

Chapter 2

Theoretical Background

In this chapter the theoretical concepts and physical principles used in this thesis are presented. The first part deals with the physical description of the studied systems, while the second part provides an introduction into the principles of X-ray and neutron scattering, the primary experimental method applied in this thesis.

2.1 Lipid Membranes

2.1.1 Physics of Lipids and Lipid Membranes

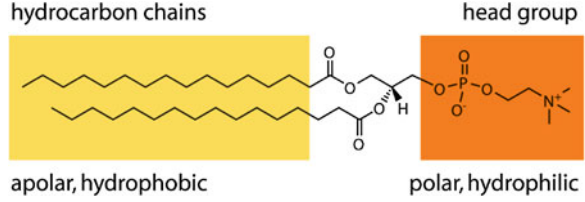
In this thesis, membrane-bound saccharides are studied using model systems prepared from various types of lipids. In the following, an introduction into the physics of lipids and lipid membranes is given.

2.1.1.1 Membrane Formation by Lipid Self-Assembling

Lipids are the main structuring component of biological membranes. Despite their enormous structural variety, all membrane lipids possess amphiphilic architecture, with one hydrophobic and one hydrophilic building block, essential for the molecular self-assembling.¹ The hydrophobic part is constituted by apolar hydrocarbon chains, while the hydrophilic part, commonly called head group, consists of polar moieties. This is illustrated in Fig. 2.1 for DPPC, a commonly studied lipid with two hydrocarbon chains and a phosphatidylcholine head group.

¹ Archaea possess lipids with two hydrophilic moieties, which leads to different molecular self-assembly.

Fig. 2.1 Schematic structure of a lipid. The amphiphilic molecules possess a hydrophobic part, constituted by apolar hydrocarbon chains, and a hydrophilic head group exhibiting polar moieties



Due to the hydrophobic effect [1, 2], lipids exhibit a very low solubility in water. Isolated lipids dissolved in the aqueous solution are only found in very low concentrations, while the vast majority of lipids form aggregates whose shapes depend on the lipid geometry characterized by the lipid packing parameter [2]. Here, we focus on the biologically most relevant cylindrical lipid geometry, which leads to the formation of bilayer structures (see Fig. 2.2). In the following, the self-assembling of lipids is discussed under thermodynamic aspects. Biological processes usually take place at constant temperature T and constant (atmospheric or hydrostatic) pressure. Under these boundary conditions, the processes are driven by a minimization of the Gibbs free energy G .

$$G = H - TS,$$

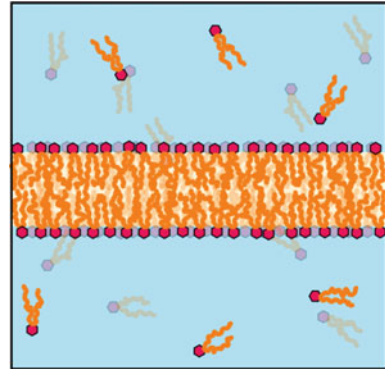
where H denotes the enthalpy and S the entropy. The solubility of the lipids can be quantified in terms of the critical aggregate concentration (CAC), which defines an upper limit for the concentration of isolated lipids dissolved in the aqueous solution [1, 3].

$$\text{CAC} \cong c_0 \exp(-\Delta g/k_B T)$$

$$\Delta g = g_{\text{sol}} - g_{\text{agg}}$$

Here, $k_B T$ denotes the thermal energy and Δg the change in the Gibbs free energy that would result from the transfer of one lipid from an aggregate into the solution. c_0 denotes the concentration of lipids within the aggregates, usually at

Fig. 2.2 Bilayer formation due to the hydrophobic effect. Isolated lipids dissolved in the aqueous solution are only found in very low concentration below the critical aggregate concentration (CAC), while the vast majority of the lipids are assembled in aggregates such as the shown lipid bilayer



the order of 1 M. Typical lipids with two hydrocarbon chains have CAC values at the order of 10^{-12} M. Δg can be decomposed into an enthalpic contribution Δh and an entropic contribution $T\Delta s$:

$$\Delta g = \Delta h - T\Delta s$$

Δh is determined by the enthalpy of lipid/lipid interactions, water/water interactions, and lipid/water interactions. Δs is determined by the change in the number of available system configurations that would result from the transfer of one lipid into solution. A dissolved lipid exposes its apolar hydrocarbon chains to the adjacent water molecules, which thus get limited in the choice of H-bonds they can form. Thus, the number of available system configurations gets reduced if a lipid is brought into solution. As a consequence, Δs is always negative. Usually the absolute of $T\Delta s$ is much higher than the absolute of Δh , and Δg is dominated by the entropic contribution which always favors the formation of aggregates. This phenomenon, known as hydrophobic effect, is the driving force for the self-assembling of lipids into aggregates, such as bilayer membranes (see Fig. 2.2) or other structures.

2.1.1.2 Phase Behavior of Lipid Membranes

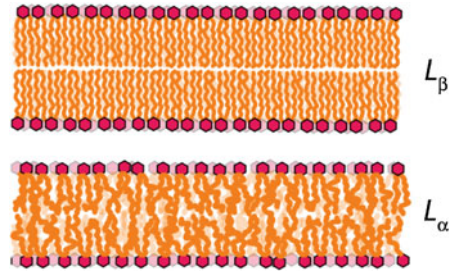
Depending on the lipid structure, lipid membranes can assume several phase states in many cases. These phase states are usually classified as follows [4, 5]: The L_c -phase represents a two-dimensional crystalline arrangement of the lipid molecules including hydrocarbon chains and head groups. The gel-like L_β -phase represents a two-dimensional crystalline ordering of the hydrocarbon chains, while the headgroups have no fixed orientation or position. The hydrocarbon chains are arranged in a lateral hexagonal-like (generally “orthorhombic”) structure with a fixed, linear configuration, denoted as all-trans configuration. This is illustrated in Fig. 2.3 (top membrane). Often the chains possess a defined tilt with respect to the membrane normal, due to a mismatch between the projected area required by the hydrocarbon chains and that required by the head groups.² The biologically most relevant L_α -phase represents a two-dimensional fluid, where the hydrocarbon chains can assume a large number of configurations (trans and gauche rotations at each carbon–carbon bond in the hydrocarbon chains) [6], and the lipids diffuse along the membrane plane. This is illustrated in Fig. 2.3 (bottom membrane). Due to the high number of gauche configurations, membranes are significantly thinner in fluid L_α -phase than in gel-like L_β -phase [3].

Lipid bilayers can transit from one phase state to another one via thermotropic phase transitions.³ Here, which phase state is assumed by the bilayer depends on

² This is the case for lipids with phosphatidylcholine headgroups (such as DPPC), where this tilted phase is denoted as L_β' -phase.

³ Phase transitions can also be induced by other thermodynamic parameters, such as pressure or concentration.

Fig. 2.3 A lipid membrane in gel-like L_β -phase and in fluid L_α -phase



the temperature T , while other parameters (lipid concentration, pressure) are kept constant. In the following we consider the biologically very important thermotropic phase transition from L_β -phase to L_α -phase. This first order phase transition is known as chain-melting transition. Let Δg denote the difference in Gibbs free energy per lipid between the two phase states for a given temperature T .

$$g_\alpha - g_\beta = \Delta g = \Delta h - T\Delta s$$

Δh has a positive value, as the in L_α -phase gauche configurations with higher energy levels are occupied, while in the L_β -phase, the hydrocarbon chains mainly take trans configurations with lowest energy. Hence, the enthalpic contribution of the Gibbs free energy favors the L_β -phase. On the other hand, the large number of possible chain configurations in L_α -phase [6] coincides with a significantly higher entropy per lipid and results in a positive value of Δs . Thus, the entropic contribution of the Gibbs free energy favors the L_α -phase. As a consequence, the temperature determines which contribution is dominant in this competition. At the phase transition temperature T_m , where the lipids are found in either phase with the same probability, Δg is zero, and thus:

$$T_m = \Delta h / \Delta s$$

The transition temperature is determined by the transition enthalpy Δh and the transition entropy Δs , which are both encoded in the molecular structure of the lipids. Conversely, measurements of T_m provide valuable information on the thermodynamics of the bilayers formed by the studied lipids. Below T_m bilayers assume L_β -phase and above T_m they assume L_α -phase. Near T_m , a coexistence of the two phases is found. The width of this coexistence region depends on the transition cooperativity, i.e., on the size of the group of lipids that undergo the transition in a cooperative process [5].

2.1.2 Inter-Membrane Interactions

In this thesis, the influence of membrane-bound saccharides on the interaction of membranes is investigated. In the following, an introduction into the physics of inter-membrane interactions is given.

