i\mathbf{q}\mathbf{R}} e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{K} \rangle = e^{-\frac{it}{\hbar} \cdot \frac{\hbar^2 K^2}{2M}} \cdot e^{\frac{it}{\hbar} \cdot \frac{\hbar^2 (\mathbf{K} - \mathbf{q})^2}{2M}}$$

$$= \exp\left[\frac{it}{\hbar} \left(\frac{\hbar^2 q^2}{2M} - \frac{2\hbar^2 \mathbf{K} \mathbf{q}}{2M}\right)\right].$$

$$(4.34)$$

Calculating the Fourier transform of this matrix element in time domain gives the delta function:

$$\int_{-\infty}^{+\infty} \langle \mathbf{K} | e^{i\mathbf{q}\mathbf{R}} \cdot e^{\frac{i}{\hbar}\hat{H}t} e^{-i\mathbf{q}\mathbf{R}} e^{-\frac{i}{\hbar}\hat{H}t} | \mathbf{K} \rangle \cdot e^{i\omega t} dt$$
$$= \int_{-\infty}^{+\infty} \exp\left[\frac{it}{\hbar} \left(\frac{\hbar^2 q^2}{2M} - \frac{2\hbar^2 \mathbf{K} \mathbf{q}}{2M} + \hbar\omega\right)\right] dt \qquad (4.35)$$
$$= 2\pi\hbar\delta \left(\frac{\hbar^2 q^2}{2M} - \frac{2\hbar^2 \mathbf{K} \mathbf{q}}{2M} + \hbar\omega\right),$$

so the inelastic incoherent scattering form factor from a free nucleus is (see Eq. (4.31))

$$S_{inc}(\mathbf{q},\omega) = \delta \Big(\frac{\hbar^2 q^2}{2M} - \frac{2\hbar^2 \mathbf{K} \mathbf{q}}{2M} + \hbar\omega\Big).$$
(4.36)

It is easy to check, that the delta function in Eq. (4.36) is non-zero only if the conservation of energy and momentum is fulfilled. In a particular case of an initially motionless nucleus ( $\mathbf{K} = 0$ ), the scattered neutrons can only give some energy to the nucleus ( $\hbar\omega < 0$ ). Therefore, after the scattering, the nucleus will have a kinetic energy  $E_{nuc}^{kin} = \hbar\omega$ . Moreover, the momentum transfer of the scattered neutrons will satisfy the condition  $\frac{\hbar^2 q^2}{2M} = -\hbar\omega =$  $E_{nuc}^{kin}$ , which is the dispersion law for a free nucleus. This gives an illustration, how measuring the inelastic neutron scattering can experimentally provide one with information about the dispersion of certain excitation in the system.

The obtained result can be easily transferred to a system consisting of many non-interacting nuclei. In this case, the positions of any to different nuclei are not correlated, i.e.

$$\langle \nu | e^{i\mathbf{q}\hat{\mathbf{R}}_m(0)} \cdot e^{-i\mathbf{q}\hat{\mathbf{R}}_n(t)} | \nu \rangle = 0, \text{ for } n \neq m.$$
(4.37)

Therefore, only the diagonal elements with m = n will contribute to the double sum in Eq. (4.26), therefore the cross section will again be proportional to the incoherent scattering form factor given by Eq. (4.36):

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{k_{out}}{k_{in}} \langle b^2 \rangle \cdot N \cdot S_{inc}(\mathbf{q}, \omega).$$
(4.38)

Moreover, one can consider the Maxwell distribution of the initial wavevectors of the nuclei:

$$\rho(\mathbf{K}) = \left(\frac{\hbar^2}{2\pi M k_B T}\right)^{3/2} \exp\left(-\frac{\hbar^2 K^2}{2M k_B T}\right). \tag{4.39}$$

Including this particular ensemble averaging into Eq. 4.26) will lead to the following incoherent scattering structure factor<sup>14</sup>:

$$S_{inc}(\mathbf{q},\omega) = \sqrt{\frac{M}{2\pi k_B T}} \cdot \frac{1}{\hbar q} \cdot \exp\left[-\frac{M}{2k_B T q^2 \hbar^2} \left(\frac{\hbar^2 q^2}{2M} + \hbar \omega\right)^2\right].$$
(4.40)

This structure factor still exhibits maximum along the line  $\frac{\hbar^2 q^2}{2M} = -\hbar\omega$ , similar to the result obtained in Eq. (4.36). Obviously, the result obtained



Fig. 4.3: Incoherent scattering structure factor  $S_{inc}(\mathbf{q},\omega)$  for an ideal gas (Eq. (4.40)) at a cold temperature  $T \to 0$  (a) and at  $T \gg 0$  (b). In the first case, the atoms in the ideal gas almost do not move, so the structure factor is non-zero only along a line defined by Eq. (4.36) for  $\mathbf{K} = 0$ , which defines a dispersion curve for the atoms of a gas.

<sup>&</sup>lt;sup>14</sup>This can be shown by substituting Eq. (4.34) and Eq. (4.39) into Eq. (4.26).

for the Maxwell distribution does not feature a term  $\mathbf{Kq}$ , because in this case,  $\langle \mathbf{Kq} \rangle = 0$ .

Finally, it is interesting to note, that the classical approximation (Eq. 4.27)) gives a different result. The calculations are much easier in this case. Indeed, for a free nucleus with a constant wavevector  $\mathbf{K}$ , the difference between its positions at two moments of time is  $\mathbf{R}(t) - \mathbf{R}(0) = \frac{\hbar \mathbf{K}}{M}t$ . Therefore, the matrix element in Eq. 4.27) equals to  $e^{-it\hbar\mathbf{q}\mathbf{K}/M}$ , and its Fourier transform (i.e. the scattering form factor) is

$$S_{inc}^{cl}(\mathbf{q},\omega) = \delta \Big( -\frac{2\hbar^2 \mathbf{K} \mathbf{q}}{2M} + \hbar\omega \Big).$$
(4.41)

The analogous calculations for the ideal gas with the Maxwell distribution give:

$$S_{inc}^{cl}(\mathbf{q},\omega) = \sqrt{\frac{M}{2\pi k_B T}} \cdot \frac{1}{\hbar q} \cdot \exp\left[-\frac{M\omega^2}{2k_B T q^2}\right].$$
 (4.42)

Therefore, the classical approximation coincides with the exact solution only when  $q \ll K$ , i.e. the momentum transferred to the system by the neutron is much smaller than the typical momentum of the particles in the system. In other words, the classical approximation means that the experimental probe (neutrons) do not influence the state of the system.

#### 4.2 Van Hove correlation function

Analogously to how it was done in section 3.2.2, let us introduce so-called van Hove generalized correlation function<sup>15</sup>  $G(\mathbf{r}, t)$ :

$$G(\mathbf{r},t) = \frac{1}{N} \Big\langle \sum_{m,n=1}^{N} \delta \big( \mathbf{r} - [\mathbf{R}_m(t) - \mathbf{R}_n(0)] \big) \Big\rangle, \tag{4.43}$$

where  $\langle \ldots \rangle$  denote ensemble averaging [43]. Its definition almost coincides with the expression for the correlation function  $G(\mathbf{r})$  in Eq. (3.44). The difference between those two lies in the fact, that  $G(\mathbf{r})$  was defined for a static system, so the positions  $\mathbf{R}_n$  and  $\mathbf{R}_m$  of two atoms are correlated at the same moment of time. In the van Hove generalized correlation function  $G(\mathbf{r}, t)$ , the position of the atoms  $\mathbf{R}_n(t)$  and  $\mathbf{R}_m(0)$  are considered at two different times. Of course, for t = 0 the van Hove correlation function matches with the static correlation function:

$$G(\mathbf{r},0) = \delta(\mathbf{r}) + \langle n \rangle \cdot g(\mathbf{r}), \qquad (4.44)$$

so it can be expressed via the pair distribution function  $g(\mathbf{r})$  defined in Eq. 3.46).

The van Hove correlation function contains information about the structure of the system and how this structure changes with time, i.e. the dynamics in the system. In the following sections we will establish the relation between the van Hove function  $G(\mathbf{r}, t)$  and the inelastic neutron scattering.

<sup>15</sup> If instead of the classical vectors  $\mathbf{R}_n(t)$  one keeps the Heisenberg operators  $\hat{\mathbf{R}}_n(t)$ , the corresponding "quantum" van Hove correlation function can be introduced as

$$G(\mathbf{r},t) = \frac{1}{N} \sum_{m,n=1}^{N} \int d\mathbf{r}' \left\langle \delta \left( \mathbf{r}' - \hat{\mathbf{R}}_m(0) \right) \delta \left( \mathbf{r}' + \mathbf{r} - \hat{\mathbf{R}}_n(t) \right) \right\rangle$$



Fig. 4.4: Illustration of the movement of atoms in a liquid: (a) the initial positions of the atoms at  $t \ll \tau$ , (b) the shift of the atoms from their initial positions at  $t \sim \tau$  (c) further displacement of the atoms at  $t \gg \tau$ . One atom is marked with darker color, so it is easier to track its movement.

#### 4.2.1 Self and distinct correlation functions

The double sum in Eq. (4.43) naturally splits into two parts: N diagonal terms with m = n and the remaining  $N^2 - N$  terms with  $m \neq n$ . This justifies the splitting of the van Hove correlation function  $G(\mathbf{r}, t)$  into two terms [43]:

$$G(\mathbf{r},t) = G_s(\mathbf{r},t) + G_d(\mathbf{r},t), \qquad (4.45)$$

where

$$G_s(\mathbf{r},t) = \frac{1}{N} \Big\langle \sum_{n=0}^{N} \delta \big( \mathbf{r} - [\mathbf{R}_n(t) - \mathbf{R}_n(0)] \big) \Big\rangle, \qquad (4.46)$$

$$G_d(\mathbf{r},t) = \frac{1}{N} \Big\langle \sum_{\substack{m,n=1\\m\neq n}}^N \delta\big(\mathbf{r} - [\mathbf{R}_n(t) - \mathbf{R}_m(0)]\big)\Big\rangle, \qquad (4.47)$$

where the subscripts "s" and "d" stand for "self" and "distinct", respectively.

To illustrate the physical meaning of these two components, let us consider a partially ordered condensed system (liquid). For consistency, let us assume that this liquid consists of N atoms, although qualitatively the same conclusions could be made for a molecular liquid. To characterize the dynamics of this liquid, let us assume that the movement of atoms happens over some time-scale  $\tau$  (Fig. 4.4).

The correlation function  $G_s(\mathbf{r}, t)$  in Eq. (4.46) describes the average displacement of an atom from its initial position  $\mathbf{R}_n(0)$  to some new position  $\mathbf{R}_n(t)$ . At the time  $t \to 0$  the position of the atom matches with its initial position, so  $G_s(\mathbf{r}, t) \to \delta(\mathbf{r})$  (first term in Eq. (4.44)). For the times  $t \sim \tau$ , the delta-like peak of  $G_s(\mathbf{r}, t)$  becomes broader, which corresponds to displacement of the atoms from their initial positions. Finally, at  $t \gg \tau$ , the positions of the atoms is not related to their initial positions, so  $G_s(\mathbf{r}, t) \to 0$ . This means, that because at such long time scale, all information about the original position of the atoms is "lost". To summarize,  $G_s(\mathbf{r}, t)$  describes self-diffusion of individual atoms in the system. Its evolution in time is schematically shown in Fig. 4.5.

The correlation function  $G_d(\mathbf{r}, t)$  in Eq. (4.47) describes the average correlation between potions of two distinct particles  $\mathbf{R}_n(t)$  and  $\mathbf{R}_m(0)$  at two different moments of time. In the limit  $t \ll \tau$ , these two moments of time are matching  $(t \to 0)$ , so  $G_d(\mathbf{r}, t) \to \langle n \rangle g(\mathbf{r})$  (second term in Eq. (4.44)). This means that  $G_d(\mathbf{r}, t)$  describes a static structure of the system at  $t \to 0$ . At larger times,  $t \sim \tau$ , the atoms move from it positions, so the peaks of the correlation function  $G_d(\mathbf{r}, t)$  become less pronounced. Finally, at  $t \gg \tau$ , the correlation between any two atoms are lost. This means that the probability of finding an atom at time  $t \gg \tau$  at some position does not depend on the initial positions of the atoms. Therefore this probability is only defined by the density of atoms, so  $G_d(\mathbf{r}, t) \to \langle n \rangle$ . A sketch of the function  $G_d(\mathbf{r}, t)$  at different times is also shown in Fig. 4.5.

#### 4.2.2 Density operator

There is an alternative way to define the van Hove correlation function, which we partially introduced in section 3.2.2. This formalism includes a number density operator (see Eq. (3.42)), and it is sometimes used in condesed matter physics.

To keep the general quantum approach, we will define number density operator (i.e. we keep the Heisenberg operators here):

$$n(\mathbf{r},t) = \sum_{m=1}^{N} \delta(\mathbf{r} - \hat{\mathbf{R}}_m(t)).$$
(4.48)



Fig. 4.5: Sketch of  $G_s(\mathbf{r},t)$ ,  $G_d(\mathbf{r},t)$  and  $G(\mathbf{r},t)$  for a liquid: (a) at the short times  $t \ll \tau$ , (b) at the intermediate times  $t \sim \tau$  (c) at long times  $t \gg \tau$ . The asymptotic value of the correlation function at large distances equals to the average concentration  $\langle n \rangle$ . The corresponding illustration in real space is shown in Fig. 4.4.

