

Analyzing Surface Dynamics using X-ray Photon Correlation Spectroscopy

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Ingrid Dax
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Dekan:

Prof. Dr. Thilo Stehle

1. Berichterstatter/-in:

Prof. Dr. Dr. h.c. Frank Schreiber

2. Berichterstatter/-in:

Prof. Dr. Martin Oettel

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Abstract

This thesis deals with structural investigations of organic thin films and analyzes the evolution of their surface morphology during various processes such as thin film growth and thermal annealing. In addition to the fundamental understanding of the underlying microscopic processes, these organic thin films also play a central role in applications such as optoelectronics, photovoltaics, sensor technology and microelectronics. Research in this area, therefore, opens up opportunities for progress, for example in, the production of organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and organic solar cells (OSCs).

The growth of thin films is a statistical non-equilibrium process, the understanding of which plays a crucial role in predicting the final morphology and thus provides access to control the properties of the thin film. Organic materials can exhibit both, layer-by-layer development and rapid roughening, which is influenced by a variety of parameters such as the choice of material or growth temperature. Understanding the structure formation during growth is a fundamental challenge. Therefore, this research aims to reveal the growth behavior of representative systems in the field of organic semiconductors.

In order to understand these fundamental microscopic processes, thermal annealing, in addition to the investigation of thin film growth, can enable a targeted investigation of individual processes, as its implementation depends on fewer parameters, which makes the analysis more accessible. With this method, a constant total amount of deposited material is maintained and fewer experimental parameters are required. The transition of structure and morphology to an equilibrium state is also observed, simplifying the investigation of specific diffusion processes. Consequently, thin film annealing serves as a gateway to explore microscopic surface dynamics, revealing phenomena such as surface diffusion and clustering.

A key method used in this study is coherent X-ray scattering, in particular in situ characterization techniques based on X-ray photon correlation spectroscopy (XPCS). This approach provides real-time insights into the dynamic evolution of thin films during growth and annealing.

The investigation focuses on dynamics occurring on the micrometer length scale and is particularly concerned with molecular cluster arrangements such as surface islands. Using XPCS, characteristic dynamic and kinetic time scales associated with the underlying (re)organization processes are extracted. However, mapping these time scales and specific features in the experimental data to scenarios in real space is a complicated task.

The interpretation of XPCS data in the context of surface investigations is therefore a major challenge. To overcome this, simulations proved to be a valuable tool. Therefore, a part of this work focuses on the construction of a simulation structure for different surface reorganization processes, with an emphasis on the growth or shrinkage of surface island (or hole) structures. With this approach, experiments with coherent scattering are modelled and the results are compared to experimental data. This comparative analysis makes it possible to assign experimental observations to physically plausible processes on the surface, providing deep insights into the evolving morphology of thin films during the growth and annealing processes.

Zusammenfassung in deutscher Sprache

Diese Arbeit befasst sich mit strukturellen Untersuchungen von organischen Dünnschichten. In diesem Kontext wird die Entwicklung ihrer Oberflächemorphologie während verschiedener Prozesse wie dem Filmwachstum und dem thermischen Ausglühen analysiert. Neben dem fundamentalen Verständnis der zugrundeliegenden mikroskopischen Prozesse spielen dünne organischen Schichten zudem eine zentrale Rolle in Anwendungen wie der Optoelektronik, der Photovoltaik, der Sensorik und der Mikroelektronik. Die Forschung in diesem Bereich eröffnet daher Möglichkeiten für Fortschritte, beispielsweise bei der Herstellung von organischen Leuchtdioden (OLEDs), organischen Feldeffekttransistoren (OFETs) und organischen Solarzellen (OSCs).

Das Wachstum dünner Schichten ist ein statistischer Nicht-Gleichgewichtsprozess, dessen Verständnis eine entscheidende Rolle bei der Vorhersage der endgültigen Morphologie spielt und somit Kontrollmöglichkeiten der Eigenschaften von dünnen Schicht bietet. Organische Materialien können sowohl eine schichtweise Entwicklung, als auch eine schnelle Aufrauung während des Wachstums aufweisen, welches durch eine Vielzahl von Faktoren, wie der Wahl des Materials oder der Wachstumstemperatur, beeinflusst wird. Das Verständnis dieser Strukturbildung ist eine grundlegende Herausforderung, daher zielt diese Arbeit darauf ab, das Wachstumsverhalten repräsentativer Systeme im Bereich der organischen Halbleiter zu entschlüsseln.