In general, the physical interaction between biological membranes is the result of a complex interplay of non-specific and specific interactions. The former comprise a variety of generic physical forces, while the latter correspond to specific bonds between motifs (e.g. oligosaccharides) presented by the membranes and can be treated separately (see [Sect. 5.2](#)). For large enough membrane separations (typically $\gg 10$ Å), the non-specific interactions can be treated in a continuum mean-field approximation which neglects the atomic structure of the matter. Here, the bilayers are considered as plates with in-plane-homogenous properties (such as charge density, dielectric constant, and bending rigidity). This is a reasonable assumption for many model membranes. Commonly used continuum mean-field approaches to describe the interaction of particles in aqueous media are the Gouy–Chapman “diffuse double layer” theory, which accounts for electrostatic interactions in electrolytes, and the DLVO theory [1, 7–10], which additionally accounts for the van der Waals interaction. However, for the description of the interaction between planar membranes, additional contributions, not covered by the above mentioned theories, become important, like hydration or undulation forces.

2.1.2.1 Hardcore Repulsion

Hardcore repulsion between membranes is important for vanishing inter-membrane separations, where the continuum description of most of the other force contributions fails. However, once hardcore repulsion becomes relevant, it dominates over all the other contributions. Hardcore repulsion originates from an overlap of orbitals of the adjacent membrane molecules. Empirically, the resulting potential can be described with a power law:

$$\Pi_{\text{HC}}(d_{\text{W}}) = d_{\text{W}}^{-(n+1)}, \quad 9 < n < 16$$

Even though the theoretical basis for this description is very poor, it is commonly used because of its mathematical convenience [1, 11].

2.1.2.2 Van der Waals Interaction

The van der Waals interaction accounts for the combination of three contributions [1]:

1. The interaction arising from the orientation of permanent dipoles, known as orientation force.
2. The interaction between permanent dipoles with induced dipoles, known as induction force.
3. The interaction between induced dipoles with induced dipoles, which is always present and known as dispersion force.

The Lifshitz theory describes the van der Waals interaction between homogenous media in a continuum approximation. This description is based on the calculation of Hamaker constants A , which depend on the dielectric properties of the interacting media [1, 12, 13]. The interaction can be attractive or repulsive, in general. However, in case of two identical media (here: lipid membranes) with the same thickness d_H , separated by a third medium (here: water) of thickness d_W , the interaction is always attractive. For lipid membranes several models have been developed [14, 15]. As demonstrated by Demé et al. [16], a double film model with one Hamaker constant $A = 5.1 \times 10^{-21}$ J is sufficient to account for the van der Waals attraction between phospholipid membranes in fluid L_α -phase:

$$\Pi_{VDW}(d_W) = -\frac{A}{6\pi} \left[\frac{1}{d_W^3} - \frac{2}{(d_W + d_H)^3} + \frac{1}{(d_W + 2d_H)^3} \right]$$

Here, the membrane separation d_W is defined as the thickness of the aqueous region separating the hydrophobic membrane regions characterized by the “hydrophobic thickness” d_H .

2.1.2.3 Hydration Repulsion

Hydration repulsion between hydrophilic surfaces is believed to result from the free energy required to modify the H-bonding network of liquid water in the vicinity of polar, H-bonding surface groups. Empirically, the hydration interaction obeys an exponential decay [1] characterized by the extrapolated pressure Π_0 at $d_W = 0$ and a decay length λ_{HYD} :

$$\Pi_{HYD}(d_W) = \Pi_0 \exp(-d_W/\lambda_{HYD})$$

For interacting phosphatidylcholine lipid membranes in fluid L_α -phase, $\Pi_0 = 4.5 \times 10^9$ Pa is an established value, if the membrane separation d_W is defined in the same way as for the van der Waals interaction [16]. For λ_{HYD} , values around 2.0 Å were reported [17, 18, 53].

2.1.2.4 Undulation Repulsion

Up to here it was sufficient to treat the interacting lipid membranes as perfectly flat layers. However, the undulation repulsion can only be understood, if thermal membrane fluctuations are taken into account. These out-of-plane “undulations” depend on the membrane bending rigidity κ . The undulation repulsion between two membranes originates from the suppression of undulation modes (which represents a decrease in entropy) as the membrane separation d_W decreases. The strength of the repulsion depends on the geometry in which the membranes are confined. For a stack of N membranes, an algebraic expression was derived by Helfrich [19–21],

$$\Pi_{\text{UND}}(d_{\text{W}}) = \frac{2N}{N+1} \alpha_N \frac{(k_{\text{B}}T)^2}{\kappa d_{\text{W}}^3}.$$

Here, the membrane separation d_{W} is defined as the thickness of the aqueous region between the “steric surfaces” of the adjacent membranes. In case of solid-supported membrane multilayers, where N is large enough, this can be approximated with the limit of $N \rightarrow \infty$:

$$\Pi_{\text{UND}}(d_{\text{W}}) = \alpha_{\infty} \frac{2(k_{\text{B}}T)^2}{\kappa d_{\text{W}}^3},$$

with the analytic estimate $\alpha_{\infty} = 3\pi^2/128 \approx 0.23$ provided by Helfrich. More recent calculations by Bachmann et al. [19] indicate a lower value of $\alpha_{\infty} \approx 0.104$. Generally, the undulation repulsion becomes important for larger separations, where the membranes are coupled only weakly by the other force contributions.

2.1.2.5 Electrostatic Interaction

Electrostatic interactions occur if the interacting membranes carry electric charges. This can be due to charged headgroup residues or due to the adsorption of ions to the membrane surface (see Sect. 5.2.2.2). In membrane multilayers with homogenous molecular composition, the membranes are like-charged and the electrostatic interaction is therefore repulsive. In a continuum approximation the in-plane distribution of the elementary charges is neglected, and a homogenous surface charge density σ is assumed, which is confined in a defined plane of the membrane. The electrostatic interaction between adjacent membranes across the aqueous medium depends in a complicated way on the surface charge and on the ion concentrations of the buffer solution. Since there are no general algebraic solutions available, this problem is further developed in Sect. 4.2.

2.1.2.6 The Disjoining Pressure

The disjoining pressure constitutes the net force (per unit area) resulting from all interactions n between two planes (here: membrane surfaces) and is defined as the negative derivative of the Gibbs free energy with respect to the plane separation d_{W} while the chemical potential μ for water is kept constant:

$$\Pi = \sum_n \Pi_n = \left(\frac{\partial G}{\partial d_{\text{W}}} \right)_{\mu}$$

A stable equilibrium separation is found wherever:

$$\Pi = 0 \quad \text{and} \quad \frac{\partial \Pi}{\partial d_{\text{W}}} < 0$$

In contrast to the individual force contributions Π_n , the disjoining pressure is accessible to experimental measurements. If sufficient information about the interacting membranes is available, the experimentally determined disjoining pressure profile $\Pi(d_W)$ can be represented theoretically with a superposition of the relevant force contributions.

2.1.2.7 Force–Distance Relationships

The disjoining pressure profile can be determined in measurements of the membrane separation d_W while various well-known external compressional forces Π_{ext} are exerted to the membranes. In the presence of an external force, the equilibrium membrane separation is shifted to the value, where $\Pi + \Pi_{\text{ext}} = 0$. This yields the identity $\Pi(d_W) = -\Pi_{\text{ext}}(d_W)$.

Typically d_W is determined indirectly by measuring the lamellar periodicity d of membrane multilayers and subsequent subtraction of the membrane thickness. The so recorded data points provide quantitative relationships between the membrane separation and the disjoining pressure, referred to as force–distance relationships. Low compressive forces ($\Pi < 10^6$ Pa) can be applied by adding impermeable solutes (e.g. water soluble polymers impermeable across the membrane) to the aqueous solution [11, 22]. This approach is known as osmotic stress method. On the other hand, measurements at controlled relative humidity h_{rel} (i.e., in the absence of condensed water) allow for the application of high compressive forces ($\Pi > 10^6$ Pa) [23]:

$$\Pi_{\text{osm}} = -\frac{k_B T}{V_{\text{water}}} \ln(h_{\text{rel}})$$

In practice, force–distance relationships are commonly presented as $\Pi(d)$ since this representation is equivalent and closer to the experimentally accessible lamellar periodicity d (see Chaps. 5, 6).

2.1.3 Mechanics of Solid-Supported Membrane Multilayers

In this thesis, the influence of membrane-bound saccharides on the mechanical properties of (interacting) membranes is studied using solid-supported membrane multilayers as model systems (see Chaps. 5, 6). In the following, an introduction into the mechanics of planar membrane multilayers is given.

2.1.3.1 The Discrete Smectic Hamiltonian

Within the framework of a continuum model approximation, the total free energy of a set of oriented membrane multilayers can be described with the discrete smectic Hamiltonian H , according to Lei et al. [54]:

$$H = \int_A d^2r \sum_{n=1}^{N-1} \left(\frac{B}{2d} (u_{n+1} - u_n)^2 + \frac{\kappa}{2} (\nabla_{xy}^2 u_n)^2 \right).$$

N is the total number of membranes, d their equilibrium periodicity, and A the area occupied by the set of multilayers. At any moment in time, each point of a membrane, defined by the in-plane coordinates x and y , is displaced from the average membrane z -position by an increment $u_n(x, y)$, due to thermal fluctuations. This is illustrated in Fig. 2.4.