The van Hove correlation function can be then expressed as (see footnote 15 on page 61):

$$G(\mathbf{r},t) = \frac{1}{N} \int \left\langle n(\mathbf{r}',0)n(\mathbf{r}'+\mathbf{r},t) \right\rangle d\mathbf{r}'.$$
(4.49)

In the next section, we will also use the Fourier transform of the number density operator:

$$n(\mathbf{q},t) = \int n(\mathbf{r},t)e^{-i\mathbf{q}\mathbf{r}}d\mathbf{r} = \sum_{m=1}^{N} e^{-i\mathbf{q}\mathbf{R}_{m}(t)}.$$
(4.50)

#### 4.3 Dynamic structure factor

#### 4.3.1 Intermediate scattering function

For the sake of simplicity, let us neglect for a moment that the neutron scattering length  $b_n$  in Eq. (4.28) is not the same for all nuclei (there could be different chemical elements and isotops, or different orientation of nuclear spin (see section 1.2.2) for details). Then we can define so-called intermediate scattering function, which naturally appears in Eq. (4.28:

$$F(\mathbf{q},t) = \frac{1}{N} \sum_{m,n=1}^{N} \left\langle e^{-i\mathbf{q} \left[ \mathbf{R}_{n}(t) - \mathbf{R}_{m}(0) \right]} \right\rangle.$$
(4.51)

It contains information about the structure and dynamics of the system (the positions of the atoms and how they move with time). Therefore, the intermediate scattering function is directly related to the van Hove correlation function.

Indeed, similarly to Eq. (3.47), we can show that the spatial Fourier transform of the van Hove correlation function is exactly intermediate scattering function:

$$\int G(\mathbf{r},t)e^{-i\mathbf{q}\mathbf{r}}d\mathbf{r} = \frac{1}{N}\sum_{m,n=1}^{N} \left\langle \int \delta\left(\mathbf{r} - [\mathbf{R}_{n}(t) - \mathbf{R}_{m}(0)]\right)e^{-i\mathbf{q}\mathbf{r}}d\mathbf{r} \right\rangle$$
$$= \frac{1}{N}\sum_{m,n=1}^{N} \left\langle e^{-i\mathbf{q}\left[\mathbf{R}_{n}(t) - \mathbf{R}_{m}(0)\right]} \right\rangle$$
$$= F(\mathbf{q},t).$$
(4.52)

Inverting Eq. (4.45), we can express the van Hove correlation function via the inverse Fourier transform of the intermediate scattering function  $F(\mathbf{q}, t)$  (see Appendix A):

$$G(\mathbf{r},t) = \frac{1}{(2\pi)^3} \int F(\mathbf{q},t) e^{i\mathbf{q}\mathbf{r}} d\mathbf{q},$$

$$F(\mathbf{q},t) = \int G(\mathbf{r},t) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}.$$
(4.53)

The pair of Eqs. (4.53) shows that the van Hove correlation function  $G(\mathbf{r}, t)$ and the intermediate scattering function  $F(\mathbf{q}, t)$  are connected to each other via spatial Fourier transform (in space domain). One can go a step further and perform a temporal Fourier transform (in time domain) of  $F(\mathbf{q}, t)$  and obtain a dynamic structure factor  $S_{coh}(\mathbf{q}, t)$ . For the reasons, explained in the following section, we will denote it as *coherent* structure factor. The connection between the coherent dynamic structure factor  $S_{coh}(\mathbf{q}, \omega)$  and the intermediate scattering function  $F(\mathbf{q}, t)$  can be written as

$$S_{coh}(\mathbf{q},\omega) = \frac{1}{2\pi\hbar} \int F(\mathbf{q},t)e^{i\omega t}dt,$$

$$F(\mathbf{q},t) = \hbar \int S_{coh}(\mathbf{q},\omega)e^{-i\omega t}d\omega.$$
(4.54)

Combining Eqs. (4.53) and (4.53), we can obtain the relation between the correlation function and the dynamic structure factor:

$$S_{coh}(\mathbf{q},\omega) = \frac{1}{2\pi\hbar} \int G(\mathbf{r},t) e^{-i\mathbf{q}\mathbf{r}+i\omega t} d\mathbf{r} dt,$$

$$G(\mathbf{r},t) = \frac{\hbar}{(2\pi)^3} \int S_{coh}(\mathbf{q},\omega) e^{i\mathbf{q}\mathbf{r}-i\omega t} d\mathbf{q} d\omega.$$
(4.55)

#### 4.3.2 Coherent and incoherent dynamic structure factor

Let us go back to Eq. (4.29) for the double-differential neutron scattering cross section. Even in the case, when the scattering system consists only from the atoms of a single chemical element, there might be different isotopes or orientations of the nuclear spin with respect to the spin of a neutron (parralel or anti-parallel). This was already discussed in section 1.2.2. In result, one has to average Eq. (4.29) over all possible orientations of the nuclear spin and isotopes:

$$\left(\frac{\partial^2 \sigma}{\partial \Omega \partial E'}\right) = \frac{k_{out}}{k_{in}} \frac{1}{2\pi\hbar} \sum_{m,n=1}^{N} \langle b_m^* b_n \rangle \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q} \left[\mathbf{R}_n(t) - \mathbf{R}_m(0)\right]} \right\rangle \cdot e^{i\omega t} dt.$$
(4.56)

The averaging of the scattering lengths can be conveniently done using Eq. 1.49, written in a compact form:

$$\langle b_m^* b_n \rangle = |\langle b \rangle|^2 + \delta_{nm} \left( \langle |b|^2 \rangle - |\langle b \rangle|^2 \right) = \frac{\sigma_{coh}}{4\pi} + \delta_{mn} \frac{\sigma_{inc}}{4\pi}, \tag{4.57}$$

where we expressed coherent and incoherent scattering length via the corresponding cross-sections.  $^{16}$ 

Substituting Eq. (4.57) into Eq. (4.56) results in breaking the double sum over m and n into two parts: the first part is proportional to  $\sigma_{coh}$  and it contains the double sum over all nuclei in the system, and the second part is proportional to  $\sigma_{inc}$  and due to the delta function it only contains the terms with m = n:

$$\left(\frac{\partial^{2}\sigma}{\partial\Omega\partial E'}\right) = \frac{k_{out}}{k_{in}} \frac{\sigma_{coh}}{4\pi} N \sum_{m,n=1}^{N} \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q}\left[\mathbf{R}_{n}(t)-\mathbf{R}_{m}(0)\right]} \right\rangle \cdot e^{i\omega t} dt + \frac{k_{out}}{k_{in}} \frac{\sigma_{inc}}{4\pi} N \sum_{n=1}^{N} \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q}\left[\mathbf{R}_{n}(t)-\mathbf{R}_{n}(0)\right]} \right\rangle \cdot e^{i\omega t} dt}{S_{inc}(\mathbf{q},\omega)} = \frac{k_{out}}{k_{in}} \frac{N}{4\pi} \left( \sigma_{coh} S_{coh}(\mathbf{q},\omega) + \sigma_{inc} S_{inc}(\mathbf{q},\omega) \right).$$

$$(4.58)$$

 $<sup>^{16}</sup>$ For the majority of isotopes, neutron scattering length b is a real number, so one can ommit the complex conjugation, which simplifies the equations.

We have already considered the first term in Eq. (4.58) containing the double sum (see section 4.3.1). We called it the coherent structure factor<sup>17</sup>  $S_{coh}(\mathbf{q},\omega)$ :

$$S_{coh}(\mathbf{q},\omega) = \sum_{m,n=1}^{N} \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q} \left[\mathbf{R}_{n}(t) - \mathbf{R}_{m}(0)\right]} \right\rangle \cdot e^{i\omega t} dt$$

$$= \frac{1}{2\pi\hbar} \int G(\mathbf{r},t) e^{-i\mathbf{q}\mathbf{r} + i\omega t} d\mathbf{r} dt.$$
(4.59)

The incoherent structure faction  $S_{inc}(\mathbf{q}, \omega)$  can be obtained in the same way, but since it has only a single sum over n, it will be proportional to the self-correlation function  $G_s(\mathbf{r}, t)$  (see Eq. (4.46)):

$$S_{inc}(\mathbf{q},\omega) = \sum_{n=1}^{N} \frac{1}{2\pi\hbar N} \int_{-\infty}^{+\infty} \left\langle e^{-i\mathbf{q} \left[\mathbf{R}_{n}(t) - \mathbf{R}_{n}(0)\right]} \right\rangle \cdot e^{i\omega t} dt$$

$$= \frac{1}{2\pi\hbar} \int G_{s}(\mathbf{r},t) e^{-i\mathbf{q}\mathbf{r} + i\omega t} d\mathbf{r} dt.$$
(4.60)

The coherent dynamic structure factor  $S_{coh}(\mathbf{q}, \omega)$  is a function of a total correlation function  $G(\mathbf{r}, t)$ , therefore it describes the structure of the system and the evolution of this structure with time. Thus, the coherent neutron scattering depends on structure and dynamics of the system. The incoherent dyncmic structure factor  $S_{inc}(\mathbf{q}, \omega)$  is a function of self-correlation function  $G_s(\mathbf{r}, t)$ , so it describes how individual atoms in the system move with time. The incoherent neutron scattering depends on dynamics of the system.

Using inverse Fourier transform, we can invert Eqs. (4.59) and (4.60):

$$G(\mathbf{r},t) = \frac{\hbar}{(2\pi)^3} \int S_{coh}(\mathbf{q},\omega) e^{i\mathbf{q}\mathbf{r}-i\omega t} d\mathbf{q} d\omega,$$

$$G_s(\mathbf{r},t) = \frac{\hbar}{(2\pi)^3} \int S_{inc}(\mathbf{q},\omega) e^{i\mathbf{q}\mathbf{r}-i\omega t} d\mathbf{q} d\omega.$$
(4.61)

In a neutron scattering experiment, one measures both coherent and incoherent neutron scattering, so both terms contribute to the total crosssection in Eq. (4.57). However, one can choose isotopes in such a way, that the coherent or incoherent scattering dominates. For example, the incoherent scattering cross-section  $\sigma_{inc}$  of  $_1^1$ H is almost 40 times larger than the coherent scattering cross-section  $\sigma_{coh}$  (see Table 2). This allows one to study self-diffusion of hydrogen by measuring incoherent inelastic neutron scattering. This is important for various biological systems, where hydrogen is usually present is significant amount (for example, diffusion of protein molecules in solution).

#### 4.3.3 Principle of detailed balance

The van Hove correlation function  $G(\mathbf{r}, t)$ , as well as the intermediate scattering function  $F(\mathbf{q}, t)$  and the dynamic structure factor  $S(\mathbf{q}, \omega)$ , fulfill certain analytical properties which follow from their definition. An extensive list of such properties can be found in [9]. These properties are important, because in many cases the exact correlation function cannot be calculated, so one has to use an approximation or a model. In this case, these analytical properties serve as a constrain which help to make the model more realistic.

In this section, we will only discuss principle of detailed balance, which has a deep physical meaning. To illustrate it, let us make a few steps back

<sup>&</sup>lt;sup>17</sup>Sometimes  $S_{coh}(\mathbf{q},\omega)$  is called a coherent scattering function.

and write the coherent coherent dynamic structure factor as:

$$S_{coh}(\mathbf{q},\omega) = \frac{1}{Z} \sum_{\nu} e^{-E_{\nu}/k_B T} \sum_{\nu'} \left| \sum_{n}^{N} \langle \nu' | e^{i\mathbf{q}\mathbf{R}_n} | \nu \rangle \right|^2 \cdot \delta(E_{\nu} - E_{\nu'} - \hbar\omega),$$

$$(4.62)$$

where we assumed Boltzmann's statistics. Let us assume that  $\hbar \omega > 0$ , meaning that we consider a process, in which neutron gains energy  $\hbar \omega$  and momentum **q** while the system changes its state from  $|\nu\rangle$  to  $|\nu'\rangle$  and lowers its energy by  $E_{\nu} - E_{\nu'}$  (see Fig. 4.6(a)).

An inverse process, in which neutron loses energy  $\hbar\omega$  (or, in other words, gains a negative energy  $-\hbar\omega$ ) and changes its momentum by  $-\mathbf{q}$ , is described by the following coherent dynamic structure factor:

$$S_{coh}(-\mathbf{q},-\omega) = \frac{1}{Z} \sum_{\nu'} e^{-E_{\nu'}/k_B T} \sum_{\nu} \left| \sum_{n}^{N} \langle \nu | e^{i\mathbf{q}\mathbf{R}_n} | \nu' \rangle \right|^2 \cdot \delta(E_{\nu'} - E_{\nu} + \hbar\omega).$$

$$(4.63)$$

In this process, the system increases its energy and changes its state from  $|\nu'\rangle$  to  $|\nu\rangle$  (see Fig. 4.6(b)). Using the energy conservation,  $E_{\nu} = E_{\nu'} + \hbar\omega$ , replacing all matrix elements with the conjugated ones, and using the fact that  $\delta(x) = \delta(-x)$ , we obtain:

$$S_{coh}(-\mathbf{q},-\omega) = \frac{1}{Z} \sum_{\nu'} e^{-E_{\nu'}/k_B T} e^{\hbar\omega/k_B T} \sum_{\nu} \left| \sum_{n}^{N} \langle \nu | e^{i\mathbf{q}\mathbf{R}_n} | \nu' \rangle^* \right|^2 \cdot \delta(E_{\nu'} - E_{\nu} + \hbar\omega)$$
$$= e^{\hbar\omega/k_B T} \frac{1}{Z} \sum_{\nu'} e^{-E_{\nu'}/k_B T} \sum_{\nu} \left| \sum_{n}^{N} \langle \nu' | e^{-i\mathbf{q}\mathbf{R}_n} | \nu \rangle \right|^2 \cdot \delta(E_{\nu} - E_{\nu'} - \hbar\omega)$$
$$= e^{\hbar\omega/k_B T} S_{coh}(\mathbf{q},\omega).$$

The physical meaning of this result is that for a pair of states in the scattering system, the values of the matrix elements  $|\langle \nu | e^{i\mathbf{q}\mathbf{R}_n} | \nu' \rangle|$  and  $|\langle \nu' | e^{-i\mathbf{q}\mathbf{R}_n} | \nu \rangle|$  are the same, so the *a priori* probabilities of such transition to be caused by a neutron are the same. However, the probability of the system being initially in the higher energy state is lower than its probability of being in the lower energy state. This is why  $S_{coh}(\mathbf{q},\omega)$  is smaller than  $S_{coh}(-\mathbf{q},-\omega)$  by the factor  $e^{\hbar\omega/k_BT}$ .