Um diese grundlegenden mikroskopischen Prozesse zu verstehen, kann neben der Untersuchung des Schichtwachstums auch das thermische Ausglühen eine gezielte Untersuchung einzelner Prozesse ermöglichen, da seine Durchführung von einer geringeren Zahl an Parametern abhängt, was die Analyse zugänglicher macht. Bei dieser Methode wird eine konstante Gesamtmenge an abgeschiedenem Material beibehalten und es sind weniger Versuchsparameter erforderlich. Es wird auch der Übergang von Struktur und Morphologie in einen Gleichgewichtszustand beobachtet, dabei vereinfacht sich die Untersuchung auf spezifische Diffusionsprozesse. Folglich dient das Dünnschichtglühen der Erforschung mikroskopischer Oberflächendynamiken, wobei Phänomene wie Oberflächendiffusion und -clusterbildung entschlüsselt werden.

Eine Schlüsselmethode, die in dieser Studie eingesetzt wird, ist die kohärente Röntgenstreuung, insbesondere in situ-Charakterisierungstechniken auf der Grundlage

der Röntgenphotonenkorrelationsspektroskopie (XPCS). Dieser Ansatz ermöglicht Echtzeiteinblicke in die dynamische Entwicklung dünner Schichten während des Wachstums und des Ausglühens.

Die Untersuchung konzentriert sich auf die Dynamik, die auf der Mikrometer-Längenskala auftritt, und befasst sich insbesondere mit Molekülcluster-Anordnungen wie Oberflächeninseln. Mithilfe von XPCS werden charakteristische dynamische und kinetische Zeitskalen extrahiert, die mit den zugrunde liegenden (Re-)Organisationsprozessen verbunden sind. Die Abbildung dieser Zeitskalen und spezifischer Merkmale in den experimentellen Daten auf Szenarien im realen Raum ist jedoch eine komplizierte Aufgabe.

Die Interpretation von XPCS-Studien im Kontext von Oberflächenuntersuchungen ist daher eine große Herausforderung. Um diese zu bewältigen, haben sich Simulationen als wertvolles Werkzeug erwiesen. Daher konzentriert sich ein Teil dieser Arbeit auf die Konstruktion einer Simulationsstruktur für verschiedene Oberflächenreorganisationsprozesse, wobei der Schwerpunkt auf dem Wachstum oder der Schrumpfung von Oberflächeninseln (oder Lochstrukturen) liegt. Mit diesem Ansatz werden Experimente mit kohärenter Streuung modelliert und die Ergebnisse mit experimentellen Daten verglichen. Diese vergleichende Analyse ermöglicht es, experimentelle Beobachtungen physikalisch plausiblen Prozessen an der Oberfläche zuzuordnen, was tiefe Einblicke in die sich entwickelnde Morphologie dünner Schichten während des Wachstums- und Glühprozesses ermöglicht.

Part I

Introduction and Theory

Chapter 1

Motivation

Research of thin films is a necessary step towards improving the existing technologies and developing new applications. In this context, organic materials are gaining prominence, due to their processability, flexibility and low costs. Those thin films are indispensable in optoelectronics, photovoltaics, sensor technology, and microelectronics, which opens up opportunities for advancement, particularly in applications such as OLEDs, OFETs, and OSCs [1–9].

Mastering and controlling growth processes and fine-tuning the morphology and properties of organic thin films is not just a pursuit of purely scientific interest but a crucial step towards maximizing performance in various fields [10, 11].

The focus of this work lies in the investigation of growth and annealing processes of thin films. The growth of organic materials is a complex process that can happen by several growth mechanisms, including layer-by-layer growth, statistical growth, rapid roughening and mixed regimes. Understanding the non-equilibrium evolution of thin film growth by deposition is crucial, and deciphering the growth behavior of representative systems for organic semiconductors is a scientific frontier to be explored.

Thermal annealing of thin films adds another layer of complexity and requires a deep understanding of the dynamics of surface reorganization.