Within the continuum framework, vertical compression is characterized by the compression modulus B , while bending is characterized by the membrane bending modulus κ . ∇_{xy} denotes the two-dimensional Nabla operator in x and y directions. In a harmonic approximation, B can also be expressed in terms of the derivative of the disjoining pressure with respect to the membrane separation d_W at the equilibrium lamellar periodicity d :

$$B = -d \left(\frac{\partial \Pi}{\partial d_W} \right)_d$$

The properties of the membrane fluctuations represent the underlying mechanical parameters, which are commonly characterized by the Caillé parameter η and the de Gennes parameter λ of smectic liquid crystals, as these quantities are more directly accessible to experiments (see Sect. 4.1).

$$\eta = \frac{\pi k_B T}{2d^2 \sqrt{\kappa B/d}} \quad \text{Caillé parameter}$$

$$\lambda = \sqrt{\frac{\kappa}{Bd}} \quad \text{de Gennes parameter}$$

For a given Temperature T , a high η value corresponds to a “soft” system and leads to strong fluctuations with a high amplitude, while a low value corresponds to a “stiff” system with weak fluctuations. On the other hand, the de Gennes parameter indicates if the stiffness of a system is rather dominated by the compression modulus (for low λ values) or rather dominated by the bending modulus (for high λ values). The de Gennes parameter also determines how strongly the fluctuations of

Fig. 2.4 Parameterization of a set of rough layers or interfaces

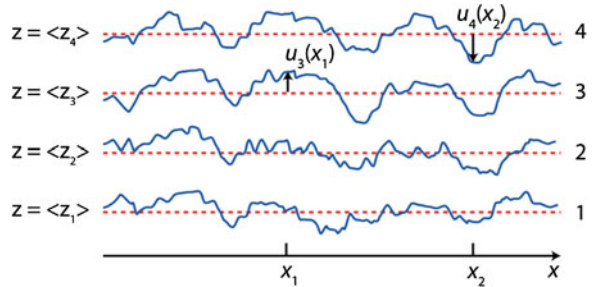
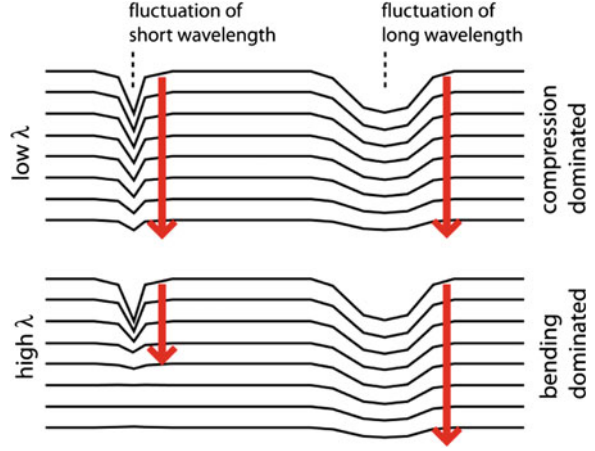


Fig. 2.5 Influence of the de Gennes parameter λ on the inter-membrane correlation of fluctuations at different wavelength



a membrane are correlated with those of its neighbors, depending on the fluctuation wavelength. This is qualitatively illustrated in Fig. 2.5, where the local displacements of a membrane and the resulting displacements of its neighbors are depicted for different displacement wavelengths and de Gennes parameters. In case of a low λ value the transmission depth of the displacement is only weakly dependent on the wavelength, whereas in case of a high λ value a displacement of short wavelength is damped much more strongly than that of long wavelength. In other words, long-wavelength membrane fluctuations have a stronger inter-membrane correlation than short wavelength fluctuations.⁴

2.1.3.2 Height–Height Correlation Functions

Correlation functions provide a model-independent statistical description of the height profile of rough layers or interfaces (see Fig. 2.4). A single rough layer or interface is described the height–height correlation function.

$$C(x, y) := \langle u(x_0 - x, y_0 - y) \cdot u(x_0, y_0) \rangle_{x_0, y_0}$$

The topological root mean square (rms) roughness σ of a layer or an interface is also defined via the height–height correlation function:

$$\sigma := \sqrt{\langle u^2 \rangle} = \sqrt{C(0, 0)}$$

For stratified systems, the correlation functions include self-correlation functions ($n = m$) within a layer or an interface and cross-correlation functions ($n \neq m$) between a layer or interface and its k th neighbor.

⁴ This is the reason why the extent, to which the width of a Bragg sheet increases with $q_{||}$ (the reciprocal space analogue to an in-plane wavelength), increases along with the de Gennes parameter.

$$C_{nm}(x, y) := \langle u_n(x_0 - x, y_0 - y) \cdot u_m(x_0, y_0) \rangle_{x_0, y_0}$$

For laterally isotropic systems the correlation functions possess radial symmetry:

$$C(x, y) \rightarrow C(r) := \langle u(\vec{r}_0 - \vec{r}) \cdot u(\vec{r}_0) \rangle_{\vec{r}_0}$$

$$C_{nm}(x, y) \rightarrow C_{nm}(r) := \langle u_n(\vec{r}_0 - \vec{r}) \cdot u_m(\vec{r}_0) \rangle_{\vec{r}_0}$$

with $r = |\vec{r}|$

An example of such a radial symmetric height–height correlation function is shown in Fig. 4.2.

2.1.3.3 Membrane Displacement Correlation Functions

In analogy, a statistical, time-averaged description of the fluctuations of interacting membranes is provided by the membrane displacement correlation functions

$$g_{nm}(r) := \left\langle [u_n(\vec{r}_0 - \vec{r}) - u_m(\vec{r}_0)]^2 \right\rangle_{\vec{r}_0}.$$

Lei et al. have derived an expression [54] which is valid in the special case of oriented multilayers that are infinitely expanded in all directions. However, this case does not apply to solid-supported membrane multilayers used for experiments. In Sect. 4.1 of this work a way to overcome this issue is presented.

2.1.4 Membrane Models

This thesis deals with several types of planar model systems of membranes and cell surfaces. Here, an introduction into selected oriented membrane models is given. Other commonly used, but non-oriented membrane models, such as unilamellar or multilamellar lipid vesicles are not discussed. Membrane models serve as simplified, well-defined models of biological membranes and allow for the detailed investigation of selected physical membrane properties. The choice of the membrane model determines which aspects of biological membranes can be studied.

2.1.4.1 Langmuir Lipid Monolayers

Langmuir lipid monolayers are insoluble monomolecular lipid films at the air/water interface [24, 25]. Here, as a consequence of the hydrophobic effect, the amphiphilic lipid molecules expose their hydrophobic tails to the gas phase.

This is illustrated in Fig. 2.6. The surface area available per lipid molecule, A , is controlled with a movable barrier.

By monitoring the surface pressure of the lipid film, π , as a function of A , the in-plane interaction of the molecules, confined in two dimensions, can be studied. Often, the lipid monolayer undergoes a phase transition as the A decreases, from a more disordered, liquid expanded (L_e , Fig. 2.6 top) phase to an ordered, liquid condensed (L_c , Fig. 2.6 bottom) phase, where the ordering refers to the hydrocarbon chains. This phase transition can be described with the two-dimensional analogue of the three-dimensional van-der-Waals (or Dieterici) equation, which accounts for the two phases and for a coexistence regime. An idealized Langmuir isotherm, i.e., a π versus A plot, recorded at a constant temperature, is schematically shown in Fig. 2.7. The curve shows the regimes of L_e and L_c phases, as well as a plateau region corresponding to the phase coexistence. As the surface area per molecule approaches to the minimum molecular area, denoted by A_0 , the surface pressure diverges. The maximum achievable surface pressure is limited by the surface tension of the air/water interface ($\sigma \cong 72$ mN/m), but usually the monolayer collapses far below that value in practice. Often no phase transition is observed, due to the molecule-intrinsic incapability to form ordered structures of their hydrocarbon chains (e.g., double bonds in the hydrocarbon chains or bulky head groups), and the monolayer remains in L_e -phase throughout the isotherm.

When a lipid monolayer is compressed to a surface area per molecule, which is representative for the molecular area found in biological membranes, the hydrophilic monolayer surface exposed to the aqueous bulk phase constitutes a well-defined model of a membrane surface. This surface can be characterized by various (surface-sensitive) techniques (such as fluorescence microscopy, Brewster angle microscopy, X-ray and neutron scattering, Kelvin probe, ellipsometry, and interfacial shear rheometry) in terms of structural, dynamical, mechanical, and dielectric properties. The surface is accessible from the aqueous side and can be the starting point for studies on the interaction of various solutes (ions, proteins, drug molecules) with the membrane surface [26, 27].