The factor  $e^{\hbar\omega/k_BT}$  becomes especially notable at low temperatures. For example, in a neutron scattering by a crystal, a phonon with energy  $\hbar\omega$  can be created by a neutron (Stokes scattering) or absorbed by it (anti-Stokes scattering). At low temperatures,  $k_BT\hbar\omega$ , the amount of photons in the crystal is low, so the probability of absorption of already existing phonon is much lower than a probability of creation of a phonon. This leads to the fact that the anti-Stokes scattering peaks (absorption of a phonon) have lower intensity than the Stokes peaks (creation of a phonon); and at very low temperatures the former can completely disappear from the scattering spectrum (Fig. 4.7).

The principle of detailed balance (Eq. (4.64)) can be also derived more formally. For this, let us write the intermediate scattering function via the number density operator (see Eqs (4.53) and (4.50)):

$$F(\mathbf{q},t) = \frac{1}{N} \langle n(\mathbf{q},0)n(-\mathbf{q},t) \rangle.$$
(4.65)



Fig. 4.6: (a) Sketch of a neutron scattering process in which the neutron gains energy  $\hbar\omega$  and the system lowers its state from  $|\nu\rangle$  to  $|\nu'\rangle$ . (b) Sketch of an inverse neutron scattering process in which neutron loses energy  $\hbar\omega$  and the system increases its state from  $|\nu'\rangle$  to  $|\nu\rangle$ .



(4.64)

Fig. 4.7: Dynamic structure factor of a neutron scattering experiment on optical phonons at low temperature. The elastic scattering is represented by a peak at  $\omega = 0$ . At the given q-value, there are two phonon modes with frequencies  $\omega_1$  and  $\omega_2$ . The inelastic scattering is only possible when a phonon is created (Stokes scattering,  $\omega > 0$ ) or absorbed (anti-Stokes scattering,  $\omega < 0$ ). The intensity of Stokes peaks is higher than the intensity of anti-Stokes peaks.

Now, using properties (H.11) and (H.10), we can write

$$\left\langle n(\mathbf{q},0)n(-\mathbf{q},t)\right\rangle = \left\langle n(-\mathbf{q},t)n\left(\mathbf{q},\frac{i\hbar}{k_BT}\right)\right\rangle = \left\langle n(-\mathbf{q},0)n\left(\mathbf{q},-t+\frac{i\hbar}{k_BT}\right)\right\rangle,\tag{4.66}$$

which means

$$F(\mathbf{q},t) = F\left(-\mathbf{q}, -t + \frac{i\hbar}{k_B T}\right).$$
(4.67)

This leads to the principle of detailed balance for the coherent dynamic structure factor using Eq. (4.54):

$$S_{coh}(\mathbf{q},\omega) = \frac{1}{2\pi\hbar} \int F(\mathbf{q},t)e^{i\omega t}dt = \frac{1}{2\pi\hbar} \int F\left(-\mathbf{q},\underbrace{-t+\frac{i\hbar}{k_BT}}_{t'}\right)e^{i\omega t}dt$$
$$= \frac{1}{2\pi\hbar} \int F(-\mathbf{q},t')e^{-i\omega t'}e^{i\omega \cdot i\hbar/k_BT}dt' = e^{-\hbar\omega/k_BT}S_{coh}(-\mathbf{q},-\omega).$$
(4.68)

The principle of detailed balance implies certain conditions on the correlation function, since the structure factor and the correlation function are connected via the Fourier transform (Eq. (4.59)). Many models use the correlation functions  $G(\mathbf{r}, t)$  which are even in coordinate and time, i.e.  $G(-\mathbf{r}, t) = G(\mathbf{r}, t)$  and  $G(\mathbf{r}, -t) = G(\mathbf{r}, t)$ . It is easy to check, that the dynamic structure factor obtained from such an even correlation function will violate the principle of detailed balance, since in this case, the it will be also an even function, i.e.  $S_{coh}(-\mathbf{q}, -\omega) = S_{coh}(\mathbf{q}, \omega)$ . Peter Schofield suggested [44] that a better approximation can be obtained by using a modified correlation function

$$G_{\text{Schofield}}(\mathbf{r}, t) = G\left(r, t - \frac{i\hbar}{2k_BT}\right).$$
 (4.69)

The dynamic structure factor obtained from the Schofield approximation of the correlation function (Eq. (4.69)) satisfies the principle of detailed balance (Eq. (4.64)).

### 4.3.4 Implications of the general formalism and special cases

Eqs. (4.59) and (4.60) show that the dynamic structure factor is proportional to the Fourier transform of the van Hove correlation function (in space and time domains). This fact can be simplified in the following formula, where we omit the prefactors and do not distinguish the coherent and incoherent scattering:

$$S(\mathbf{q},\omega) \sim \int G(\mathbf{r},t)e^{-i(\mathbf{qr}-\omega t)}d\mathbf{r}dt.$$
 (4.70)

This simplified notation allows us to distinguish "modes of the experiment". For instance, for purely elastic scattering ( $\omega = 0$ ) we obtain  $\int G(\mathbf{r}, t) dt$ which means we measure the time-averaged structure. Another instructive special case is that of a harmonic oscillation with frequency  $\omega_0$  (such as, e.g., a phonon) in the structure. If G(r, t) thus features this frequency  $\omega_0$ , the scattering signal  $S(q, \omega)$  will exhibit a peak at  $\omega = \omega_0$ , which corresponds to the spectroscopy of phonons. The connection between different experimental consitions of the scattering experiment and the corresponding correlation function are shown in Table 5.

#### 4.3.5 Example: diffusion of atoms

To illustrate the relation between the van Hove correlation function and the scattering structure factor, let us consider random motion of particles.

Correlation	Structure factor
$G(\mathbf{r},t)$	$S(\mathbf{q},\omega)$
$G(\mathbf{r},t=0)$	$\int S({f q},\omega)d\omega$
$G(\mathbf{r}=0,t)$	$\int S({f q},\omega) d{f q}$
$G(\mathbf{r}=0,t=0)$	$\int \int S({f q},\omega) d{f q} d\omega$
$\int G({f r},t)dt$	$S({\bf q},\omega=0)$
$\int G({f r},t) d{f r}$	$S(\mathbf{q}=0,\omega)$

Table 5: Relation between the correlation functions in real space and the structure factor in reciprocal space

If the particles do not interact with each other, they move independently. This means, that the positions of two different particles  $\mathbf{R}_m(t)$  and  $\mathbf{R}_n(t)$   $(m \neq n)$  are not correlated at any moment of time, so that the distinct correlation function  $G_d(\mathbf{r}, t)$  is zero (Eq. (4.47)). Therefore, to calculate the self-correlation function  $G_s(\mathbf{r}, t)$  (Eq. (4.46)), we only need to consider an average motion of a single particle, because all other particles in the system will on average behave in a similar way.

Let us chose the origin of the coordinates in such a way, that ar t = 0 the particle is in the origin  $\mathbf{r} = 0$ . Its motion is described by Fick's second law of diffusion:

$$D\nabla^2 n(\mathbf{r}, t) = \frac{\partial}{\partial t} n(\mathbf{r}, t), \qquad (4.71)$$

where D is the diffusion coefficient and  $n(\mathbf{r}, t)$  is the concentration, which is proportional to the probability to find the particle in the vicinity of point  $\mathbf{r}$ at the moment of time t. For the boundary condition  $n(\mathbf{r}, t)|_{t=0} = \delta(\mathbf{r})$ , the solution of the diffusion equation (4.71) is well-known<sup>18</sup>:

$$n(\mathbf{r},t) = \frac{1}{(4\pi Dt)^{3/2}} \exp\left[-\frac{r^2}{4Dt}\right].$$
(4.72)

It is easy to check, that for this solution, the average displacement of the particle from the origin is zero,  $\langle \mathbf{r} \rangle = 0$  and the mean squared displacement is proportional to the diffusion time,  $\langle \mathbf{r}^2 \rangle = Dt$ , as it should be for the Brownian motion.

The self-correlation function  $G_s(\mathbf{r}, t)$  (see definition given by Eq. (4.46)) satisfies the same differential equation as the concentration, therefore it can also be written as

$$G_s(\mathbf{r},t) = \frac{1}{(4\pi D|t|)^{3/2}} \exp\left[-\frac{r^2}{4D|t|}\right].$$
(4.73)

Here we extended it for the negative times, by substituting t with |t|.

Combining Eqs. (4.73) and (4.60), we can evaluate the incoherent scattering structure factor, using the spherical system of coordinates:

$$S_{inc}(\mathbf{q},\omega) = \frac{1}{2\pi\hbar} \int G_s(\mathbf{r},t) e^{-i\mathbf{q}\mathbf{r}+i\omega t} d\mathbf{r} dt$$
  

$$= \frac{1}{2\pi\hbar} \cdot \frac{1}{(4\pi Dt)^{3/2}} \int_{-\infty}^{+\infty} dt e^{i\omega t} \int e^{-\frac{r^2}{4D|t|}} e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r}$$
  

$$= \frac{1}{2\pi\hbar} \cdot \frac{1}{(4\pi Dt)^{3/2}} \int_{-\infty}^{+\infty} dt e^{i\omega t} \cdot \frac{4\pi}{q^3} \cdot \frac{\sqrt{\pi}}{4} (4Dt)^{3/2} \cdot e^{-D|t|q^2}$$
  

$$= \frac{1}{2\pi\hbar} \cdot \frac{1}{q^3} \int_{-\infty}^{+\infty} e^{-D|t|q^2} e^{i\omega t} dt = \frac{1}{2\pi\hbar} \cdot \frac{1}{q^3} \frac{2Dq^2}{(Dq^2)^2 + \omega^2}$$
  

$$= \frac{1}{\pi\hbar} \frac{Dq^2}{(Dq^2)^2 + \omega^2}.$$
(4.74)

By fitting the experimentally measured  $S_{inc}(\mathbf{q}, \omega)$  with Eq. (4.74) for different scattering vectors q, one can determine the diffusion coefficient of the particles in the system (see Fig. 4.8).

 $^{18}\mathrm{It}$  is easy to check that Eq. (4.72) satisfies the differential equation Eq. (4.71, where

$$\nabla^2 = \Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left( f^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2}$$

in spherical coordinates.



Fig. 4.8: (a) Sketch of the self-correlation function  $G_s(\mathbf{r},t)$  at three different moment of time (Eq. (4.73)). (b) Sketch of the incoherent scattering structure factor  $S_{inc}(\mathbf{q},\omega)$  at three different *q*-values (Eq. (4.74)). (c) Determination of the diffusion coefficient *D* from the width of the peak of  $S_{inc}(\mathbf{q},\omega)$  at different *q*-values.

# 4.3.6 Experimental realization

There are various technical realizations of energy-resolved neutron scattering (see Table 6). They provide different energy resolution (and dynamical ranges) for different dynamical processes, from lattice dynamics (phonons) in triple-axis spectrometry (TAS) to macromolecular dynamics (neutron backscattering (NBS) and neutron spin-echo (NSE)). For details we refer to M. Grimaldo *et al.* [45] and references therein.

Technique	Energy
	resolution
Triple-axis	
spectrometry	$\Delta E \lesssim 1~{\rm meV}$
(TAS)	
Time-of-flight	
spectrometry	$\Delta E \lesssim 100 \ \mu {\rm eV}$
(TOF)	
Neutron	
backscattering	$\Delta E \lesssim 1 \ \mu \mathrm{eV}$
(NBS)	
Netron	
spin-echo	$\Delta E \sim 1~{\rm neV}$
(NSE)	

Table 6: Various inelastic neutron scattering techniques and coarse estimate of the corresponding energy resolution (all values depend on experimental condition).
# 5 Scattering from crystals

In this section, we will consider a scattering from crystals - 3D periodic arrays of atoms. Scattering from crystals is a very important case, which has been covered in many excellent books dedicated to this subject. On top of that, almost every book on condensed matter considers scattering of X-rays or neutrons to a certain extend. Therefore, we will not go into too many details here and just provide a short overview of this broad field.

# 5.1 Translation symmetry of crystals

### 5.1.1 Crystal structure

The main property of crystal structure is a periodic arrangement of atoms. It means, that the infinite 3D crystal can be constructed by periodic translation of an elementary unit cell over all vectors given by

$$\mathbf{R}_{\mathbf{n}} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3, \tag{5.1}$$

where  $n_1$ ,  $n_2$  and  $n_3$  are integer numbers and  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  are three noncollinear vectors. These three vectors form an affine system of coordinates, in which the axes may be not orthogonal to each other. The choice of an elementary unit cell is not unique - it is easy to imagine that any combination of several adjacent to unit cells can be used to build up a periodic crystals with different (larger) translation vectors.

One of the possible ways to select a unit cell is to build a 3D parallelopiped on the translation vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  (Fig. 5.1a). In this case, the full translational symmetry of the crystal lattice is defined by three unit cell parameters  $a_1$ ,  $a_2$  and  $a_3$  and three angles between them  $\alpha$ ,  $\beta$ ,  $\gamma$ .

The unit cell and the corresponding crystal lattice is just a mathematical construct. In order to describe the real crystal structure we have to indicate the position of atoms within the unit cell - the basis. Since only a finite number of atoms can be within a unit cell (this number can be quite large, especially for the molecular crystals), the basis is just a set of vectors  $\rho_j$ . It is common to express the basis vectors  $\rho_i$  through the unit cell vectors:

$$\boldsymbol{\rho}_j = x_j \mathbf{a}_1 + y_j \mathbf{a}_2 + z_j \mathbf{a}_3, \tag{5.2}$$

where  $\{x_j, y_j, z_j\}$  are fractional coordinates between 0 and 1, since the atoms are located inside the unit cell. An example of a unit cell with a basis of two atoms is shown in Fig. 5.2a, and the corresponding crystal structure built from this unit cell - in Fig. 5.2b.