For this purpose, coherent X-ray scattering is used – an approach that enables the investigation of dynamics in real-time. In the world of organic thin films, the use of state-of-the-art in situ characterization technique XPCS opens up new possibilities [12]. Traditionally, this technique has been used to analyze solutions containing colloidal particles to study their continuous movement [13–17]. But there have been several investigations of other objects using XPCS, such as the investigation of polymers [18], molecular and magnetic glasses [19, 20], capillary waves in liquid crystals [21, 22], magnetic or orbital order domains [23, 24] etc. Following these successful applications, XPCS has recently been adapted to the study of thin films [25, 26]. Specifically, in the context of this work, the focus lies on thin films composed of organic materials.

Through the use of in situ X-ray experiments and the development of simulations, the study presented here enables real-time observation of molecular island formation, extraction of dynamic and kinetic time scales, and provides profound

insights into the evolving morphology of thin films during growth and annealing. The presented approach enables a comprehensive understanding of thin film development, ranging from changes in island dimensions and roughness to the coverage rates of individual layers and diffusion modes. This provides a better understanding of the intricate processes that determine the formation and arrangement of thin films.

This thesis is structured as follows: The first part contains the theoretical foundations. As the main focus is on surface effects, Chap. 2 provides insights into surfaces – what happens on them (the targeted measurements) and how surface scattering experiments work. Chap. 3 examines how X-rays interact with matter and the role they play in materials analysis. The crucial concept of coherence, which is essential to the study of dynamics, is explained in Chap. 4. Chap. 5 deals with analytical techniques, in particular XPCS, which uses coherence to extract dynamical parameters.

In the second part of the thesis, the investigated materials are introduced (Chap. 6), and common methods for thin film analysis are explained. This includes the introduction of experimental methods in Chap. 7 and the exploration of simulations to compare experimental data in Chap. 8.

In the third part, various results are presented, starting with an investigation of the dynamics during the growth of a diindenoperylene (DIP) film in Chap. 9. This is succeeded by an exploration of the annealing process of N,N'-dioctyl-3,4,9,10-perylenedicarboximide (PTCDI-C8) films in Chap. 10. The last chapter in the results part (Chap. 11) compiles complementary data and provides insights into the annealing and growth processes of different materials.

Finally, part five, which includes Chap. 12 summarizes the results and gives an overall conclusion.

Chapter 2

Effects on Surfaces

This thesis focuses on the investigation of surfaces, which is why a separate chapter is dedicated to this aspect. The description of effects on surfaces is discussed, aiming at creating a basic understanding of the essential aspects of the investigation. Accordingly, the first section focuses on the description of different diffusion processes that can appear on surfaces, while the subsequent section introduces a classification of diverse growth scenarios.

2.1 Surface Diffusion

In exploring the complexity of non-equilibrium processes, this section focuses on the dynamics related to thin film growth and the associated effects of diffusion phenomena on the surface morphology. In this context, time-dependent equations are necessary to capture the evolving thin film comprehensively. They serve as a basis for describing various processes essential for the growth of thin films, such as cluster formation, cluster and edge diffusion, and movement across or towards a step-edge. The temperature dependence of these processes adds an additional layer of complexity and influences the overall kinetics of thin film development. A visual representation of these processes can be found in Fig. 2.1. For a deeper insight into the topic, it is referred to Ref. [27–34].

The investigation of diffusion phenomena is of central importance in understanding the growth of thin films. A distinction can be made between diffusion within a single layer (intralayer diffusion) and diffusion between different layers (interlayer diffusion).

First, we will focus on intralayer diffusion in thin films. The diffusion coefficient D , which is a measure of how particles (for example molecules) diffuse across the film's surface, depends on the temperature T , as [27, 32]

$$D = D_0 \exp\left(-\frac{E_D}{k_B T}\right), \quad (2.1)$$

with the Boltzmann constant k_B and a prefactor D_0 . The activation energy for diffusion E_D is the minimum energy required for particles to move from one position to another within the layer. Hence, it is a measure of the energy barrier