Fig. 2.6 Sketch of a Langmuir film balance. In many cases, lipids undergo a transition from disordered L_e -phase to ordered L_c -phase upon compression

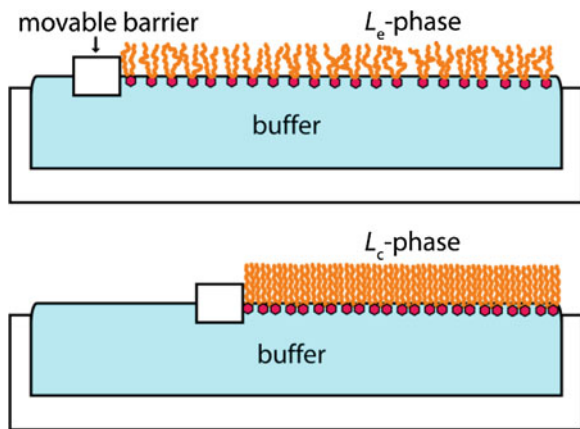
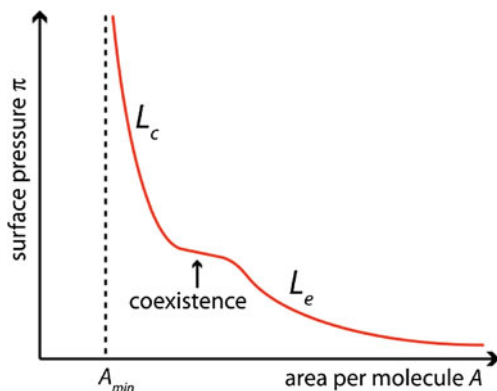


Fig. 2.7 Idealized Langmuir isotherm showing an L_c regime for large molecular areas, an L_e regime for small molecular areas, and a plateau region corresponding to the phase coexistence for intermediate molecular areas



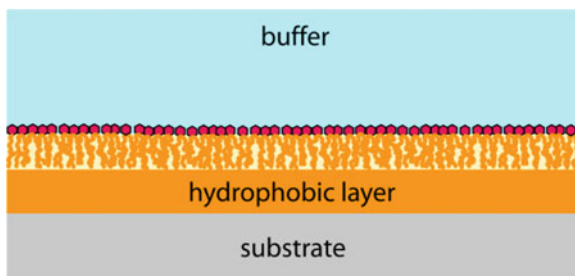
2.1.4.2 Solid-Supported Lipid Monolayers

Solid-supported lipid monolayers constitute models of biological membrane surfaces at the interface between a solid substrate and the aqueous phase [28]. This is illustrated in Fig. 2.8. Solid-supported lipid monolayers can be created by spreading small unilamellar lipid vesicles (SUVs) onto hydrophobic solid substrates under bulk buffer. The formation of the monolayer is driven by the hydrophobic effect. The resulting in-plane density of lipid molecules is very similar to that found in lipid bilayer membranes. Alternative methods for the deposition of lipid monolayers onto hydrophobic substrates are the Langmuir–Blodgett or Langmuir–Schaefer transfer [29], which enable the control of the in-plane density of the lipids. In contrast to Langmuir lipid monolayers, solid-supported lipid monolayers can be rotated in space, and therefore lend themselves towards scattering experiments, which often require sample rotations (see Sect. 3.3.1.1).

2.1.4.3 Solid-Supported Lipid Bilayers

Solid-supported lipid bilayers constitute well-defined models of biological lipid membranes confined in two dimensions [30]. This is illustrated in Fig. 2.9 (left).

Fig. 2.8 Sketch of solid-supported monolayer deposited onto a flat hydrophobic solid substrate



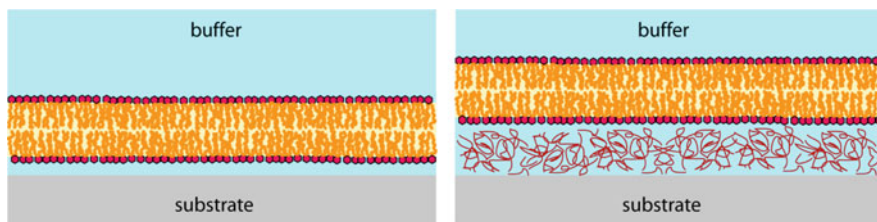


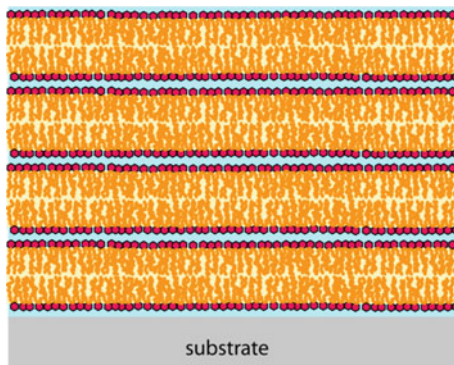
Fig. 2.9 Sketch of a solid-supported (*left*) and a polymer-supported (*right*) lipid bilayer

They are well suited to study the diffusion of lipids and membrane-associated proteins [31]. Solid-supported lipid bilayers can be created by the fusion of SUVs, or by Langmuir–Blodgett/Langmuir–Schaefer transfers. The bilayer is confined at the solid surface due to strong van der Waals attraction. To reduce the influence of this strong interaction with the substrate on the bilayer behavior, and to create a more physiological environment for the bilayer, soft polymer interlayers between solid support and bilayer (see Fig. 2.9 right) have gained importance in recent years [32, 33].

2.1.4.4 Solid-Supported Membrane Multilayers

Solid-supported membrane multilayers constitute model systems of interacting biological membranes. This is illustrated in Fig. 2.10. These systems, which can be prepared either by evaporating organic lipid solutions on the solid surface or by multiple Langmuir–Blodgett transfers, can be studied in humidified air but also under bulk buffer solution, if they retain their oriented lamellar structure under these conditions. This is the case if a finite equilibrium membrane separation is established by the inter-membrane interactions (see Sect. 2.1.2). To investigate structure and mechanics of interacting lipid membranes, the samples can be studied by X-ray and neutron scattering techniques (see Chaps. 5, 6).

Fig. 2.10 Sketch of solid-supported multilayers aligned parallel with the flat substrate



2.2 Principles of X-Ray and Neutron Scattering

X-ray and neutron scattering techniques are the principal experimental methods applied in this thesis. In the following, the common theoretical concepts of the used scattering techniques are introduced. Since this thesis deals with oriented membrane models, the main focus is put on specular and off-specular scattering from planar, oriented systems.

2.2.1 Basic Principles

X-ray and neutron scattering techniques are ideal for the structural characterization of a sample at molecular length scales. They provide structural information with high spatial resolution in a non-destructive manner and have access to buried structures in contrast to other techniques. A good introduction to X-ray and neutron scattering is given in the following references [34–37]. When probing a sample at length scales which are large compared to atomic structures (≈ 1 Å), the description of the sample in terms of continuous media has proven very powerful. Here, the atomic structure of the sample is neglected and the sample is parameterized with a refractive index $n(\vec{r})$, which is a complex function of the spatial coordinates $\vec{r}$:

$$n = 1 - \delta + i\beta$$

$$\delta = \frac{\lambda^2}{2\pi}\rho$$

$$\beta = \frac{\lambda}{4\pi}\mu$$

λ denotes the wavelength of the X-ray or neutron beam, ρ the scattering length density (SLD) of the medium, and μ the absorption coefficient of the medium for the beam. In case of X-rays, μ mainly accounts for the photoelectric consumption of X-ray photons, while the SLD is proportional to the electron density $\rho = r_0\rho_{\text{el}}$, where r_0 denotes the classical electron radius (or Thomson scattering length). In case of cold or thermal neutrons, μ accounts for neutron capture processes, while the SLD depends on the nuclear composition of the medium:

$$\rho = \sum_j \rho_j b_j$$

Here, ρ_j denotes the volume density of the nuclide species j , and b_j its coherent scattering length, which is tabulated for the vast majority of nuclides [38].