The position of each atom in the crystal can be given by

$$\mathbf{r}_{n,j} = \mathbf{R}_{\mathbf{n}} + \boldsymbol{\rho}_j = \underbrace{n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3}_{\text{crystal lattice}} + \underbrace{\boldsymbol{\rho}_j}_{\text{basis}}.$$
 (5.3)

Therefore, the position of all atoms in a crystal, i.e. the crystal structure, is defined by the *crystal lattice* and the *basis*.

Usually the smallest possible unit cell is selected, in this case it is called a *primitive* unit cell. Sometimes, the arrangement of the atoms within a unit cell gives rise to a certain point symmetry of the crystal, i.e. the mirror planes, rotational axes etc.<sup>19</sup> In this case, a larger unit cell, which contains all point symmetry of the crystal is selected. Such unit cells is called a *conventional* unit cell.



Fig. 5.1: (a)A 3D unit cell determined by three unit cell vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  with angles  $\alpha$ ,  $\beta$  and  $\gamma$  between them.

(b) Crystal lattice formed by translation of the unit cell.



Fig. 5.2: (a)A 3D unit cell with a basis consisting of two atoms of different kind. The atom with  $\rho_1 = 0$  is located in the origin of the unit cell (filled circle), and the atom with  $\rho_2 = 0.5 \cdot \mathbf{a}_1 + 0.5 \cdot \mathbf{a}_2 + 0.5 \cdot \mathbf{a}_3$  is located in the center of the unit cell (open circle). (b) Crystal structure formed by translation of the unit cell.

<sup>&</sup>lt;sup>19</sup>A typical example of such situation is the hexagonal lattice with  $a_1 = a_2 \neq a_3$ ,  $\alpha = \beta = 90^{\circ}$  and  $\gamma = 120^{\circ}$ . The presence of a sixfold rotational symmetry around  $\mathbf{a}_3$  axis is not apparent from the primitive unit cell, as shown in Fig. 5.1a.

In the following, we will use a concept of crystal planes. Crystal plane is defined as a plane passing through three sites of the crystal lattice  $\mathbf{R_n}$ that are not lying on the same line. Each crystal plane passes through the infinite number of lattice points. The crystal lattice can be split into a series of parallel crystal planes in such a way, that each lattice cite belongs to one of the planes in this series.<sup>20</sup> This is illustrated in Fig. 5.3.

Each family of parallel crystal planes can be uniquely characterized by three integer numbers (hkl) called Miller indices. To find these indices, one has to consider the intersections of the plane with the main crystal axis in the units of the lattice cell parameters. In the example shown in Fig. 5.3a, these intersections are U = 2, V = 2, W = 4. The equation of this plane in the system of coordinates defined by the unit cell vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$  is

$$\frac{x}{U} + \frac{y}{V} + \frac{z}{W} = 1. (5.4)$$

The Miller indices (hkl) are defined as h = K/U, k = K/V and l = K/W, where the integer number K is selected in such a way, that (hkl) are the smallest possible integers (relative primes). In the case shown in Fig. 5.3a, K = 4 and  $(hkl) = K \cdot (\frac{1}{U}\frac{1}{V}\frac{1}{W}) = K \cdot (\frac{1}{2}\frac{1}{2}\frac{1}{4}) = (221)$  If the plain is parallel to one of the axis, the intersection can be formally set to be at the infinite distance. This means, that the corresponding Miller index equals to zero (formally,  $\frac{1}{\infty} = 0$ ). Miller indices can also be negative. Any crystal plane belonging to the (hkl) family can be described with

an equation

$$hx + ky + lz = D, (5.5)$$

where D is some constant. For example, the plane passing through the origin of coordinates has D = 0.

#### **Reciprocal lattice** 5.1.2

The translational symmetry of a periodic crystal lattice has a deep impact on all processes happening in crystals. To illustrate this, let us consider any function  $\psi(\mathbf{r})$ , which has the same translation symmetry as the crystal lattice, i.e.

$$\psi(\mathbf{r} + \mathbf{R}_{\mathbf{n}}) = \psi(\mathbf{r}). \tag{5.6}$$

For example,  $\psi(\mathbf{r})$  can be local concentration of electrons in a crystal. Any periodic function can be expanded into a Fourier series<sup>21</sup>

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}\mathbf{r}},\tag{5.7}$$

where complex-valued coefficients  $C_{\mathbf{G}}$  do not depend on  $\mathbf{r}$ .

Similarly to 1D case, the Fourier series (Eq. (5.7)) contains infinite but countable number of terms. The translation symmetry of a periodic crystal

$$f(x) = \sum_{n = -\infty}^{+\infty} C_n e^{i\frac{2\pi}{L}nx},$$

$$C_n = \frac{1}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) e^{-i\frac{2\pi}{L}nx} dx$$



Fig. 5.3: (a) Crystal plane with Miller indices (hkl) passing through three lattice points on the main crystal axes.

(b) A family of parallel crystal planes (*hkl*), (c) Side view of the same (hkl) crystal planes family

where

 $<sup>^{20}</sup>$ Note that crystal planes go thought the sites of the crystal lattice, not the atoms. The atoms in the crystal structure can lie between the crystal planes.

 $<sup>^{21}</sup>$ This is just a generalization of a well-known Fourier expansion a function with period L in 1D case:

allows only terms with certain vectors  $\mathbf{G}$  to be present in the sum. From Eq. (5.7), we obtain

$$\psi(\mathbf{r} + \mathbf{R}_{\mathbf{n}}) = \sum_{\mathbf{G}} C_{\mathbf{G}} e^{i\mathbf{G}(\mathbf{r} + \mathbf{R}_{\mathbf{n}})} = \sum_{\mathbf{G}} (C_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}_{\mathbf{n}}}) e^{i\mathbf{G}\mathbf{r}}.$$
 (5.8)

Fourier series given by Eqs. (5.7) and (5.8) should be equal, therefore the values of the Fourier coefficients should be equal as well. It means, that only vectors **G** which satisfy the condition

$$e^{i\mathbf{GR_n}} = 1$$
 or  $\mathbf{GR_n} = 2\pi \cdot m$  for any  $\mathbf{R_n} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$  (5.9)

can be present in the Fourier expansion of a periodic function  $\psi(\mathbf{r})$ . All vectors **G** which satisfy the condition (5.9) form reciprocal lattice.<sup>22</sup>

Let us define an explicit expression for the reciprocal lattice vectors  $\mathbf{G}$ . For this let us first find three non-collinear vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$  that satisfy the condition 5.9. These three vectors are called the reciprocal unit vectors. Their choice is not unique, but one of the possible (and the most practical) solutions is

$$\mathbf{b}_{1} = \frac{2\pi}{\Omega} \left[ \mathbf{a}_{2} \times \mathbf{a}_{3} \right],$$
  

$$\mathbf{b}_{2} = \frac{2\pi}{\Omega} \left[ \mathbf{a}_{3} \times \mathbf{a}_{1} \right],$$
  

$$\mathbf{b}_{3} = \frac{2\pi}{\Omega} \left[ \mathbf{a}_{1} \times \mathbf{a}_{2} \right],$$
(5.10)

where  $\Omega = \mathbf{a}_1 \cdot [\mathbf{a}_2 \times \mathbf{a}_3]$  is the volume of the unit cell in real space (Fig. 5.4). By direct calculations, it is easy to show that the unit cell vectors  $\mathbf{a}_i$  (i = 1, 2, 3) and reciprocal unit vectors  $\mathbf{b}_j$  (j = 1, 2, 3) fulfill the following condition:

$$\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{i,j}. \tag{5.11}$$

It is also easy to check, that any linear combination of the reciprocal unit vectors with integer coefficients h, k and l also satisfies the condition 5.9:

$$\mathbf{G}_{hkl} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3,\tag{5.12}$$

 $\mathbf{G}_{hkl} \cdot \mathbf{R}_{\mathbf{n}} = (h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot (n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3) = 2\pi \cdot (hn_1 + kn_2 + ln_3).$ (5.13)

Moreover, Eq. (5.12) defines all possible reciprocal space vectors **G**. Indeed, let us assume that there is any other vector **G**, which cannot be represented as in Eq. (5.12). It can anyway be represented as a liner combination of three non-collinear reciprocal unit vectors, but at least one coefficient, h, k or l is non-integer. Let us assume that h s non-integer. In this case,  $\mathbf{G} \cdot \mathbf{a}_1 = 2\pi \cdot h \neq 2\pi \cdot m$ , which contradicts definition (5.9), which should be true for any  $\mathbf{R}_n$ , including  $\mathbf{R}_n = \mathbf{a}_1$ .

Therefore, we obtained that all possible vectors of reciprocal lattice can be written as a linear combination of three reciprocal unit vectors with integer coefficients, called Miller indices. It means that reciprocal vectors form a periodic lattice in reciprocal space, similar to the crystal lattice in real space defined by Eq. (5.1). Using Eqs. (5.10), it can be shown that the volume of the reciprocal unit cell is  $2\pi/\Omega$  (volume of the parallelopiped formed by vectors  $b_1$ ,  $b_2$  and  $b_3$ ). Moreover, if all angles between the unit cell vectors are straight ( $\alpha = \beta = \gamma = 90^{\circ}$ ), the reciprocal unit vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$  are parallel to  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ , and have lengths  $b_1 = 2\pi/a_1$ ,



Fig. 5.4: (a) Unit cell in real space with volume  $\Omega$ . (b) Corresponding unit cell in reciprocal space with volume  $2\pi/\Omega$ .



Fig. 5.5: (a) Orthorhombic unit cell in real space  $(\alpha = \beta = \gamma = 90^{\circ})$ . (b) Corresponding unit cell in reciprocal space. The reciprocal unit cell vectors  $b_1 = 2\pi/a_1$ ,  $b_2 = 2\pi/a_2$  and  $b_3 = 2\pi/a_3$  are orthogonal to each other.

 $<sup>^{22}\</sup>mathrm{The}$  reciprocal lattice is reciprocal to the corresponding real lattice defined by Eq. (5.1).

 $b_2 = 2\pi/a_2$  and  $b_3 = 2\pi/a_3$  (Fig. 5.5). In the general case of an obliqueangled unit cell, the relation between the real and reciprocal unit cell vectors is more complex.

Eq. (5.12) defines all possible wave vectors of the plane waves  $e^{i\mathbf{G}_{hkl}\mathbf{r}}$  with the periodicity of the lattice, i.e. which are invariant to the translation over any vector in Eq. (5.1). Let us now prove another geometrical interpretation of the reciprocal lattice vectors, namely, their connection to crystal planes. Indeed, for any constant D, equation

$$\mathbf{G}_{hkl}\mathbf{r} = D \tag{5.14}$$

defines a plane oriented perpendicular to the vector  $\mathbf{G}_{hkl}$ . From all collinear vectors  $\mathbf{G}_{hkl}$ , let us consider  $\mathbf{G}_{hkl}^{\min}$  with the minimal length. The plane defined above has Miller indices (hkl), which can be proved by substituting  $\mathbf{r} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3$  into Eq. (5.14) and obtaining Eq. (5.5).

Due to condition  $\mathbf{G}_{hkl}^{\min} \mathbf{R}_{\mathbf{n}} = 2\pi m$  in Eq. (5.9), every lattice point  $\mathbf{R}_{\mathbf{n}}$  will belong to one of such planes. Let us consider two neighboring parallel lattice planes, which are characterized by two consecutive integer numbers m and m + 1:

$$\mathbf{G}_{hkl}^{\min} \mathbf{R}_n = 2\pi \cdot m, 
\mathbf{G}_{hkl}^{\min} \mathbf{R}'_n = 2\pi \cdot (m+1).$$
(5.15)

From Fig. 5.6, the distance between these two adjacent crystal planes is

$$d_{hkl} = \left(\mathbf{R}'_n - \mathbf{R}_n\right) \cdot \frac{\mathbf{G}_{hkl}^{\min}}{\left|\mathbf{G}_{hkl}^{\min}\right|} = \frac{2\pi}{\left|\mathbf{G}_{hkl}^{\min}\right|}.$$
(5.16)

Thus, we proved that each reciprocal vector  $\mathbf{G}_{hkl}$  corresponds to a family of parallel lattice planes (hkl), and the distance between these planes can be calculating using Eq. (5.16).

Often the fact that the crystal planes should always go though the crystal lattice points is neglected. This relaxation of the crystal plane definition usually does not lead to misunderstanding, because the real atoms are also not always placed at the sites of the crystal lattice. In this case, the distance between such planes is  $d_{hkl} = 2\pi/|\mathbf{G}_{hkl}|$ .

For orthorhombic crystal lattice  $(a_1 \neq a_2 \neq a_3 \text{ and } \alpha = \beta = \gamma = 90^\circ)$ , this gives for the distance between (hkl) planes:

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a_1}\right)^2 + \left(\frac{k}{a_2}\right)^2 + \left(\frac{l}{a_3}\right)^2}} \quad \text{(orthorhombic)}, \tag{5.17}$$

which simplifies even further for the cubic lattice  $(a_1 = a_2 = a_3 = a \text{ and } \alpha = \beta = \gamma = 90^\circ)$ :

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$
 (cubic). (5.18)

For the lattices with non-orthogonal unit cell vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ , the equation for calculation of the interplane distance  $d_{hkl}$  becomes more complex.

### 5.2 Scattering from a single crystal

# 5.2.1 Bragg's law

The easiest way to interpret diffraction from a crystal is to split the crystal lattice into a family of parallel crystal planes and consider the interference



Fig. 5.6: Two adjacent (hkl) crystal planes defined by Eqs. (5.15).

of the waves scattered from different crystal planes. This is analogous to the scattering from multilayer (section 2.4), but even easier, because the scattering angles are typically large, so we can neglect the total external reflection and effects of multiple scattering.<sup>23</sup>

The wave is scattered by a crystal plane in such a way, that the angle of incidence equals to the outcoming angle (this follows from the symmetry considerations, because the projection of the wave vector onto the crystal plane should be conserved in a scattering process). From Fig. 5.7, the path difference for the waves scattered from two adjacent crystal planes is  $2d_{hkl} \cdot \sin \theta$ . A constructive interference is observed when the path difference is a multiple of the wavelength

$$2d_{hkl} \cdot \sin \theta = m \cdot \lambda. \tag{5.19}$$

This condition is known as Bragg's law. The integer number m is a diffraction order. The maxima of the scattered intensity, observed for the experimental conditions given by Eq. (5.19) are called Bragg peaks.