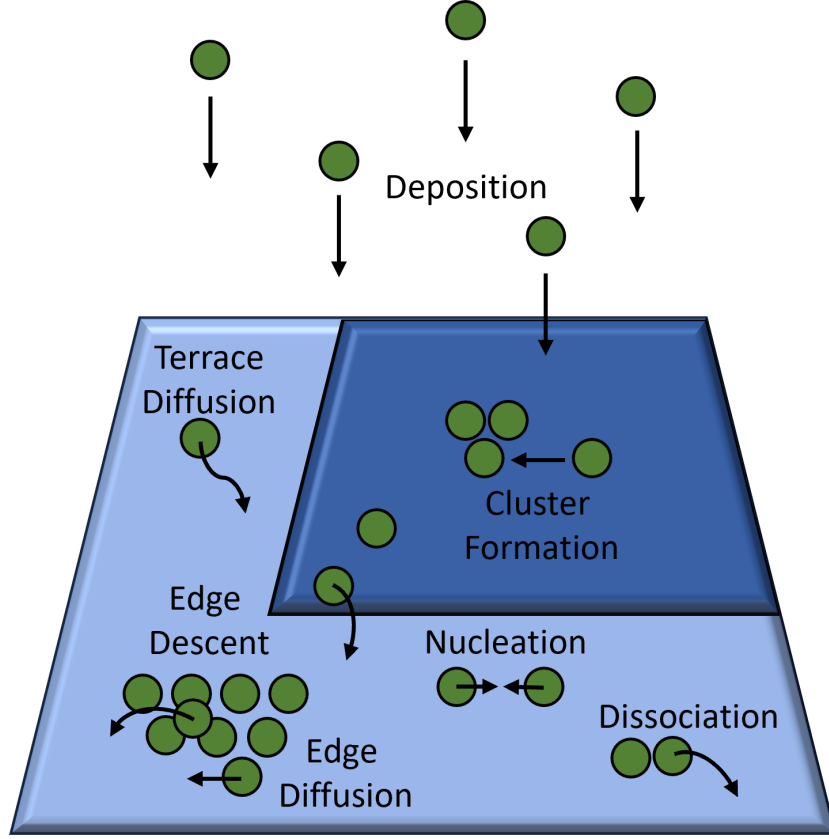


Figure 2.1: Schematic representation of possible effects on surfaces during molecular deposition on a thin film, including the formation of clusters, diffusion of clusters and edges, and movement across or toward a stepped edge (based on [27]).

that particles must overcome to diffuse. As the temperature increases, the fraction in Eq. (2.1) decreases, leading to an increase in the diffusion coefficient. This aligns with the understanding that higher temperatures provide particles with more thermal energy, making it easier for them to overcome barriers and move in the film layer.

Interlayer diffusion, on the other hand, is described by

$$D' = D \cdot \exp\left(-\frac{\Delta E_{ES}}{k_B T}\right), \quad (2.2)$$

which incorporates the Ehrlich-Schwoebel barrier ΔE_{ES} [35, 36]. This barrier represents an additional energy barrier for particles trying to diffuse across the edge into the next layer. Consequently, it is more probable for particles to stay in their initial layer than to move to another one, i.e., $D' < D$. Further, the ratio between ΔE_{ES} and E_D plays a crucial role. If ΔE_{ES} is significantly greater than E_D , diffusion between the layers is hindered, leading to the so-called statistical (or 3D) growth. Hence, the influence of the Ehrlich-Schwoebel barrier on the morphology

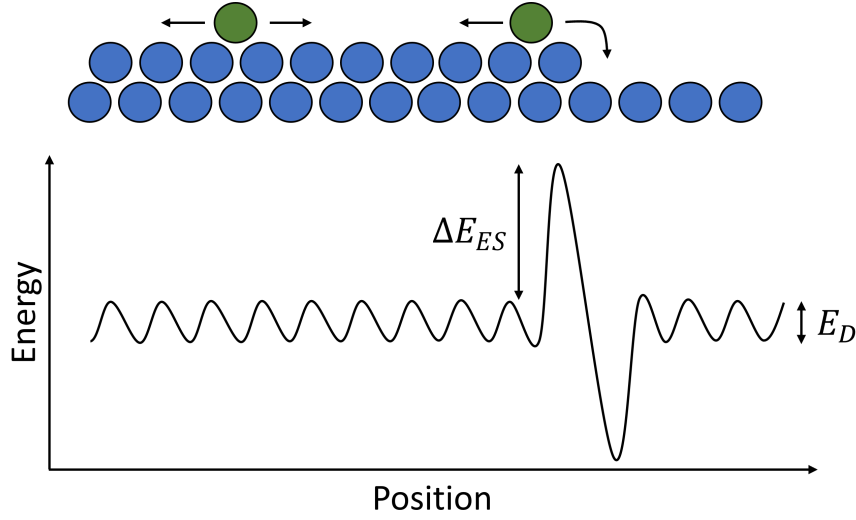


Figure 2.2: Potential particle dynamics on a thin film (based on [37]). The motion of the particles is influenced by their energy levels and the energy barriers within the layers. The particles can either diffuse within the same layer, depending on E_D , or cross a step edge into another layer, depending on the height of the Ehrlich-Schwoebel barrier ΔE_{ES} .

of the thin film can be clearly anticipated. Both, intra- and interlayer diffusion, including the energy barriers, is schematically represented in Fig. 2.2.