2.2.1.1 X-Ray versus Neutrons

Commonly used X-ray and neutron beams have comparable wavelengths in the Armstrong range. However, the ways X-rays and neutrons interact with matter are fundamentally different. While X-rays are scattered by the electron shells of atoms and molecules via electromagnetic interactions, neutrons are scattered by the atomic nuclei via strong interaction and the interaction between the magnetic dipole moments of the nucleus and the neutron [39]. Fortunately, despite these differences, the essentially same mathematical formalism can be used for both radiation types if the scattering signals are interpreted using the before mentioned continuum description. Besides these fundamental differences there are quite a few practical differences which become important in an experiment. Currently, the photon flux provided by modern X-ray sources (e.g., synchrotrons) is by orders of magnitude higher than the neutron flux provided by the most powerful neutron sources (nuclear reactors and spallation sources). For this reason, to record scattering signals with a desired signal to noise ratio typically takes much longer with neutrons, and, as a consequence, the spatial resolution achieved with X-rays is generally higher. On the other hand, the absorption coefficients of the matter are typically much lower for neutrons than for X-rays. This renders neutrons superior for the investigation of deeply buried structures. Moreover, the fact that the neutron scattering length can strongly differ between two isotopes of the same chemical element offers the unique possibility to manipulate the scattering contrast within the sample. This method is known as “contrast variation”, and is particularly powerful for soft-matter samples and biological samples. Here, molecules or parts of molecules can be highlighted by isotopic labeling without significantly influencing their chemical behavior. This works particularly well when hydrogen is replaced by deuterium (called deuteration), as these nuclides possess extremely different scattering lengths. Generally, whether X-rays or neutrons are more suited for an experiment depends on the sample and on the experimental conditions, and in many cases it is desirable to investigate a sample with both methods.

2.2.1.2 Scattering from Oriented Planar Samples

Oriented planar samples (e.g., thin films on a flat substrate) offer the possibility to distinguish between out-of-plane (z) and in-plane (x and y) directions. Here, the scattering signals contain structural information simultaneously for both out-of-plane and in-plane directions. The former can be extracted from the specular scattering intensity, while the latter is contained in the off-specular (diffuse) scattering intensity [34, 40–43].

Oriented samples are commonly modeled with “slab models” [44–47], where each slab represents a layer of constant refractive index n . Such a slab model is illustrated in Fig. 2.11. Since, for X-rays and thermal neutrons all materials possess refractive indices close to unity and, in thin layers, absorption can be neglected, the sample structure is typically described in terms of SLD profiles

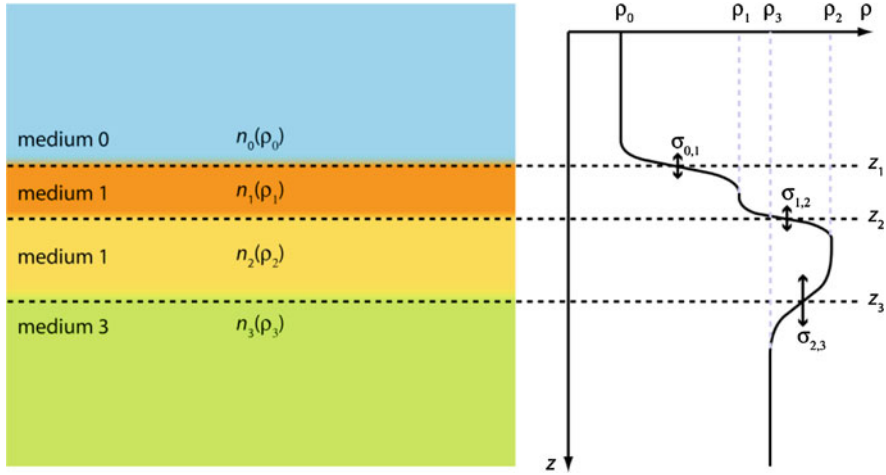


Fig. 2.11 (Left) schematic slab model illustration of an oriented sample. (Right) corresponding SLD profile, parameterized by the constant SLDs ρ of the stratified media and the SLD gradients across the interfaces (characterized by the width σ)

rather than in terms of refractive index profiles. The continuous transition of ρ at the interface between a slab and its neighbors is typically accounted for with an error function (characterized by transition width σ). Figure 2.12 shows the geometry considered in the following for a scattering experiment with an oriented sample.

Let a monochromatic beam with wave vector $\vec{k}_i$ impinge to an oriented sample with the incident angle θ_i . The plane of incidence is defined by $\vec{k}_i$ and the normal to the sample. We further consider that the beam is scattered into a direction which is part of the plane of incidence⁵ and has an angle θ_f with the sample surface as indicated in Fig. 2.12. $\vec{k}_f$ denotes the wave vector of the scattered beam. In the here considered elastic scattering processes the length of the wave vector is conserved:

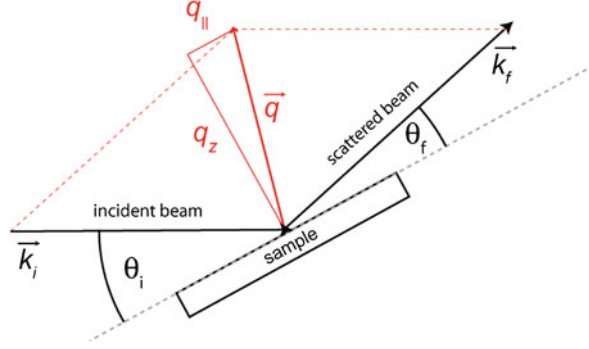
$$|\vec{k}_f| = |\vec{k}_i| = \frac{2\pi}{\lambda}$$

The momentum transfer corresponding to the scattering process is characterized by the scattering vector $\vec{q}$:

$$\vec{q} = \vec{k}_f - \vec{k}_i,$$

⁵ Within the frame of this thesis and for the explanations below it is not necessary to consider the scattering into directions which are not part of the plane of incidence.

Fig. 2.12 Sketch of the scattering geometry considered in this thesis



which can be decomposed into an out-of-plane component q_z , and a in-plane component $q_{\parallel}$. These two components are the reciprocal space coordinates and can be expressed in terms of the scattering angles θ_i and θ_f :

$$q_z = k_f^z - k_i^z = \frac{2\pi}{\lambda}(\sin\theta_f + \sin\theta_i),$$

$$q_{\parallel} = k_f^{\parallel} - k_i^{\parallel} = \frac{2\pi}{\lambda}(\cos\theta_f - \cos\theta_i)$$

2.2.2 Specular Scattering

The (in-plane averaged) out-of-plane structure of an oriented sample can be extracted from the specular scattering intensity, where only the intensity of the mirror-like reflection is considered (i.e., $\theta_f = \theta_i =: \theta$). In this case $q_{\parallel} = 0$ and q_z simplifies to:

$$q_z = \frac{4\pi}{\lambda} \sin\theta$$

2.2.2.1 Specular Reflectivity from a Single Ideal Interface

We consider an ideal (i.e., perfectly smooth) planar interface between two homogenous media denoted with 0 and 1, and a beam impinging onto the interface coming from medium 0. The out-of-plane component k_j^z of the wave vector in each medium depends on q_z and on the refractive indices of the media, n_0 and n_1 :

$$k_j^z = \frac{2\pi}{\lambda} \sqrt{\left(\frac{q_z \lambda}{4\pi}\right)^2 + n_j^2 - 1}$$

This can be simplified if absorption is neglected:

$$k_j^z = \sqrt{\left(\frac{q_z}{2}\right)^2 - 4\pi\rho_j}$$

The complex amplitudes of the reflected and transmitted waves are given as the Fresnel amplitude reflection and transmission coefficient:

$$r_{0,1}^F = \frac{k_0^z - k_1^z}{k_0^z + k_1^z} \quad \text{and} \quad t_{0,1}^F = 1 + r_{0,1}^F.$$

In contrast to the case of visible light, these coefficients do not depend significantly on the polarization of the X-ray or neutron beam [34]. The specular reflectivity R , defined as the ratio between the reflected intensity I_r and the incident intensity I_i , is the absolute square of the complex Fresnel amplitude reflection coefficient:

$$R(q_z) := I_r/I_i = |r_{0,1}^F|^2$$

If the refractive index of medium 1 is lower than that of medium 0, the beam is totally reflected ($R = 1$) below a critical q_z value, denoted with q_z^c . This value can be approximated in terms of the SLDs of the media:

$$q_z^c \cong \sqrt{16\pi(\rho_1 - \rho_0)}$$

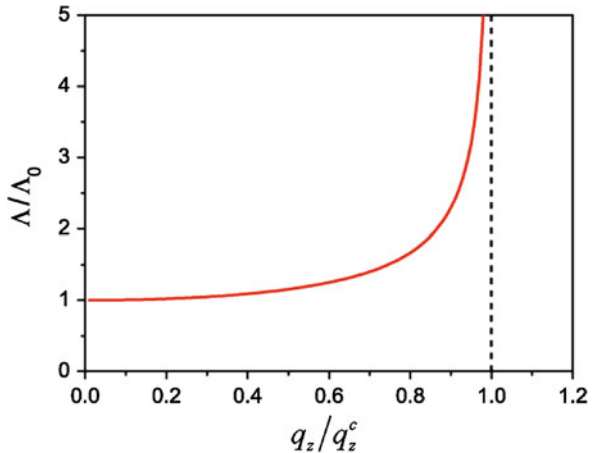
Below q_z^c , medium 1 is illuminated only in close vicinity of the interface is by an evanescent field of q_z -dependent intensity decay length Λ .

$$\Lambda = \Lambda_0 \left(1 - (q_z/q_z^c)^2\right)^{-1/2}, \quad \text{with } \Lambda_0 = 1/q_z^c$$

This dependency is shown in Fig. 2.13, and it is seen that the decay length diverges as q_z approaches q_z^c . Above q_z^c the beam propagates into medium 1.