In practice, it is always possible to set m = 1 and by considering the scattering by the planes with higher values of the Miller indices (hkl), as shown in Fig. 5.8. In this case, the Bragg law can be written as

$$2d_{hkl} \cdot \sin \theta = \lambda, \tag{5.20}$$

where  $d_{hkl}$  are defined via the corresponding vector of reciprocal lattice as

$$d_{hkl} = \frac{2\pi}{|\mathbf{G}_{hkl}|}.$$
(5.21)

Eqs. (5.20-5.21) give a connection between the unit cell parameters (which are needed to calculate  $\mathbf{G}_{hkl}$ ) and the scattering angles.

Bragg's law provides a pictorial connection between the scattering angles and a certain set of lattice planes. This is why it is often used for the analysis of the diffraction patterns from crystals. At the same time, it doesn't provide any information about the intensity of the scattered waves. The intensities can be calculated only when the positions or real atoms are taken into account, which will be done in the following section.

### 5.2.2 Laue condition

Let us consider scattering in the same manner as it was done in section 3.2.1. To be specific, we will focus on X-ray scattering, however the same derivation can be done for neutrons or any other wave.

Neglecting the constants, such as intensity of the incoming beam, and the polarization factor, the magnitude of the scattered wave is

$$E \propto \sum_{\mathbf{n},j} f_j(q) e^{-i\mathbf{q}\mathbf{r}_{\mathbf{n},j}},\tag{5.22}$$

where  $f_j(q)$  is the scattering form factor of the atom "j". Substituting the positions of the atoms from Eq. (5.3), we can regroup the sum over all atoms in the crystal into the sum over a single unit cell (internal sum) and the sum over all unit cells in the crystal (external sum):

$$E \propto \underbrace{\sum_{\mathbf{n}} e^{-i\mathbf{q}\mathbf{R}_{\mathbf{n}}}}_{\text{lattice sum}} \cdot \underbrace{\sum_{j} f_{j}(q) e^{-i\mathbf{q}\boldsymbol{\rho}_{j}}}_{\text{structure fator}}.$$
(5.23)

 $^{23}$ One has to take into account the effects of multiple scattering when crystals are large. This is considered in dynamical theory of scattering



Fig. 5.7: (a) Scattering of a wave from crystal lattice place. (b) Increased view of the scattering from two adjacent crystal planes for derivation of Eq. (5.19). The path difference is marked with red.



Fig. 5.8: (a) First (m = 1) and second (m = 2) diffraction order by scattering from parallel crystal planes (hkl). (b) Alternative representation of the same scattering process, where the second diffraction order is considered as the first diffraction order from the planes with twice smaller distance (or twice higher Miller indices (2h 2k 2l)).

In order to observe the non-zero scattered intensity, both factors in Eq. (5.23) should be non-zero. Let us focus first on the lattice sum, and the crystal structure factor will be considered in section 5.2.5.

The maximum of the scattered intensity is achieved when all complex exponentials in Eq. (5.23) have the same phase. Since for the term with  $\mathbf{R_n} = 0$  the complex phase is zero, it means that it should be also zero (or  $2\pi \cdot m$ ) for all other terms. Thus, we can expect the maximum intensity of the scattered waves for such values of the scattering vector  $\mathbf{q}$ , which fulfill the condition  $e^{-i\mathbf{qR_n}}$  for all vectors  $\mathbf{R_n}$ . This is identical to condition (5.9), meaning that the maxima of the scattered intensity (Bragg peaks) when

$$\mathbf{q} = \mathbf{G}_{hkl}.\tag{5.24}$$

This equation is called Laue condition. More detailed analysis of the lattice sum will be done in section 5.2.3. It can be shown [46, 6, 47, 42], that the Laue condition in reciprocal space (5.24) and the Bragg condition in real space (5.19) are equivalent.

### 5.2.3 Influence of crystal size (Scherrer's broadening)

Using the periodic arrangement of the unit cells in the crystal given by Eq. (5.1), we can write the lattice sum in Eq. (5.23) as

$$\sum_{\mathbf{n}} e^{-i\mathbf{q}\mathbf{R}_{\mathbf{n}}} = \sum_{n_1}^{N_1} e^{-i\mathbf{q}\mathbf{a}_1 n_1} \cdot \sum_{n_2}^{N_2} e^{-i\mathbf{q}\mathbf{a}_2 n_2} \cdot \sum_{n_3}^{N_3} e^{-i\mathbf{q}\mathbf{a}_3 n_3}, \quad (5.25)$$

where  $N_1$ ,  $N_2$  and  $N_3$  are the size of the crystal in three dimensions.

Each factor in Eq. (5.25) can be calculated using the formula for the sum of the geometric series:

$$\sum_{n=1}^{N} \left( e^{-i\mathbf{q}\mathbf{a}} \right)^n = e^{-i\mathbf{q}\mathbf{a}} \cdot \frac{1 - \left( e^{-i\mathbf{q}\mathbf{a}} \right)^N}{1 - e^{-i\mathbf{q}\mathbf{a}}} = e^{-i\mathbf{q}\mathbf{a}(N-1)/2} \cdot \frac{\sin\left(\frac{\mathbf{q}\mathbf{a}N}{2}\right)}{\sin\left(\frac{\mathbf{q}\mathbf{a}}{2}\right)}.$$
 (5.26)

The complex exponent  $e^{-i\mathbf{q}\mathbf{a}(N-1)/2}$  does not enter the final result for the intensity of the scattered wave, since  $I \propto |E|^2$ . Finally, for the intensity of the scattered wave from a 3D crystal we can write:

$$I \propto \left| \frac{\sin\left(\frac{\mathbf{q}\mathbf{a}_1 N_1}{2}\right)}{\sin\left(\frac{\mathbf{q}\mathbf{a}_1}{2}\right)} \right|^2 \cdot \left| \frac{\sin\left(\frac{\mathbf{q}\mathbf{a}_2 N_2}{2}\right)}{\sin\left(\frac{\mathbf{q}\mathbf{a}_2}{2}\right)} \right|^2 \cdot \left| \frac{\sin\left(\frac{\mathbf{q}\mathbf{a}_3 N_3}{2}\right)}{\sin\left(\frac{\mathbf{q}\mathbf{a}_3}{2}\right)} \right|^2.$$
(5.27)

The scattered intensity reaches maximum when the denominators in Eq. (5.27) are close to zero, i.e. at the points

$$\begin{cases} \mathbf{q}\mathbf{a}_1 = 2\pi h \\ \mathbf{q}\mathbf{a}_2 = 2\pi k \quad \Leftrightarrow \mathbf{q} = \mathbf{G}_{hkl}. \\ \mathbf{q}\mathbf{a}_3 = 2\pi l \end{cases}$$
(5.28)

This is equivalent to Bragg peaks from an infinite crystal. The value in the maximum can be obtained from the L'Hôpital rule:

$$I_{\rm max} \propto (N_1 N_2 N_3)^2.$$
 (5.29)

The width of the peaks  $\Delta \mathbf{q}$  can be estimated as a distance between two points around the Bragg peak when the nominator equals to zero:

$$\Delta q = \frac{2\pi}{aN}.\tag{5.30}$$



Fig. 5.9: Intensity of the scattered wave obtained from Eq. (5.27) in 1D case for different values of N.

The width of the peak can be different in three different directions of the reciprocal space vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$  and  $\mathbf{b}_3$ .

Dependence of the scattered intensity given by Eq. (5.27) is shown in Fig. 5.9 for a 1D case. It follows that the Bragg peaks are narrow for the large crystals  $(N \gg 1)$ , while for the smaller crystals the Bragg peaks get broader. This effect is called Scherrer's broadening. By measuring the width of the Bragg peaks, one can estimate the size of the crystals  $L \approx aN$  (or crystalline domains). This is often written as the Scherrer equation:

$$L = \frac{K\lambda}{\Delta(2\theta)\cos\theta}.$$
(5.31)

Here  $K \sim 1$  is a dimensionless constant which depends on the shape of the crystal,  $\theta = \arcsin\left(\frac{q\lambda}{4\pi}\right)$  is the scattering angle of the Bragg peak, and  $\Delta(2\theta) = \frac{2\Delta q\lambda}{4\pi\cos\theta}$  is the width of the Bragg peak (in the units of the scattering angle) Eqs. (5.30) written in reciprocal space and (5.31) written in real space are equivalent to each other.

# 5.2.4 Ewald's sphere and scans across the reciprocal space

In most practical cases, X-ray scattering can be considered to be elastic. This means that the wave vectors of the incoming and scattered photons have the same length,  $|\mathbf{k}_{in}| = |\mathbf{k}_{out}| = k = 2\pi/\lambda$ . From this it follows that the end of the scattering vector  $\mathbf{q} = \mathbf{k}_{out} - \mathbf{k}_{in}$  in reciprocal space lies on a sphere with radius  $k = 2\pi/\lambda$ , called Ewalds' sphere. The construction of Ewald's sphere is shown in Fig. 5.10. From this scheme one can see, that by placing the detector at different positions, i.e. by scanning scattering angle  $2\theta$ , one always probes the points of reciprocal space lying on the Ewald sphere.

Ewald's sphere is extremely useful when a scan of a reciprocal space of a crystalline sample is performed [48]. Three most common type of scans with a point detector (1D detector) are detector scans, specular scans and rocking scans. Let us discuss the in more detail.

• Detector scan ( $2\theta$  scan): the sample is fixed, the incoming beam is also fixed, the 1D detector is moving around the sample, so that the scattering angle  $2\theta$  is changing. This situation is essentially illustrated by Fig. 5.10. In this type of scan, one probes reciprocal space along the curved Ewald sphere.

In the case of a 2D detector, the image recorded by the detector is therefore a cross-section of the reciprocal space by the curved Ewald sphere.

• Specular scan  $(\theta - 2\theta \text{ scan})$ : the sample is fixed, the incoming beam and the 1D detector are rotated simultaneously by the same angle  $\Delta\Theta$ , so that the scattering vector **q** changes its length but not the direction. In a laboratory setup, this is most commonly done by rotating the Xray tube and the detector simultaneously around the fixed sample, as illustrated in Fig. 5.11. The same scan can be also performed if the incoming beam is fixed, and the sample is rotated by an angle  $\theta$ while the detector is simultaneously rotated by twice the angle  $2\theta$ . In this type of scan, one probes reciprocal space along a straight line in reciprocal space, usually normal to the sample's surface.

Illustration of the probed reciprocal space in the case of a 2D detector is shown in Fig. 5.13



Fig. 5.10: (a) Scheme of the scattering in real space (detector scan). (b) 2D scheme of the construction of Ewald's sphere in reciprocal space. The sphere passes through the origin  $\mathbf{q} = 0$ . Blue points indicate the vectors  $\mathbf{G}_{hkl}$  of the reciprocal lattice. According to Eq. (5.24), a Bragg peak occurs only if  $\mathbf{q} = \mathbf{G}_{hkl}$ , i.e. only if the Ewald sphere intersects with one of the sites of the reciprocal lattice.



Fig. 5.11: Scheme of a specular  $(\theta - 2\theta)$  scan, during which the incoming beam and the detector are rotated simultaneously by the same angle  $\Delta\Theta$ . In this case, the scattering vector **q** changes its length, but not the direction.

• Rocking scan ( $\omega$  scan): the sample is being rotated (rocked), while the incoming beam and the detector are fixed. This type of scan is illustrated in Fig. 5.12. The same effect can be achieved on a fixed sample, when the incoming beam and the detector are rotated around the angle over the same angle  $\omega$  but in opposite directions. In this scan, the length of the scattering vector **q** remains constant, but its direction changes during the scan. In a way, this gives one a crosssection of the reciprocal space in the direction perpendicular to the direction of a specular scan.

Illustration of the probed reciprocal space for the rocking scan in the case of a 2D detector is shown in Fig. 5.13

## 5.2.5 Crystal structure factor (forbidden reflections)

Let us turn back to Eq. (5.23), and consider the intensity of a Bragg reflection:

$$I \propto \left| \sum_{\substack{\mathbf{n} \\ \text{lattice sum}}} e^{-i\mathbf{q}\mathbf{R}_{\mathbf{n}}} \right|^{2} \cdot \left| \sum_{\substack{j \\ \text{structure fator}}} f_{j}(q) e^{-i\mathbf{q}\boldsymbol{\rho}_{j}} \right|^{2} \propto N^{2} \cdot |F_{hkl}|^{2}.$$
(5.32)

We have already shown that the diffraction pattern from an ideal crystal consists of sharp Bragg peaks observed when  $\mathbf{q} = \mathbf{G}_{hkl}$  (Eq (5.24)), i.e. when the scattering from all unit cells happens in phase. The magnitude of the scattered wave is therefore proportional to the number of unit cells N, and intensity is proportional to  $N^2$ .

The second factor which determines the intensity of a Bragg reflection - the structure factor  $F_{hkl}$  - represents the scattering from a single unit cell. Here we should not that for an ideal crystal it only makes sense to consider the structure factor only at the positions of the Bragg peaks, i.e. for  $\mathbf{q} = \mathbf{G}_{hkl}$ , because otherwise the scattering intensity is zero regardless the structure factor.

For these given values  $\mathbf{q} = \mathbf{G}_{hkl}$ , the structure factor can be directly calculated, because it consists of a finite number of terms, which is equal to the amount of atoms within a unit cell.

For a simple unit cell, which contains only a single atom with an atomic scattering factor f(q), the structure factor equals to  $fe^{-i\mathbf{q}\boldsymbol{\rho}}$ . By selecting the origin of the unit cell at the point where the atom is, we can set  $\boldsymbol{\rho} = 0$ , which results in  $F_{hkl} = f$ .