In the following, the study of deposition on the substrate under molecular flux F is considered, where t denotes time. In particular, a scenario is specified in which the molecules diffuse predominantly within their own layer due to a high Ehrlich-Schwoebel barrier, and diffusion between layers is effectively suppressed, i.e., $D \gg D'$. Consequently, the focus lies on pure intralayer diffusion. The introduction of the layer coverage, denoted by Θ_n , which represents the extent of occupancy within a layer n ranging from 0 to 1, enables the calculation of the exposed layer coverage, given by

$$\phi_n = \Theta_n - \Theta_{n+1}. \quad (2.3)$$

The description of the coverage can be expressed by the differential equation

$$\frac{d\Theta_n}{dt} = F\Omega \cdot (\Theta_{n-1} - \Theta_n), \quad (2.4)$$

where F describes the flux of the molecules towards the substrate and Ω the probability of adsorption. A solution to Eq. (2.4) is given by

$$\Theta_n = 1 - \exp(-\theta) \sum_{k=0}^{n-1} \frac{\Theta^k}{k!}, \quad (2.5)$$

with the total coverage of the surface given by $\Theta = \sum_{n=1}^{\infty} \Theta_n = F\Omega \cdot t$. Inserting Eq. (2.5) into Eq. (2.3), the result is that the exposed layer coverage follows a Poisson distribution

$$\phi_n = \frac{\exp(-\Theta)\Theta^n}{n!}. \quad (2.6)$$

The standard deviation, which serves as a general measure of roughness, is given by

$$\sigma^2 = d_{\text{ML}}^2 \cdot \sum_{n=0}^{\infty} (n - \Theta)^2 \phi_n, \quad (2.7)$$

with the thickness of one monolayer (ML) d_{ML} . Inserting Eq. (2.6) in Eq. (2.7) results in $\sigma = d_{\text{ML}}\sqrt{\Theta}$. This shows that the roughness remains independent of the diffusion rate within the layer, which means that the diffusion within the layer does not change the roughness. However, considering interlayer diffusion offers the possibility of reducing the surface roughness.

2.2 Thin Film Growth

Thin film growth, at its essence, involves the absorption of film material onto a solid surface (substrate). However, understanding and explaining the growth of organic thin films can be very complicated. This complexity arises from the occurrence of either smooth film growth or rapid roughening phenomena, depending on many external parameters as already mentioned in the last section. The statistical growth described above is obviously a great simplification, because it does not include the diffusion between the layers. Depending on the inter- and intralayer diffusion, deposition rate, as well as the energy cost of unclosed islands, three major growth scenarios can be distinguished during the deposition of a material onto a substrate [38]. These arise depending on the strength of the interaction between the adatoms and the surface:

- 1.) Frank-van-der-Merwe growth: In this scenario, adatoms preferentially attach to the surface, resulting in smooth and developed layers. The corresponding films exhibit two dimensional (2D)-growth, i.e. they grow layer-by-layer.
- 2.) Stranski-Krastanov growth: This process is an intermediate process due to its growth in 2D-layers as well as in three dimensional (3D)-islands. The transition between layer-by-layer and island-based growth occurs at a critical layer thickness. This depends mainly on the chemical and physical

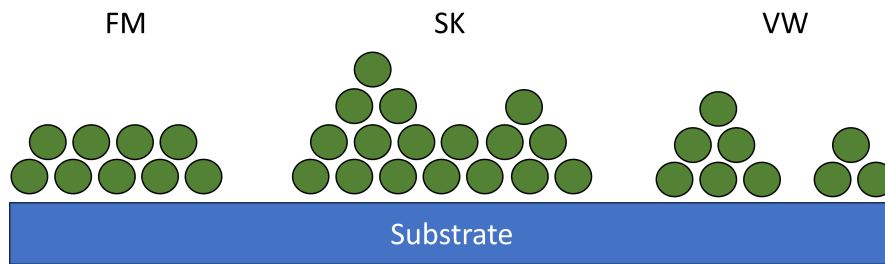


Figure 2.3: Different growth scenarios showing the varying arrangements of the molecules on a substrate (based on [39]). It can be separated between the Frank-van-der-Merwe growth (FM), the Stranski-Krastanov growth (SK), and the Vollmer-Weber growth (VW).

properties of the substrate and the layer, such as surface energies and lattice parameters.