In Fig. 2.14 (left) the reflectivity of an ideal interface ($\rho_0 = 0$, $\rho_1 = 20 \times 10^{-6} \text{ \AA}^{-2}$, $n_0 > n_1$) is plotted as a function of q_z . For high q_z values ($q_z \gg q_z^c$), the reflected intensity is weak. In this limit the reflectivity decays as q_z^{-4} , see dashed

Fig. 2.13 Intensity decay length of the evanescent field as a function of q_z . The decay length diverges as q_z approaches q_z^c



line in Fig. 2.14 (left). In the regime of weak reflection the kinematic approximation, also known as First Born Approximation is valid. In this approximation, the incident beam is assumed to be “inexhaustible” and the reduction of the transmitted intensity due to reflections is neglected. Within the range of its validity, the kinematic approximation is very powerful, as it enables the treatment of many scattering problems in terms of simple algebraic expressions. However, the so calculated scattering intensities cannot be scaled with respect to the incident beam intensity.

2.2.2.2 Interfacial Roughness

Realistic (non-ideal) interfaces between two homogenous media do not possess a sharp jump in the SLD (and thus, in the refractive index) but a gradual transition (see Fig. 2.11). To describe this transition, error functions characterized by the transition width σ are typically used. For this case, Nevot and Croce [48] have derived how the amplitude reflection coefficient for an interface should be modified:

$$r_{0,1}^F \rightarrow r_{0,1}^F \cdot \exp\left(-\frac{1}{2} q_z^2 \sigma_{0,1}^2\right)$$

The effect of the interfacial roughness is shown in Fig. 2.14 (right) for $\sigma = 3 \text{ \AA}$. It should be pointed out that the specular intensity contains information only on the in-plane averaged sample structure. This averaged structure does not distinguish between an SLD gradient across the interface (i.e., an identical z -dependence of the SLD for all x and y) and topological roughness (i.e., the in-plane heterogeneity of the z -position of the interface). Only the interpretation of off-specular (diffuse) scattering intensities enables this distinction (see Sect. 2.2.3).

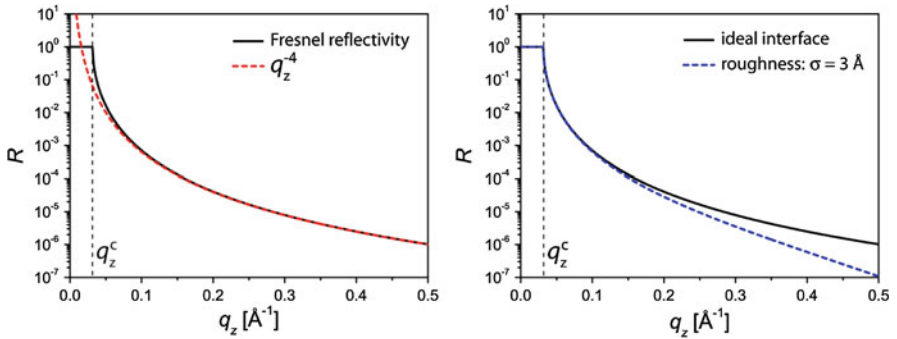


Fig. 2.14 (Left) Fresnel reflectivity from a single ideal interface. (Right) influence of interfacial roughness

2.2.2.3 Stratified Interfaces

The reflectivity signals from N stratified interfaces (see Fig. 2.11) can be calculated using the formalisms introduced by Parratt [34, 49]. Based on the Fresnel amplitude reflection coefficients,

$$r_{j,j+1}^F = \frac{k_j^z - k_{j+1}^z}{k_j^z + k_{j+1}^z} \cdot \exp\left(-\frac{1}{2}q_z^2 \sigma_{j,j+1}^2\right)$$

the effective amplitude reflection coefficient of the stratified system $r_{0,N}$ is calculated recursively starting from the last interface (between medium $N - 1$ and medium N):

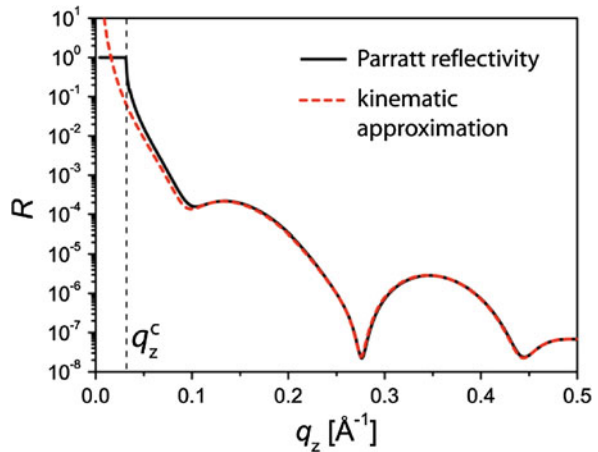
$$r_{j,N} = \frac{r_{j,j+1}^F + r_{j+1,N} \cdot e^{2ik_{j+1}^z d_{j+1}}}{1 + r_{j,j+1}^F \cdot r_{j+1,N} \cdot e^{2ik_{j+1}^z d_{j+1}}}$$

j counting downwards from $N - 2$ to 0, $d_j = z_{j+1} - z_j$ denotes the thickness of medium j .

The reflectivity is then given as: $R(q_z) = |r_{0,N}|^2$.

A calculated reflectivity signal from 3 stratified interfaces ($\rho_0 = 0$, $\rho_1 = 10 \times 10^{-6} \text{ \AA}^{-2}$, $\rho_2 = 25 \times 10^{-6} \text{ \AA}^{-2}$, $\rho_3 = 20 \times 10^{-6} \text{ \AA}^{-2}$, $d_1 = 35 \text{ \AA}$, $d_2 = 25 \text{ \AA}$, $\sigma_{0,1} = \sigma_{1,2} = \sigma_{2,3} = 3 \text{ \AA}$) is presented in Fig. 2.15. In contrast to the signal from a single interface, the shown curve possesses various features like oscillations and deep minima (known as Kiessig fringes), caused by the interference of the waves reflected at different interfaces. The Parratt formalism constitutes a fully dynamical description of the scattering process where the intensity of the incident beam is conserved, and the reflections from each interface (including multiple back- and forth reflections within the slabs) as well as the interference of

Fig. 2.15 Specular reflectivity from a set stratified rough interfaces



all reflected and transmitted waves are considered. An equivalent formalism was presented by Abeles, based on layer matrices [50]. In the regime of weak reflection ($q_z \gg q_z^c$), the reflectivity signals from stratified interfaces can be expressed in the kinematical approximation using the Master Formula [34]. Here, the signal is described with the asymptotic scaling of the reflectivity of a single, ideal interface, and with the Fourier-transformed SLD gradient.⁶

$$R(q_z) \propto \frac{1}{q_z^4} \left| \int_{-\infty}^{\infty} \frac{d\rho}{dz} \exp(-iq_z z) dz \right|^2 \quad (2.1)$$

In case of slab models, this expression can be calculated very efficiently, as the derivatives of error functions are Gaussian functions that can be Fourier-transformed analytically. The resulting signal is also shown in Fig. 2.15. As the signal possesses no absolute scale, it was multiplied by a pre-factor such that it coincides with the dynamically calculated curve in the valid range.

2.2.2.4 Periodic Multilayers

In case many interfaces are arranged periodically ($z_{j+1} - z_j = d$ for all j), the interference of the waves reflected from the interfaces results in peaks of high reflection intensity, known as Bragg peaks. The positions of the peaks maxima, $q_z^{\max}$, are located periodically along q_z :

$$q_z^{\max} = 2m\pi/d, \quad m = 1, 2, \dots \quad (2.2)$$

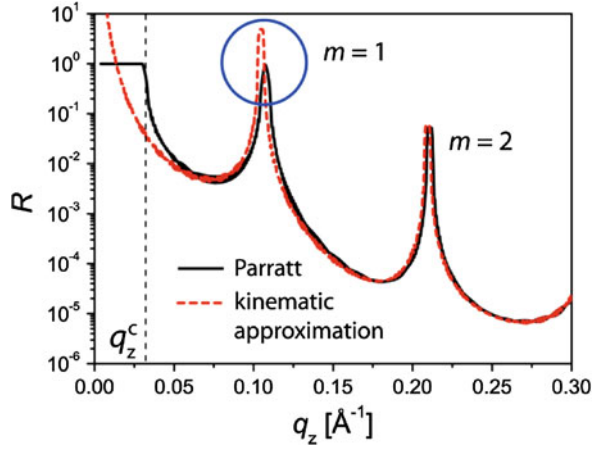
This is shown in Fig. 2.16 (solid black line) for a periodic system of 100 double layers ($\rho_A = 20 \times 10^{-6} \text{ \AA}^{-2}$, $\rho_B = 0$, $d_A = 35 \text{ \AA}$, $d_B = 25 \text{ \AA}$) between two semi-infinite media ($\rho_0 = 0$, $\rho_1 = 20 \times 10^{-6} \text{ \AA}^{-2}$) and $\sigma = 3 \text{ \AA}$ for all interfaces. The intensity of the Bragg peaks (especially of the first Bragg peak with $m = 1$) often becomes comparable to that of the incident beam. In this case the kinematic approximation fails even for $q_z \gg q_z^c$, as it predicts too high intensities (see dashed red line in Fig. 2.16).