For a body-centered structure, such as represented in Fig. 5.2, the basis  $\rho_i$  consists of two atoms:

$$\boldsymbol{\rho}_{j} = \begin{cases} 0, & \text{for } j = 1, \\ \frac{1}{2}(\mathbf{a}_{1} + \mathbf{a}_{2} + \mathbf{a}_{3}), & \text{for } j = 2. \end{cases}$$
(5.33)

Using  $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi \delta_{i,j}$  (Eq. (5.11), the structure factor can be easily calculated:

$$F_{hkl} = \sum_{j=1}^{2} f_j \exp\left[-i(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3)\boldsymbol{\rho}_j\right]$$
  
=  $f_1 \exp\left[-i(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot 0\right]$   
+  $f_1 \exp\left[-i(h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3) \cdot \frac{1}{2}(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)\right]$   
=  $f_1 + f_2 \exp\left[-\pi(h + k + l)\right].$  (5.34)



Fig. 5.12: (a) Scheme of a rocking ( $\omega$ ) scan when the sample is rocked by an angle  $\omega$ , while the incoming beam and the detector remain still. (b) The same scan in the geometry when the sample is fixed, and the X-ray source and the detector are rotated by the angle  $\omega$  but in opposite directions.

Since the Miller indices are integer numbers, the exponential in Eq. (5.34) can take only two values: +1 if (h+k+l) is an even number or -1 if (h+k+l) is an odd number. The intensity of the corresponding Bragg reflections is therefore proportional to  $(f_1 + f_2)^2$  or  $(f_1 - f_2)^2$ . If the two atoms in the body-centered unit cell are the same (i.e.  $f_1 = f_2$ ), the intensity of some Bragg peaks will be zero. Such peaks, for which there is a destructive interference of the waves scattered by different atoms within a crystal unit cell, are called *forbidden reflections*. These reflection are allowed by the Bragg law, but their intensity is zero because of the structure factor. Deviations of the atoms from their position may break the interference condition, and the forbidden reflections will have small but non-zero intensity. Experimentally it is sometimes easier to detect the change in the intensity of a forbidden reflection due to a structural phase transition (intensity is zero for one structure and small but non-zero for another structure), while the intensity of bright allowed reflections may change only insignificantly.

The same calculations, as performed in Eq. (5.34), can be done for other crystal structures, but the conditions for the allowed and forbidden peaks will depend on the structure. A short summary is given below:

- **simple**: all reflections are allowed.
- **body-centered**: reflections with (h + k + l) is an even number allowed, reflections with (h + k + l) is an odd number forbidden.
- face-centered: reflections for which h, k, l have the same oddity allowed (for example,  $(2, 0, \overline{4})$ ), reflections for which h, k, l are mixed forbidden (for example, (3, 0, 0)).

# 5.3 Powder diffraction

Most of materials exist in a polycrystalline form. It means that they do not crystallize in single crystal but consist of small crystal grain which can be oriented in any direction. The same description can be applied to powders, in which each particle is a small single crystal with a random orientation. Large single crystals, as were considered in the previous chapter, are rather exception. Let us consider diffraction from a polycrystalline or powder sample.

The reciprocal lattice of each small crystal grain looks as it is shown in Fig. 5.10b, and the diffraction pattern from it is determined by the crosssection of the reciprocal lattice with the Ewald sphere. To take into account the random orientation of the grain, we have to average the reciprocal lattice over all possible orientations. For each new orientation of the grain, the reciprocal lattice is rotated in 3D space around its origin at  $\mathbf{q} = 0$ . It means, that if all orientations are equally possible, each Bragg peak at  $\mathbf{q} = \mathbf{G}_{hkl}$  will be "smeared" over a sphere of radius  $|\mathbf{G}_{hkl}|$  with a center at  $\mathbf{q} = 0$ . Such a sphere always intersects with the Ewald sphere, and the intersection is always a ring around the direction  $\mathbf{k}_{in}$ , as can be seen from Fig. 5.10b. For such a ring, the scattering angle  $2\theta$  is fixed by the Bragg law (i.e. it is determined by the crystal lattice parameters), but due to a random orientation of the crystal grain, the scattering can happen in any direction with respect to the incoming beam  $\mathbf{k}_{in}$ .

This produces cones of scattering, in which the scattering is possible. On a detector, one can see not single Bragg peaks (as in the case of a single crystal), but rings around the direction of an incoming beam  $\mathbf{k}_{in}$ . These rings are called Debye-Scherrer powder diffraction rings, and their origin from individual Bragg peaks is illustrated in Fig. 5.14. If the crystal grains



Fig. 5.13: (a) 3D scheme of the scattering experiment with a 2D detector in real space. (b) Cross-sections of the reciprocal space which are recordered by the 2D detector during a specular scan and a rocking scan. The coordinate system is in the reference frame of the sample. Note that each detector image corresponds to a cross-section of the reciprocal space by a curved sphere.

have some preferred orientation, the Debye-Scherrer rings may not have a uniform intensity, or they can split into the arcs.



Fig. 5.14: (a) Scheme of the scattering from a singe crystal. Several sharp Bragg reflections are visible a detector. (b) Scattering from a polycrystalline sample, where the grains have some preferred orientation. The Bragg peaks are "smeared" in the angular direction due some "randomness" in the orientation of individual crystal grains. (c) Scattering from a powder sample, where the grains gave a random orientation. The Bragg peaks are smeared so much, that they from uniform Debye-Scherrer rings.

# **Appendices**

# A Fourier transform and its properties

The Fourier transform of the electron density naturally appears when considering diffraction of a plane monochromatic wave (see Eqs. (1.28-1.29)). The same is true for neutron diffraction (Eq. (1.48)). This is a result of two main assumptions that hold true for many scattering experiments (but not all):

- approximation of weak interaction of a plane monochromatic wave (Xrays or neutrons) with matter, which allows one to neglect absorption and multiple scattering. This approximation is called *kinematic* scattering. Including absorption and multiple scattering into the diffraction theory is subject of the *dynamical* theory.
- approximation of far field diffraction (Fraunhofer diffraction), which allows one to consider the scattered wave as plane waves. This approximation is valid when  $D^2/(R\lambda) \ll 1$ , where D is the size of the scattering system and R is the distance from the system to the observer.

Therefore, the Fourier transform appears multiple times in this text. Below we give a list of some identities related to the Fourier transform.

• Definition of the Fourier transform:<sup>24</sup>

$$F(q) = \int_{-\infty}^{\infty} f(x)e^{-iqx}dx \text{ (direct Fourier transform)}$$
(A.1)

$$f(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} F(q) e^{iqx} dq \text{ (inverse Fourier transform)}$$
(A.2)

• Properties of the Fourier transform:

$$f(x) = ag(x) + bh(x) \iff F(q) = aG(q) + bH(q) \text{ (linearity)} (A.3)$$

$$h(x) = f(x - x_0) \iff H(q) = F(q)e^{ix_0q} \text{ (shifting)}$$
 (A.4)

$$h(x) = f(ax) \iff H(k) = \frac{1}{|a|}F(q/a) \text{ (scaling)}$$
 (A.5)

$$f(x) \xrightarrow{\mathscr{F}} F(q) \iff F(q) \xrightarrow{\mathscr{F}} 2\pi f(-x) \text{ (duality)}$$
 (A.6)

$$F(0) = \int_{-\infty}^{\infty} f(x)dx \text{ (normalization)}$$
(A.7)

• Definition of the convolution:

$$f(x) \otimes g(x) \equiv (f \otimes g)(x) = \int_{-\infty}^{\infty} f(x')g(x - x')dx'$$
(A.8)

• Convolution theorem:

$$f(x) = g(x) \otimes h(x) \iff F(q) = G(q) \times H(q)$$
 (A.9)

$$\underbrace{f(x) = g(x) \times h(x)}_{=} \iff F(q) = \frac{1}{2\pi} G(q) \otimes H(q)$$
(A.10)

<sup>&</sup>lt;sup>24</sup>Other definitions are also common in literature. They may differ from the given one by the prefactor and the exponential under the integral  $(e^{-i2\pi qx}$  instead of  $e^{-iqx})$ .

• Fourier transform of a derivative:

$$f(x) = \frac{dg}{dx} \iff F(q) = iqG(q)$$
 (A.11)

• Fourier transform of the Gaussian function

$$g(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-\frac{x^2}{2\sigma^2}}$$

$$G(q) = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{\infty} e^{-\frac{x^2}{2\sigma^2}} e^{-iqx} dx = e^{\frac{q^2\sigma^2}{2}}$$
(A.12)

• Fourier transform of the Lorentzian function

$$l(x) = \frac{a}{\pi (a^2 + x^2)}$$

$$L(q) = \frac{a}{\pi} \int_{-\infty}^{\infty} \frac{1}{x^2 + a^2} e^{-iqx} dx = e^{-a|q|}$$
(A.13)

• Integral representation of the Dirac delta function

$$\int_{-\infty}^{\infty} e^{-iqx} dx = 2\pi\delta(q) \tag{A.14}$$

• Fourier transform of the Heaviside step function

$$h(x) = \begin{cases} 1, & \text{if } x \le 0\\ 0, & \text{if } x > 0 \end{cases}$$

$$H(q) = \int_{-\infty}^{\infty} h(x)e^{-iqx}dx = \frac{1}{iq} + \pi\delta(q)$$
(A.15)

• Fourier transform of the rectangular function

$$r(x) = \begin{cases} 1, & \text{if } |x| \le a/2\\ 0, & \text{if } |x| > a/2 \end{cases}$$

$$R(q) = \int_{-\infty}^{\infty} r(x)e^{-iqx}dx = a\frac{\sin\frac{qa}{2}}{\frac{qa}{2}} = a \cdot \operatorname{sinc}\left(\frac{qa}{2}\right)$$
(A.16)

### B Incoherent X-ray scattering from a many-electron atom

Let us consider coherent and incoherent (i.e. elastic and inelastic) X-ray scattering from an atom with Z electrons. As it was discussed in section 1.1.7, a coherent X-ray scattering (elastic) is related to the scattering process in which electrons of the atom remain in their ground function. More specifically, the coherent X-ray scattering cross-section can be written as

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |M_{00}|^2, \tag{B.17}$$

where  $\left(\frac{\partial \sigma}{\partial \Omega}\right)_e$  is the Thomson scattering cross-section for a single electron given by Eq. (1.18) and  $M_{00} = \langle 0 | \hat{V} | 0 \rangle$  is the corresponding matrix element. Let us denote by  $\psi_0$  a many-electron wave function of the ground state, which depends on coordinates of all electrons  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_Z$ . Let us also denote by  $\hat{V} = \sum_{n=1}^{Z} e^{-i\mathbf{q}\mathbf{r}_n}$  the operator which in the first order approximation describes the interaction of each electron with the electromagnetic field of the X-ray wave. Then the matrix element  $M_{00}$  can be explicitly written as

$$M_{00} = \sum_{n=1}^{Z} \int \psi_{0}^{*}(\mathbf{r}_{1},...,\mathbf{r}_{Z}) e^{-i\mathbf{q}\mathbf{r}_{n}} \psi_{0}(\mathbf{r}_{1},...,\mathbf{r}_{Z}) d\mathbf{r}_{1}...d\mathbf{r}_{Z}.$$
 (B.18)

The integration over all coordinates of the electrons, except of  $\mathbf{r}_n$ , can be performed. In result, one obtains the absolute squared value of a single-electron wave function  $|\phi_n(\mathbf{r}_n)|^2$ , which determines the probability of the  $n^{\text{th}}$  electron to be found at the point  $\mathbf{r}_n$ . The total electron density can be calculated as a sum of all  $|\phi_n(\mathbf{r})|^2$ :

$$\rho_{el}(\mathbf{r}) = \sum_{n=1}^{Z} |\phi_n(\mathbf{r})|^2 \tag{B.19}$$

We can then write

$$M_{00} = \sum_{n=1}^{Z} \int |\phi_n(\mathbf{r}_n)|^2 e^{-i\mathbf{q}\mathbf{r}_n} d\mathbf{r}_n = \int \rho_{el}(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} d\mathbf{r} \equiv f(\mathbf{q}).$$
(B.20)

This result matches with the X-ray scattering form factor of an atom  $f(\mathbf{q})$  derived in Eq. (1.29). Finally, the coherent X-ray scattering cross-section can be written via the atomic scattering form factor as

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{coh} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot |f(q)|^2. \tag{B.21}$$

This result has the same structure as Eq. (1.38) for an atom with a single electron.

Calculating the incoherent scattering function s(q), introduced in Eq. (1.32) is a more difficult problem. As it was discussed in section 1.1.7, an incoherent X-ray scattering (inelastic) involves transition of the electrons to the excited state  $\nu$ . To calculate the incoherent scattering cross-section, one has to sum over all possible excited states (compare with Eq. (B.17))

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{inc} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot \underbrace{\sum_{\nu>0} |M_{0\nu}|^2}_{s(\mathbf{q})} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_e \cdot s(\mathbf{q}), \quad (B.22)$$

where

$$M_{0\nu} = \langle \nu | \hat{V} | 0 \rangle = \sum_{n=1}^{Z} \langle \nu | e^{-i\mathbf{q}\mathbf{r}_{n}} | 0 \rangle$$
  
$$= \sum_{n=1}^{Z} \int \psi_{\nu}^{*}(\mathbf{r}_{1}, ..., \mathbf{r}_{Z}) e^{-i\mathbf{q}\mathbf{r}_{n}} \psi_{0}(\mathbf{r}_{1}, ..., \mathbf{r}_{Z}) d\mathbf{r}_{1} ... d\mathbf{r}_{Z}.$$
(B.23)

Here  $\psi_{\nu}(\mathbf{r}_1, ..., \mathbf{r}_Z)$  denotes the many-electron wave function in the excited state  $\nu > 0$ . The function  $s(\mathbf{q}) = \sum_{\nu>0} |M_{0\nu}|^2$  is called incoherent scattering function.