- 3.) Vollmer-Weber growth: The interactions between the adatoms are stronger than those between the adatoms and the substrate. In this mode, island formation persists throughout the entire growth process, resulting in a discontinuous, island-like thin film structure.

All three growth scenarios are shown in Fig. 2.3.

A further approach to the classification of growth modes can be found in Ref. [40]. The focus lies on the 2D nucleation of islands, which are bounded by steps. For this purpose, the residence time of an adatom on the island is taken into account. Accordingly, this theory is particularly suitable for pronounced step edge formation in the growth of thin films. Another review article on thin film growth can be found in Ref. [41]. There, non-equilibrium growth is described in more detail with particular emphasis on the theory of kinetic surface roughening.

Chapter 3

Elementary Scattering Theory

This chapter deals with structural analysis using X-rays and provides an exploration of basic methods for analysing materials at length scales relevant to the investigation. While many textbooks provide a comprehensive introduction to the theory of X-ray scattering, the content of this chapter is mainly based on Ref. [42–49].

At the beginning, the X-rays and their interaction with matter are examined, with the findings mainly based on Ref. [46]. The central part of this section focuses on the fundamental aspects introduced by the study of surface scattering. For a more detailed exploration of crystals and their structural analysis, the interested reader is referred to [45], as this aspect is not covered in detail in this thesis.

3.1 X-rays

X-rays are electromagnetic waves in the energy range of $E \approx 200 \text{ eV} - 200 \text{ keV}$ [47]. The electric field of a plane wave can be written as

$$\mathbf{E}(\mathbf{r}, t) = \hat{\mathbf{e}} \mathbf{E}_0 e^{i(\mathbf{k}\mathbf{r} - \omega t)}, \quad (3.1)$$

with the polarization $\hat{\mathbf{e}}$ and an amplitude E_0 . The wave vector is related to the wavelength via

$$|\mathbf{k}| = k = \frac{2\pi}{\lambda}. \quad (3.2)$$

X-rays do not only have wave characteristics but can also be treated as particles, i.e., photons. According to de Broglie, a quantized X-ray particle has a momentum and an energy of

$$p = \frac{h}{\lambda} \quad \text{and} \quad E = \frac{hc}{\lambda}, \quad (3.3)$$

respectively, with the Planck constant h and the velocity of light denoted by c . This helps to understand how X-rays can be used to analyze material using scattering experiments. X-rays with a typical wavelength of $1 \text{ \AA}$ can be used to study the structure of matter on a similar lengthscale of $1 \text{ \AA}$. Higher momenta lead to smaller wavelengths, and therefore smaller structures can be studied.

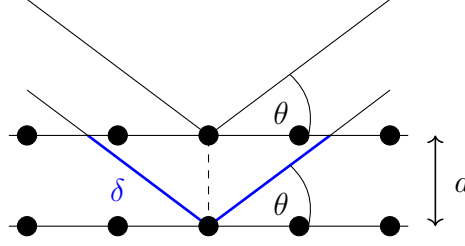


Figure 3.1: X-ray scattering on a crystal. Two parallel X-rays scatter on atoms in two neighboured lattice planes with distance d to each other. With this geometry, the Bragg condition can be derived, depending on the path length difference δ , marked in blue.

Two effects can occur if an X-ray beam is sent on a target. The radiation can be either absorbed or scattered. Depending on the X-ray energy and type of atoms, several processes are possible, i.e., photoabsorption, florescence, Compton scattering, and pair production. They all result in an emission of radiation after a relaxation process.