2.2.3 Off-Specular (Diffuse) Scattering

Real interfaces always possess topological roughness, which leads non-mirror-like scattering ($\theta_f \neq \theta_i$, $q_{\parallel} \neq 0$, see Fig. 2.12), called off-specular or diffuse scattering. To consider diffuse scattering, the intensity has to be described as a function of q_z and $q_{\parallel}$. Like the reflectivity $R(q_z)$, the (more general) scattering intensity

⁶ Often the asymptotic q_z^{-4} factor is replaced by the reflectivity curve of an ideal interface between the semi-infinite media. The results of this “hybrid” description come close to those of the full dynamical treatment in some cases.

Fig. 2.16 Specular reflectivity from a multilayered system. The signal exhibits Bragg maxima periodic in q_z . The breakdown of the kinematic approximation at the first ($m = 1$) Bragg peak is highlighted with a blue circle



$I(q_z, q_{||})$ is defined in terms of total intensity in the following. It can be expressed with the scattering function $S(q_z, q_{||})$, which is defined in terms of incident flux and the solid angle of detection [43]:

$$I(q_z, q_{||}) \propto \frac{1}{q_z^2} S(q_z, q_{||})$$

2.2.3.1 Scattering from a Single, Topologically Rough Interface

The topological roughness of an interface can be parameterized with the local out-of-plane displacement $u(x, y) = z(x, y) - \langle z \rangle$, where $z(x, y)$ denotes the height of the interface at the point (x, y) and $\langle z \rangle$ its average height. The diffuse scattering from an interface is determined by the characteristics of the topological roughness. The scattering function can be expressed [34, 40, 42, 43] in terms of the height–height correlation $C(r)$ of the interface (see Sect. 2.1.3.2). In Kinematical approximation, the scattering function is given as:

$$S(q_z, q_{||}) \propto \frac{e^{-q_z^2 \sigma^2}}{q_z^2} \int_{-\infty}^{\infty} e^{q_z^2 C(r)} e^{-iq_{||} r} dr$$

The expression comprises a Fourier-transformation which has to be evaluated numerically in general. Figure 2.17 (left) shows the calculated total (specular and diffuse) scattering intensity $I(q_z, q_{||})$ from a single topologically rough interface ($\rho_0 = 0, \rho_1 = 20 \times 10^{-6} \text{ Å}^{-2}$) in color coded logarithmic scale. Here, the height–height correlation function was parameterized⁷ as $C(r) = \sigma^2 \exp(-(r/\xi)^{2h})$, with

⁷ Such a parameterization is commonly used to describe interfaces with self-affine roughness [40], but cannot describe all types of surface topologies (see Sect. 4.1.1).

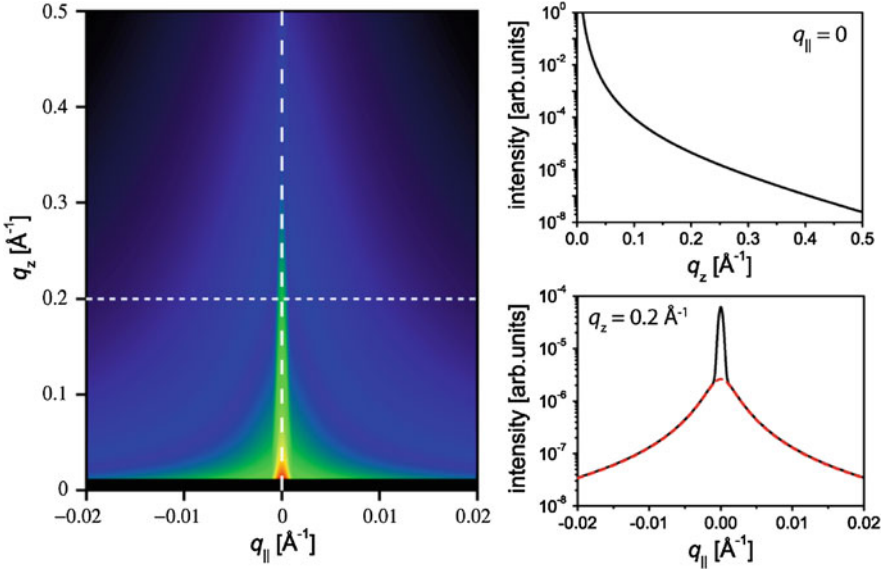


Fig. 2.17 (Left) simulated scattering intensity from a single rough interface in kinematic approximation. (Top right) central cut through the intensity map along the specular line (vertical broken line in the left panel). (Bottom right)(solid black line) intensity as a function of $q_{\parallel}$ (horizontal dashed line in the left panel). (Dashed red line) diffuse intensity alone

the topological rms roughness $\sigma = 3 \text{ \AA}$, the decay length $\zeta = 500 \text{ \AA}$, and the stretching exponent $h = 0.5$. The top right panel shows the intensity along the specular line as a function of q_z . The bottom right panel of the figure (solid black line) shows a cut through intensity map along $q_{\parallel}$ at $q_z = 0.2 \text{ \AA}^{-1}$, indicated by the horizontal dashed line in the left panel. The central maximum represents the specular peak, where the intensity is dominated by the specular contribution. Except for the peak region, the intensity corresponds to the diffuse contribution. For practical reasons, the width of the specular peak (ideally a Dirac delta function of $q_{\parallel}$) was broadened by convoluting $I(q_z, q_{\parallel})$ with an artificial point-spread function in $q_{\parallel}$. The dashed red line represents the diffuse intensity alone.

A dynamical treatment of the scattering from a topologically rough interface requires taking refraction effects and strong scattering into account. This is achieved by the Distorted Wave Born Approximation (DWBA) [40, 42], at the cost of a much higher numerical effort. In DWBA, the scattering function is given as:

$$S(q_z, q_{\parallel}) \propto |t_{0,1}^{F,i}|^2 |t_{0,1}^{F,f}|^2 \frac{1}{q_z^2} \exp\left(-\frac{1}{2}\sigma^2((q_1)^2 + (q_1^*)^2)\right) \cdot \int_{-\infty}^{\infty} e^{|q_1|^2 C(r)} e^{-iq_{\parallel}r} dr$$

$t_{0,1}^{F,i}$ and $t_{0,1}^{F,f}$ denote the Fresnel amplitude transmission coefficients for the incident and scattered beam, respectively:

$$t_{0,1}^{F,i} = 1 + \frac{k_{i,0}^z - k_{i,1}^z}{k_{i,0}^z + k_{i,1}^z}, t_{0,1}^{F,f} = 1 + \frac{k_{f,0}^z - k_{f,1}^z}{k_{f,0}^z + k_{f,1}^z}$$

$q_1 = k_{f,1}^z - k_{i,1}^z$ denotes the momentum transfer in medium 1.

These quantities are defined via the out-of-plane components of the incident and scattered wave vectors in medium 1, $k_{i,1}^z$ and $k_{f,1}^z$, which can be calculated by mathematically inverting the scattering geometry:

$$k_{i,1}^z = \sqrt{(k_i^z)^2 - 4\pi\rho_1}, \quad k_{f,1}^z = \sqrt{(k_f^z)^2 - 4\pi\rho_1}$$

$$k_i^z = k_0 \sin\theta_i, \quad k_f^z = k_0 \sin\theta_f$$

$$\begin{aligned} \theta_i &= \frac{1}{2} \arccos\left(1 - \frac{q_x^2 + q_z^2}{2k_0^2}\right) + \arctan\left(\frac{q_x}{q_z}\right), \theta_f \\ &= \frac{1}{2} \arccos\left(1 - \frac{q_x^2 + q_z^2}{2k_0^2}\right) - \arctan\left(\frac{q_x}{q_z}\right) \end{aligned}$$

$$k_0 = 2\pi/\lambda$$

Figure 2.18 (left) shows the total scattering intensity $I(q_z, q_{\parallel})$ from a single topologically rough interface (same parameters as before) calculated in DWBA.