Now we can do the same trick as in Eq. (1.37), i.e. add and subtract  $|M_{00}|^2$  and use the closure relation (see footnote 3 on page 8)

$$\sum_{\nu>0} |M_{0\nu}|^2 = \sum_{\nu\geq0} |M_{0\nu}|^2 - |M_{00}|^2 = \sum_{\nu\geq0} \langle 0|\,\hat{V}^*\,|\nu\rangle\,\langle\nu|\,\hat{V}\,|0\rangle - |f(q)|^2$$

$$= \langle 0|\,\hat{V}^*\cdot\hat{V}\,|0\rangle - |f(q)|^2.$$
(B.24)

Here, however, in contrast to Eq. (1.37),

$$\hat{V}^* \cdot \hat{V} = \sum_{m=1}^{Z} e^{i\mathbf{q}\mathbf{r}_m} \cdot \sum_{n=1}^{Z} e^{-i\mathbf{q}\mathbf{r}_n} = \sum_{n,m=1}^{Z} e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)} = Z + \sum_{\substack{n,m=1\\n \neq m}}^{Z} e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)},$$
(B.25)

where we separated Z diagonal terms for which n = m. Finally, the incoherent scattering cross-section can be written as

$$\left(\frac{\partial\sigma}{\partial\Omega}\right)_{inc} = \left(\frac{\partial\sigma}{\partial\Omega}\right)_{e} \cdot \left[Z - |f(q)|^{2} + \langle 0|\sum_{\substack{n,m=1\\n\neq m}}^{Z} e^{-i\mathbf{q}(\mathbf{r}_{n} - \mathbf{r}_{m})} |0\rangle\right]. \quad (B.26)$$

In the case of an atom with a single electron (Z = 1), this result matches with Eq. (1.38).

Evaluation of the last term in Eq. (B.26) can be generally performed under certain approximation. For example, let us assume that the ground many-electron wave function can be factorized, i.e.  $\psi_0(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_Z) \approx \phi_1(\mathbf{r}_1) \cdot \phi_2(\mathbf{r}_2) ... \phi_Z(\mathbf{r}_Z)$ , where  $\phi_n$  is a single-electron wave function of the  $n^{\text{th}}$  electron. In this case,

$$\langle 0| e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)} |0\rangle = \int \phi_n^*(\mathbf{r}_n) \phi_m^*(\mathbf{r}_m) \cdot e^{-i\mathbf{q}(\mathbf{r}_n - \mathbf{r}_m)} \cdot \phi_n(\mathbf{r}_n) \phi_m(\mathbf{r}_m) d\mathbf{r}_n d\mathbf{r}_m$$

$$= f_n(q) \cdot f_m^*(q),$$
(B.27)

where

$$f_n(q) = \int \phi_n^*(\mathbf{r}) e^{-i\mathbf{q}\mathbf{r}} \phi_n(\mathbf{r}) d\mathbf{r}$$
(B.28)

is the scattering form factor of the  $n^{\text{th}}$  electron.

The total scattering form factor of an atom is the sum scattering form factors of all electrons  $f(q) = \sum_n f_n(q)$  (see Eq. (B.20)). Thus, the term  $|f(q)|^2$  in Eq. (B.26) can be evaluated as

$$|f(q)|^{2} = \left|\sum_{n=1}^{Z} f_{n}(q)\right|^{2} = \sum_{n=1}^{Z} f_{n}(q) \cdot \sum_{m=1}^{Z} f_{m}^{*}(q) = \sum_{n,m=1}^{Z} f_{n}(q) f_{m}^{*}(q).$$
(B.29)

Finally, inserting results of Eqs. (B.27) and (B.29) into the formula (B.26) for the incoherent scattering cross-section, we can see that the off-diagonal elements with  $n \neq m$  cancel out, which leads to the final result:

$$\begin{pmatrix} \frac{\partial \sigma}{\partial \Omega} \end{pmatrix}_{inc} = \left( \frac{\partial \sigma}{\partial \Omega} \right)_{e} \cdot \left[ Z - \sum_{\substack{n,m=1\\n\neq m}}^{Z} f_{n}(q) f_{m}^{*}(q) + \sum_{\substack{n,m=1\\n\neq m}}^{Z} f_{n}(q) f_{m}^{*}(q) \right]$$

$$= \left( \frac{\partial \sigma}{\partial \Omega} \right)_{e} \cdot \underbrace{ \left[ Z - \sum_{\substack{n=1\\s(\mathbf{q})}}^{Z} |f_{n}(q)|^{2} \right]}_{s(\mathbf{q})}.$$

$$(B.30)$$

From the definition of the scattering form factor of the  $n^{\text{th}}$  electron (Eq. (B.28)), one can obtain the asymptotic behavior for small and large q-values:

$$f_n(q \to 0) = 1,$$
  

$$f_n(q \to \infty) = 0.$$
(B.31)

Therefore, one obtains the following asymptotic behavior for the atomic scattering form factor:

$$f(q \to 0) = \sum_{n=1}^{Z} f_n(0) = Z,$$
  

$$f(q \to \infty) = \sum_{n=1}^{Z} f_n(\infty) = 0,$$
(B.32)

which matches with Eq. (1.30). For the incoherent scattering function  $s(\mathbf{q})$ , using Eqs. (B.26-B.28), we obtain

$$s(q \to 0) = Z - \underbrace{|f(0)|^2}_{=Z^2} + \underbrace{\sum_{\substack{n,m=1\\n \neq m}}^{Z} f_n(0) f_m^*(0)}_{=Z^{2-Z}} = 0,$$

$$s(q \to \infty) = Z - \underbrace{|f(\infty)|^2}_{=0} + \underbrace{\sum_{\substack{n,m=1\\n \neq m}\\ n \neq m}}^{Z} f_n(\infty) f_m^*(\infty) = Z.$$
(B.33)

Eqs. (B.21) and (B.32) mean that the coherent X-ray scattering from an atom scales with the number of electrons as  $\propto Z^2$ , and it is large at small values of q. Eqs. (B.22) and (B.33) mean that the incoherent X-ray scattering scales as  $\propto Z$ , and it is large for the large values of q. Therefore, the incoherent X-ray scattering becomes significant (not much smaller than the coherent X-ray scattering) for large scattering angles and light elements. This is illustrated in Fig. 1.15 and, for example, in [8].

# C The Ostrogradsky-Gauss theorem

The Ostrogradsky-Gauss theorem states that the volume integral of the divergence div $\mathbf{F}$  equals the surface integral of  $\mathbf{F}$  over the boundary S:

$$\int_{V} \operatorname{div} \mathbf{F} d\mathbf{r} = \oint_{S} \mathbf{F} d\mathbf{S}, \qquad (C.34)$$

where **F** a smooth vector field, V is a compact volume in 3D with a piecewise smooth boundary S (Fig. C1).

Let us calculate the left hand side of Eq. (C.34) for the vector field

$$\mathbf{F} = -\frac{i\mathbf{A}}{\mathbf{q}\mathbf{A}}e^{i\mathbf{q}\mathbf{r}},\tag{C.35}$$

where  $\mathbf{A}$  is an arbitrary vector. The divergence of  $\mathbf{F}$  is

$$\operatorname{div}\mathbf{F} = \frac{\partial \mathbf{F}}{\partial \mathbf{r}} = -\frac{i\mathbf{A}}{\mathbf{q}\mathbf{A}} \cdot (i\mathbf{q})e^{i\mathbf{q}\mathbf{r}} = e^{i\mathbf{q}\mathbf{r}}.$$
 (C.36)

Substituting Eqs. (C.35) and (C.36) in (C.34), we obtain

$$\int_{V} e^{i\mathbf{q}\mathbf{r}} d\mathbf{r} = -\frac{i}{\mathbf{q}\mathbf{A}} \oint_{S} e^{iq\mathbf{r}} (\mathbf{A}d\mathbf{S}).$$
(C.37)

Multiplying Eq. (C.37) with its complex conjugation, we arrive to the integral from Eq. (2.58):

$$\iint_{V} e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')} d\mathbf{r} d\mathbf{r}' = \oint_{S} \oint_{S'} \frac{e^{-i\mathbf{q}(\mathbf{r}-\mathbf{r}')}}{(\mathbf{q}\mathbf{A})^{2}} (\mathbf{A}d\mathbf{S}) (\mathbf{A}d\mathbf{S}'). \quad (C.38)$$



Fig. C1: Volume V with a boundary S and the vector field  $\mathbf{F}$ .

### D The Helmholtz equation for X-rays

Taking the curl of the both sides of the Faraday equation

$$\operatorname{rot}\mathbf{E} = -\frac{1}{c}\frac{\partial\mathbf{B}}{\partial t},\qquad(D.1)$$

we obtain

$$\operatorname{rot}\operatorname{rot}\mathbf{E} = -\frac{1}{c}\frac{\partial}{\partial t}\operatorname{rot}\mathbf{B}.$$
 (D.2)

Then we can use Ampère's circuital law

$$\operatorname{rot}\mathbf{B} = \frac{4\pi}{c}\mathbf{j} + \frac{\varepsilon\mu}{c}\frac{\partial\mathbf{E}}{\partial t} = \frac{n^2}{c}\frac{\partial\mathbf{E}}{\partial t},\tag{D.3}$$

where we assumed a non-magnetic insulator ( $\mu = 1$  and  $\mathbf{j} = 0$ ) with the index of refraction  $n^2 = \mu \varepsilon = \varepsilon$ .

Substituting Eq. (D.3) into Eq. (D.2), we obtain

$$\operatorname{rot}\operatorname{rot}\mathbf{E} = -\frac{n^2}{c^2}\frac{\partial^2 \mathbf{E}}{\partial t^2} = n^2 k^2 \mathbf{E},\qquad(D.4)$$

where the time derivative was calculated assuming the monochromatic electric field  $\mathbf{E} \propto e^{i\omega t}$  with the dispersion  $\omega = k \cdot c$ . Using the identity

$$rot rot \mathbf{E} = grad \operatorname{div} \mathbf{E} - \nabla^2 \mathbf{E}, \qquad (D.5)$$

and the absence of free electrical charges

$$\operatorname{div}\mathbf{E} = 0, \tag{D.6}$$

we can rewrite Eq. (D.4) as

$$-\nabla^2 \mathbf{E} = n^2 k^2 \mathbf{E},\tag{D.7}$$

which is the Helmholtz equation (2.77) for the electromagnetic wave.

# E Scattering reversibility

Let us consider the exact equation (2.89) for the scattering amplitude

$$f(\mathbf{k}_1, \mathbf{k}_2) = -\frac{1}{4\pi} \left\langle e^{i\mathbf{k}_2 \mathbf{r}} | V | \psi_{\mathbf{k}_1}(\mathbf{r}) \right\rangle.$$
 (E.1)

The inversion of time does not change the probabilities, i.e.  $f(\mathbf{k}_1, \mathbf{k}_2) = f(-\mathbf{k}_2, -\mathbf{k}_1)$  (Fig. E1). Writing explicitly

$$f(\mathbf{k}_{1},\mathbf{k}_{2}) = -\frac{1}{4\pi} \int e^{-i\mathbf{k}_{2}\mathbf{r}} V(\mathbf{r}) \psi_{\mathbf{k}_{1}}(\mathbf{r}) d\mathbf{r} = -\frac{1}{4\pi} \left\langle e^{i\mathbf{k}_{2}\mathbf{r}} | V | \psi_{\mathbf{k}_{1}}(\mathbf{r}) \right\rangle$$
$$f(-\mathbf{k}_{2},-\mathbf{k}_{1}) = -\frac{1}{4\pi} \int e^{i\mathbf{k}_{1}\mathbf{r}} V(\mathbf{r}) \psi_{-\mathbf{k}_{2}}(\mathbf{r}) d\mathbf{r} = -\frac{1}{4\pi} \left\langle \psi_{-\mathbf{k}_{2}}^{*}(\mathbf{r}) | V | e^{i\mathbf{k}_{1}\mathbf{r}} \right\rangle,$$
(E.2)

we immediately arrive to the identity

$$\langle e^{i\mathbf{k}_{2}\mathbf{r}} | V | \psi_{\mathbf{k}_{1}}(\mathbf{r}) \rangle = \langle \psi_{-\mathbf{k}_{2}}^{*}(\mathbf{r}) | V | e^{i\mathbf{k}_{1}\mathbf{r}} \rangle.$$
(E.3)



Fig. E1: Illustration of the time inversion in a scattering process.

#### F Isothermal compressibility

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Let us find the relation between the averaged square fluctuations of the volume  $\langle \Delta V^2 \rangle$  and the isotermal compressibility of the system

$$\chi_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T. \tag{F.1}$$

In order to do this, we need to calculate the work W which must be supplied to compress our system from the volume  $V_0$  to  $V_0 - \Delta V$  (see Fig. F1). During the compression of the system, its pressure will increase from  $P_0$  to  $P = P_0 + \Delta P$ . In the linear approximation, we can write that the pressure in the system will be

$$P(V) = P_0 + \left(\frac{\partial P}{\partial V}\right)_T (V - V_0).$$
 (F.2)

Thus, the work needed to compress the system is

$$W = -\int_{V_0}^{V_0 - \Delta V} (P - P_0) dV$$
  
=  $-\int_{V_0}^{V_0 - \Delta V} \left(\frac{\partial P}{\partial V}\right)_T (V - V_0) dV \stackrel{v=V_0 - V}{=} -\int_0^{\Delta V} \left(\frac{\partial P}{\partial V}\right)_T (-v) d(-v)$   
=  $-\left(\frac{\partial P}{\partial V}\right)_T \cdot \frac{1}{2} \Delta V^2 = \frac{1}{\chi_T V} \cdot \frac{1}{2} \Delta V^2.$  (F.3)

Therefore, fluctuation of the system volume  $\Delta V$  has the "energy cost" of  $W = -\left(\frac{\partial P}{\partial V}\right) \cdot \frac{1}{2}\Delta V^2$ . The equipartition theorem states that the average energy related to this fluctuation (vibrational degree of freedom) equals to  $k_B T/2$ , so

$$\langle W \rangle = \frac{1}{\chi_T V} \cdot \frac{1}{2} \langle \Delta V^2 \rangle = \frac{k_B T}{2}.$$
 (F.4)

Therefore,

$$\langle \Delta V^2 \rangle = k_B T \chi_T V. \tag{F.5}$$

#### Exponential of a Hamiltonian operator G

If  $|\nu\rangle$  and  $E_{\nu}$  are the eigenfunction and eigenvalue of a system with a Hamiltonian  $\hat{H}$ , then it satisfies a stationary Schrödinger equation

$$\hat{H} |\nu\rangle = E_{\nu} |\nu\rangle.$$
 (G.1)

Applying the Hamiltonian operator  $\hat{H}$  to the both sides of Eq. (G.1), we obtain

$$\ddot{H}\ddot{H}\left|\nu\right\rangle = E_{\nu}\ddot{H}\left|\nu\right\rangle = E_{\nu}^{2}\left|\nu\right\rangle,$$
 (G.2)

which can be easily generalized to

$$\underbrace{\hat{H}...\hat{H}}_{n \text{ times}} |\nu\rangle = \hat{H}^n |\nu\rangle = E_{\nu}^n |\nu\rangle.$$
(G.3)

The exponential of the operator  $\hat{A}$  is defined by formally applying Taylor expansion

$$e^{\hat{A}} = \sum_{n=0}^{\infty} \frac{1}{n!} \hat{A}^n.$$
 (G.4)



Fig. F1: To compress the system with a piston from the volume  $V_0$  to  $V_0 - \Delta V$  one has to supply the work W. During the compression, the pressure of the system will increase from  $P_0$  to  $P_0 + \Delta P$ .