3.2 Structure Analysis

With the help of X-rays it is possible to analyze the structure of matter. The most straightforward example works with a crystal. The scattering of X-rays on two lattice planes is sketched in Fig. 3.1. There, two parallel X-rays are considered, each scattering on an atom. The atoms are located on neighboured lattice planes with lattice distance d to each other. To calculate the superposition of both X-rays after the scattering process, the difference of the paths δ is essential. From the geometry in Fig. 3.1, this can be calculated to

$$\delta = 2d \sin \theta. \quad (3.4)$$

If both X-rays interfere constructively (the wave crests add up), the path length difference needs to be a multiple of the wavelengths, i.e. $\delta = n \cdot \lambda$. This equation is called the Bragg condition. In contrast, if the condition $(2n + 1) \cdot \lambda/2$ is fulfilled the interference is destructive, and the wave crests cancel each other. With measured intensities, it is therefore possible to calculate the distance of the lattice planes and learn something about the crystal structure.

Alternatively, the Bragg condition can be derived via the scattering phase, according to

$$e^{i\mathbf{q} \cdot \mathbf{r}} = 1 \quad \Rightarrow \quad \mathbf{q} \cdot \mathbf{r} = 2\pi n \quad \Leftrightarrow \quad 2d \sin \theta = n\lambda, \quad (3.5)$$

where the scattering vector q is introduced as the difference between the outgoing and the incoming X-ray beam. Using the reciprocal space, this condition is equivalent to

$$\mathbf{r}^* \cdot \mathbf{r} = 2\pi(hn_1 + kn_2 + ln_3) \Leftrightarrow \mathbf{q} = \mathbf{r}^*. \quad (3.6)$$

This means that constructive interference of the scattered photons is only obtained if the scattering vector q equals a reciprocal lattice vector.

3.3 X-ray Scattering on Matter

In this section, the interaction of X-rays with matter is discussed. The interaction begins with a single electron, extends to an atom, and finally encompasses general matter.

3.3.1 X-ray Scattering on an Electron

First, Thomson radiation is considered. In this elementary scattering process, X-rays scatter elastically at a single electron. This can be described classically. When an X-ray hits an electron at position $\mathbf{r} = 0$, it is accelerated with

$$\mathbf{a}(\mathbf{r}=0, t) = \frac{e}{m_e} \cdot \mathbf{E}_{\text{in}}(\mathbf{r}=0, t). \quad (3.7)$$

Here, e is the elementary charge and m_e is the mass of the electron. The initial electric field can be recognized by the subscript 'in'. As a consequence of this acceleration, the electron experiences a harmonic oscillation around its equilibrium position. Behaving as a Hertzian dipole, it emits radiation with a phase difference of π , and an electric field in the point of observation $\mathbf{R}$ is

$$\mathbf{E}_{\text{rad}}(\mathbf{R}, t) \propto \hat{\epsilon}' \cdot \frac{e}{R} \cdot \mathbf{a}(\mathbf{R}, t). \quad (3.8)$$

The radiated intensity I can be measured with a detector. It is connected to the differential cross section ($d\sigma/d\Omega$) with some constants depending on the detector geometry positioned at $\mathbf{R}$. The differential cross section is itself connected to the initial and final electric field via [46]

$$I \propto \left(\frac{d\sigma}{d\Omega} \right) = \frac{|\mathbf{E}_{\text{rad}}|^2 R^2}{|\mathbf{E}_{\text{in}}|^2} = r_0^2 |\hat{\epsilon} \cdot \hat{\epsilon}'|^2. \quad (3.9)$$

In the last step, Eq. (3.8) is used. Adapting the units and considering the angle to the detector or the observation point, the ratio between incident and radiated

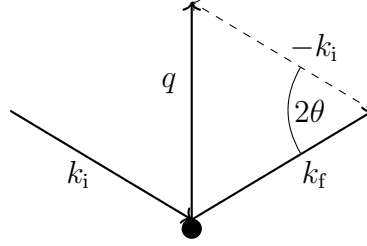


Figure 3.2: Definition of the wave vectors of X-rays scattering on an atom. The momentum transfer is defined by $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$.

electric field results in

$$\frac{E_{\text{rad}}}{E_{\text{in}}} = \frac{r_0}{r} |\hat{\epsilon} \cdot \hat{\epsilon}'|. \quad (3.10)$$

All constants are summed up into r_0 which, is the classical electron radius given by [46]

$$r_0 = \left(\frac{e^2}{4\pi\epsilon_0 m_e c^2} \right) = 2.82 \cdot 10^{-5} \text{ \AA} \quad (3.11)$$

and called Thomson radius.