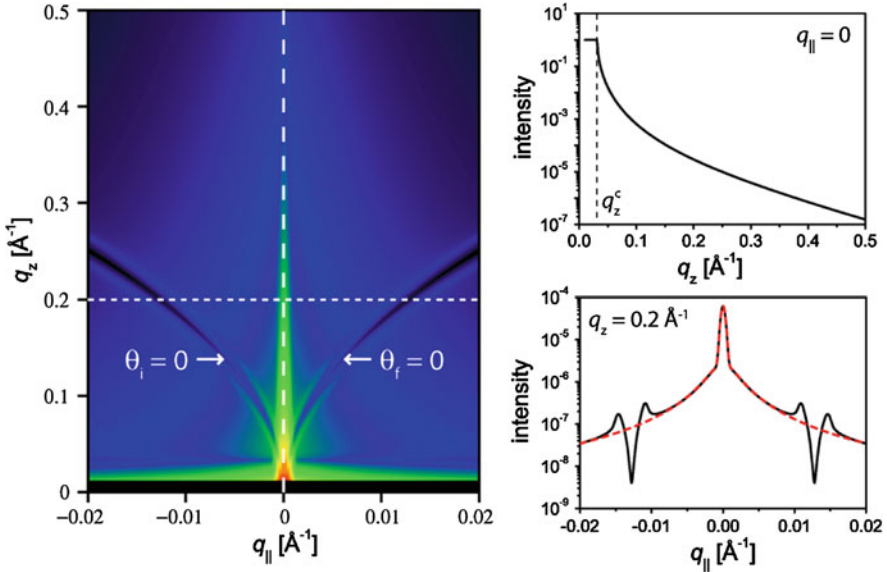


Fig. 2.18 (Left) simulated scattering intensity from a single rough interface in DWBA. (Top right) Central cut through the intensity map along the specular line (vertical broken line in the left panel). (Bottom right solid black line) intensity as a function of $q_{\parallel}$ (horizontal dashed line in the left panel). Dashed red line: kinematic approximation

The top right panel shows the intensity along the specular line as a function of q_z , which exhibits the total reflection regime in the dynamic treatment. The reciprocal space map contains additional features, most prominently the Yoneda-wings along the sample horizons ($\theta_i = 0$, $\theta_f = 0$) as indicated in the figure. They are results of the refraction effects which become important at grazing incidences near the sample horizons. Again, the right panel of the figure (solid black line) shows a cut through intensity map along $q_{||}$ at $q_z = 0.2 \text{ \AA}^{-1}$, indicated by the horizontal dashed line in the left panel. In this representation, the Yoneda wings are seen as dips in the intensity. For comparison, the result of the kinematic approximation is superimposed to the graph (dashed red line).

2.2.3.2 Scattering from Stratified Interfaces with Correlated Topological Roughness

In kinematic approximation, the scattering function of a set of N stratified interfaces with correlated topological roughness is given as:

$$S(q_z, q_{||}) \propto \frac{1}{q_z^2} \sum_{n=1}^N \sum_{m=1}^N e^{-\frac{1}{2}q_z^2(\sigma_n^2 + \sigma_m^2)} \Delta\rho_n \Delta\rho_m e^{-iq_z(z_n - z_m)} \int_{-\infty}^{\infty} e^{q_z^2 C_{nm}(r)} e^{-iq_{||}r} dr$$

with $C_{nm}(r) = \langle u_n(\vec{r}_0 - \vec{r}) \cdot u_m(\vec{r}_0) \rangle_{\vec{r}_0}$ and $r = |\vec{r}|$ (see Sect. 2.1.3)

$\Delta\rho_n$ denotes the SLD jump across the n th interface and σ_n its topological rms roughness. In the following, the slab model introduced for the calculation of the specular reflectivity is used (see Sect. 2.2.2.3). Further, we assume that each interface possesses the height–height self-correlation $C_{n=m}(r) = \sigma^2 \exp(-(r/\xi)^{2h})$ with the identical parameters $\sigma = 3 \text{ \AA}$, $\xi = 500 \text{ \AA}$, and $h = 0.5$ (like the single topologically rough interface discussed before). To highlight the role of the cross-correlation terms $C_{n \neq m}(r)$, two extreme scenarios are considered: (1) Full correlation between all interfaces. The calculated scattering intensity $I(q_z, q_{||})$ for this scenario is shown in the top left panel of Fig. 2.19. (2) Two interfaces possess fully correlated roughness, while there is no correlation between these two interfaces and the third one. The corresponding scattering intensity is shown in the top right panel of Fig. 2.19. Mathematically this can be expressed using the correlation matrices:

$$C_{nm} = C_{n=m} \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix} \quad (1)$$

$$C_{nm} = C_{n=m} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{pmatrix} \quad (2)$$

As can be seen in the figure, there are distinct differences in the diffuse scattering intensity. These differences can be highlighted by plotting the scattering intensity as a function of q_z for various $q_{\parallel}$ values. This is shown in the bottom panels of Fig. 2.19, where the scattering intensity along q_z is plotted for $q_{\parallel} \cong 0$ (central cut, see dashed white lines in top panels) and $q_{\parallel} \neq 0$ (diffuse cut, see broken white lines in top panels). In the fully correlated case 1 (bottom left panel), all features (minima and maxima) seen in the central cut (where the intensity is dominated by the specular contribution) are also reflected in the diffuse cut, which is constituted by the diffuse intensity. In contrast, in the partially correlated case 2 (bottom right panel), only the minimum at around $q_z = 0.27 \text{ \AA}^{-1}$ of the central cut

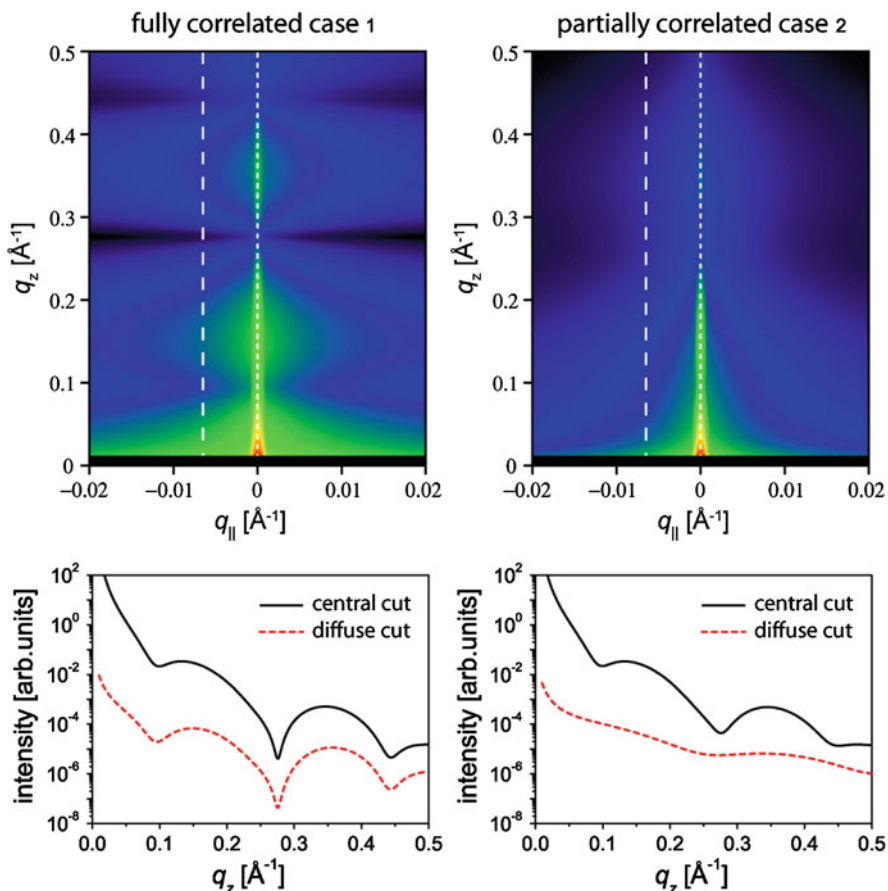


Fig. 2.19 (Top) simulated scattering intensity from a set of interfaces with correlated topological roughness in kinematic approximation. The vertical dashed lines indicate the “central cut”, while the vertical broken lines indicate the “diffuse cut”. (bottom) “Central cuts” and “diffuse cuts” through the intensity maps. (left) Case 1 with full correlation between all interfaces. (right) Case 2 with only partial correlation

is also seen in the diffuse cut, and this minimum corresponds to the interference between the two correlated interfaces. Generally, the way how the features of the diffuse scattering intensity relate to those of the specular scattering intensity is determined by the cross-correlation functions.

The dynamical treatment of the scattering from stratified interfaces with correlated topological roughness requires the use of the DWBA. This enables the correct description of strong scattering intensities and features which are characteristic for multiple scattering. However, the numerical effort for the computations is enormous and the corresponding equations are not presented in this work. For further reading the following literature can be consulted [40, 42, 51, 52].

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