Thus, using Eq. (G.3), we can define  $e^{-i\frac{\hat{H}t}{\hbar}}$  and show that

$$e^{-i\frac{\hat{H}t}{\hbar}} |\nu\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-i\hat{H}t}{\hbar}\right)^n |\nu\rangle = \sum_{n=0}^{\infty} \frac{1}{n!} \left(\frac{-iE_{\nu}t}{\hbar}\right)^n |\nu\rangle = e^{-i\frac{E_{\nu}t}{\hbar}} |\nu\rangle.$$
(G.5)

Since  $e^{-i\frac{E_{\nu}t}{\hbar}}$  is just a number (not an operator), we can change the order in the last expression in Eq. (G.5) and write

$$|\nu\rangle \cdot e^{-i\frac{E_{\nu}t}{\hbar}} = e^{-i\frac{\hat{H}t}{\hbar}} |\nu\rangle, \qquad (G.6)$$

and analogously, for  $\langle \nu |$ ,

$$e^{-i\frac{E_{\nu}t}{\hbar}} \cdot \langle \nu | = \langle \nu | e^{i\frac{\hat{H}t}{\hbar}}.$$
 (G.7)

Combining Eqs. (G.6) and (G.7), we obtain Eq. (4.19) in the main text:

$$e^{-i\frac{E_{\nu'}t}{\hbar}} \cdot \langle \nu' | \hat{A} | \nu \rangle \cdot e^{-i\frac{E_{\nu}t}{\hbar}} = \langle \nu' | e^{i\frac{\hat{H}t}{\hbar}} \cdot \hat{A} \cdot e^{-i\frac{\hat{H}t}{\hbar}} | \nu \rangle, \qquad (G.8)$$

where  $\hat{A} = e^{-i\mathbf{q}\mathbf{R}_n}$ .

# H Heisenberg picture

There are several approaches to the time-evolution in quantum mechanics. The most common approach, so-called Schrödinger picture, states that the wave function  $\psi$  of a system depends on time according to the Schrödinger equation:

$$i\hbar \frac{\partial \psi(\mathbf{x},t)}{\partial t} = \hat{H}\psi(\mathbf{x},t),$$
 (H.1)

where we denoted as **x** all the arguments of the wave function  $\psi$ , except of the time t. In Schrödinger picture, the experimentally measurable average value of any operator  $\hat{A}$  is

$$\bar{A}(t) = \int \psi^*(\mathbf{x}, t) \hat{A} \psi(\mathbf{x}, t) d\mathbf{x} = \langle \psi(\mathbf{x}, t) | \hat{A} | \psi(\mathbf{x}, t) \rangle.$$
(H.2)

There is an alternative approach, when one treats time-evolution as some operator  $\hat{T}(t)$  acting on the wave function  $\psi(\mathbf{x}, t = 0)$ . One can formally write

$$\tilde{T}(t)\psi(\mathbf{x},0) = \psi(\mathbf{x},t).$$
 (H.3)

If the Hamiltonian of the system does not explicitly depend on time (i.e. the system is conservative), one can find the solution of the partial differential equation (H.1). It is easy to check that

$$\psi(\mathbf{x},t) = e^{-i\frac{H}{\hbar}t}\psi(\mathbf{x},0) \tag{H.4}$$

fulfills the Schrödinger equation (H.1). Therefore, for the conservative system, the time-evolution operator  $\hat{T}$  is

$$\hat{T}(t) = e^{-i\frac{H}{\hbar}t}.\tag{H.5}$$

In Dirac notation, we can write

$$\begin{aligned} |\psi(\mathbf{x},t)\rangle &= \hat{T}(t) |\psi(\mathbf{x},0)\rangle = e^{-i\frac{H}{\hbar}t} |\psi(\mathbf{x},0)\rangle, \\ \langle\psi(\mathbf{x},t)| &= \langle\psi(\mathbf{x},0)| \,\hat{T}^+(t) = \langle\psi(\mathbf{x},0)| \,e^{i\frac{\hat{H}}{\hbar}t}. \end{aligned} \tag{H.6}$$

This gives us the following expression for the average value of the operator  $\hat{A}$ :

$$\bar{A}(t) = \underbrace{\langle \psi(\mathbf{x},0) | e^{i\frac{\hat{H}}{\hbar}t}}_{\langle \psi(\mathbf{x},t) |} \hat{A} \underbrace{e^{-i\frac{\hat{H}}{\hbar}t} | \psi(\mathbf{x},0) \rangle}_{|\psi(\mathbf{x},t) \rangle} = \langle \psi(\mathbf{x},0) | \hat{A}_H(t) | \psi(\mathbf{x},0) \rangle , \quad (\mathrm{H.7})$$

where

$$\hat{A}_H(t) = \hat{T}^+(t) \cdot \hat{A} \cdot \hat{T}^(t) = e^{i\frac{\hat{H}}{\hbar}t} \hat{A} e^{-i\frac{\hat{H}}{\hbar}t}$$
(H.8)

is called Heisenberg representation of the operator  $\hat{A}$ .

In Schrödinger picture (Eq. (H.2)) we assumed time-independent operator  $\hat{A}$ , and all information about the evolution in time was "recorder" in the time-dependent wave function  $\psi(\mathbf{x}, t)$ . In Heisenberg picture (Eq. (H.7)) we transferred the time-dependence into the operator  $\hat{A}_H(t)$  defined in Eq. (H.8), while the wave-function  $\psi(\mathbf{x}, 0)$  is now time-independent. This is schematically illustrated in Fig. H1.

By definition, the Heisenberg operator  $\hat{A}_H(t)$  determines the value of the quantity A at the moment of time t (Eq. (H.7)). At time t = 0 the Heisenberg and Schrödinger operators coincide, as it can be seen from Eq. (H.8):

$$\hat{A}_{H}(0) = e^{i\frac{\hat{H}}{\hbar}0}\hat{A}e^{-i\frac{\hat{H}}{\hbar}0} = \hat{A}.$$
(H.9)

To illustrate, how one works with the Heisenberg operators, it is instructive to show some calculations. For example, let us show that if  $\hat{A}_H(t_1)$  and  $\hat{B}_H(t_2)$  are two Heisenberg operators, the matrix element  $\langle \nu | \hat{A}_H(t_1) \hat{B}_H(t_2) | \nu \rangle$ can only depend on the difference  $t_2 - t_1$ . Indeed,

$$\begin{aligned} \langle \nu | \, \hat{A}_{H}(t_{1}) \hat{B}_{H}(t_{2}) \, | \nu \rangle &= \langle \nu | \, e^{i \frac{\hat{H}}{\hbar} t_{1}} \hat{A} e^{-i \frac{\hat{H}}{\hbar} t_{1}} e^{i \frac{\hat{H}}{\hbar} t_{2}} \hat{B} e^{-i \frac{\hat{H}}{\hbar} t_{2}} \, | \nu \rangle \\ &= e^{-i \frac{E_{\nu}}{\hbar} t_{1}} \, \langle \nu | \, \hat{A} e^{-i \frac{\hat{H}}{\hbar} (t_{1} - t_{2})} \hat{B} e^{-i \frac{\hat{H}}{\hbar} t_{2}} \, | \nu \rangle \\ &= \langle \nu | \, \hat{A} e^{-i \frac{\hat{H}}{\hbar} (t_{1} - t_{2})} \hat{B} e^{-i \frac{\hat{H}}{\hbar} t_{2}} e^{-i \frac{\hat{H}}{\hbar} t_{1}} \, | \nu \rangle , \qquad (\text{H.10}) \\ &= \langle \nu | \, \hat{A} e^{i \frac{\hat{H}}{\hbar} (t_{2} - t_{1})} \hat{B} e^{-i \frac{\hat{H}}{\hbar} (t_{2} - t_{1})} \, | \nu \rangle \\ &= \langle \nu | \, \hat{A}_{H}(0) \hat{B}_{H}(t_{2} - t_{1}) \, | \nu \rangle \end{aligned}$$

where we used Eqs. (G.6), (G.7) and (H.8).

Let us also prove the following identity:

$$\langle A(0)B(t)\rangle = \left\langle B(t)A\left(\frac{i\hbar}{k_BT}\right)\right\rangle,$$
 (H.11)

where angular brakets denote ensemble averaging (as it was introduced in section 4.1.3)

$$\langle C \rangle = \frac{1}{Z} \sum_{\nu} \rho_{\nu} \langle \nu | \hat{C} | \nu \rangle.$$
 (H.12)

Assuming classical Boltzman statistics, we can write:

$$\langle A(0)B(t)\rangle = \frac{1}{Z} \sum_{\nu} e^{-E_{\nu}/k_B T} \langle \nu | \hat{A}_H(0)\hat{B}_H(t) | \nu \rangle.$$
 (H.13)

Using definition of the Heisenberg operator (H.8) and the property (G.6), we can modify the expression (H.13) as following:

$$\langle A(0)B(t)\rangle = \frac{1}{Z} \sum_{\nu} \langle \nu | \hat{A} \cdot \hat{T}^{+} \hat{B} \hat{T} \cdot e^{-\hat{H}/k_{B}T} | \nu \rangle.$$
(H.14)



Fig. H1: Red arrow represents a wave function  $\psi$  of a system. Three black axis schematically shows different eigenfunctions of the operator  $\hat{A}$ . The projection of the wave function  $\psi$  onto a certain eigenfunction gives the probability to measure a certain value of the physical quantity A. In Schrödinger picture, time evolution is considered as time dependence of the wave function (its time evolution is schematically shown by a blue trajectory in upper panel). In Heisenberg picture, the wave function is considered to be constant, while the operator  $\hat{A}_{H}(t)$  depends on time, which means that the eigenfunctions also depend on time (schematically shown by blue trajectories in lower pannel).

Using the closure relation,  $^{25}$  one can exchange the order of operators:

$$\langle A(0)B(t)\rangle = \frac{1}{Z}\sum_{\nu} \langle \nu | \hat{T}^{+}\hat{B}\hat{T} \cdot e^{-\hat{H}/k_{B}T} \cdot \hat{A} | \nu \rangle.$$
(H.15)

Now we can replace  $\langle \nu |$  with  $e^{-E_{\nu}/k_BT} \langle \nu | \cdot e^{\hat{H}/k_BT}$ :

$$\langle A(0)B(t)\rangle = \frac{1}{Z} \sum_{\nu} e^{-E_{\nu}/k_B T} \langle \nu | \underbrace{e^{\hat{H}/k_B T} \cdot \hat{T}^+ \hat{B} \hat{T} \cdot e^{-\hat{H}/k_B T}}_{\hat{B}_H(t-i\hbar/k_B T)} \hat{A} | \nu \rangle , \quad (\text{H.16})$$

where we used

$$e^{\hat{H}/k_{B}T}e^{i\frac{\hat{H}}{\hbar}t}\hat{B}e^{-i\frac{\hat{H}}{\hbar}t}e^{-\hat{H}/k_{B}T} = \hat{B}_{H}\left(t - \frac{i\hbar}{k_{B}T}\right).$$
(H.17)

Thus, Eq. (H.16) can be simplified to

$$\langle A(0)B(t)\rangle = \frac{1}{Z} \sum_{\nu} e^{-E_{\nu}/k_B T} \langle \nu | \hat{B}_H \left( t - \frac{i\hbar}{k_B T} \right) \hat{A}_H(0) | \nu \rangle.$$
(H.18)

Using the fact, that the value of the matrix element in Eq. (H.18) can depend only on difference between the arguments (see Eq. (H.10)), we can finally write

$$\langle A(0)B(t)\rangle = \frac{1}{Z} \sum_{\nu} e^{-E_{\nu}/k_{B}T} \langle \nu | \hat{B}_{H}(t)\hat{A}_{H}\left(\frac{i\hbar}{k_{B}T}\right) |\nu\rangle = \left\langle B(t)A\left(\frac{i\hbar}{k_{B}T}\right) \right\rangle, \tag{H.19}$$

which proves Eq. (H.11).

 $^{25}$  for any operators  $\hat{A}$  and  $\hat{B}$  and complete orthonormal sets of eigenfunctions  $\nu$  and  $\nu'$ :

$$\sum_{\nu} \langle \nu | \hat{A}\hat{B} | \nu \rangle = \sum_{\nu,\nu'} \langle \nu | \hat{A} | \nu' \rangle \langle \nu' | \hat{B} | \nu \rangle = \sum_{\nu,\nu'} \langle \nu' | \hat{B} | \nu \rangle \langle \nu | \hat{A} | \nu' \rangle = \sum_{\nu'} \langle \nu' | \hat{B}\hat{A} | \nu' \rangle$$

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