3.3.2 X-ray Scattering on an Atom

Next, the scenario will be extended to X-ray scattering by matter. The consideration initially focuses on a single atom. Instead of a point-like scattering object, the X-rays are now scattered by an extended object. Due to the low mass of the electrons compared to the nucleus, they are most strongly influenced by the radiation. Therefore, the interest lies in the distribution of the electrons in the atom and later in the whole matter. This is described by the electron density function $\rho(\mathbf{r})$.

Characterizing the incident beam by the wave vector $\mathbf{k}_i$ and the final wave vector by $\mathbf{k}_f$, as in Fig. 3.2, the phase difference between both waves is given by [46]

$$\Delta\Phi(\mathbf{r}) = (\mathbf{k}_i - \mathbf{k}_f) \cdot \mathbf{r} = -\mathbf{q} \cdot \mathbf{r}. \quad (3.12)$$

This equation introduces the momentum transfer, given by $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$. For the special case of elastic scattering, i.e. $|\mathbf{k}_i| = |\mathbf{k}_f|$, this equation can be simplified to

$$|\mathbf{q}| = \frac{4\pi}{\lambda} \sin \theta, \quad (3.13)$$

where 2θ is the angle between both wave vectors.

If we now ensure the phase-correct summation of all electrons in the atom, we end

up with the so-called atomic form factor, given by

$$f(\mathbf{q}) = \int \rho(\mathbf{r}) e^{i\mathbf{q}\cdot\mathbf{r}} d\mathbf{r}, \quad (3.14)$$

with the phase factor $e^{i\mathbf{q}\cdot\mathbf{r}}$. The form factor is the Fourier transformation of the electron density and gives insight into the 'shape' of a single particle. The two limiting cases are given by

$$f(q) = \begin{cases} Z & q \rightarrow 0 \\ 0 & q \rightarrow \infty. \end{cases} \quad (3.15)$$

This means that all volume elements in the atom scatter in phase, the form factor reaches its highest value, given by the number of electrons Z . On the other hand, if all volume elements scatter out of phase, the lowest value is reached, given by zero.

The atomic form factor is linked to the final intensity via

$$I(\mathbf{q}) \propto |f(\mathbf{q})|^2. \quad (3.16)$$

Hence, measuring the intensity after the scattering process gives access to the form factor and, therefore, the electron density function.

3.3.3 X-ray Scattering on Matter

This scattering process can be extended to matter consisting of several atoms. Hence, a system of N particles is considered. Again, this system can be described by the electron density function $\rho(\mathbf{r})$, which can be split into the single contributions of the particles according to

$$\rho(\mathbf{r}) = \sum_{j=1}^N \rho'_j(\mathbf{r}) \quad (3.17)$$

$$= \sum_{j=1}^N \rho_i(\mathbf{r} - \mathbf{R}_j). \quad (3.18)$$

Here, $\mathbf{R}_j$ is the center of mass of the j -th particle, and thus $\rho'_j(\mathbf{r})$ is a relative scattering density with respect to the center of mass.

With the scattering density, a density auto-correlation function can be created. The function can be described by the van Hove function, given by [50]

$$G(\mathbf{r}) = \left\langle \int d\mathbf{r}' \rho(\mathbf{r}') \rho(\mathbf{r}' + \mathbf{r}) \right\rangle, \quad (3.19)$$

where, $\langle \cdot \rangle$ represents an average of all conceivable configurations of the system. Neglecting multiple scattering, i.e., using the Born Approximation, the scattered intensity can be calculated as

$$I(\mathbf{q}) = \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) G(\mathbf{r}) \quad (3.20)$$

$$= \langle \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) \int d\mathbf{r}' \rho(\mathbf{r}') \rho(\mathbf{r}' + \mathbf{r}) \rangle \quad (3.21)$$

$$\stackrel{\mathbf{r}''=\mathbf{r}'+\mathbf{r}}{=} \langle \int d\mathbf{r}'' \exp(i\mathbf{q} \cdot \mathbf{r}'') \rho(\mathbf{r}'') \int d\mathbf{r}' \exp(-i\mathbf{q} \cdot \mathbf{r}') \rho(\mathbf{r}') \rangle \quad (3.22)$$

$$= \langle A(\mathbf{q}) \cdot A^*(\mathbf{q}) \rangle \quad (3.23)$$

with the local scattering amplitude

$$A(\mathbf{q}) = \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) \rho(\mathbf{r}). \quad (3.24)$$

Inserting Eq. (3.18) in the scattering amplitude results in

$$A(\mathbf{q}) = \int d\mathbf{r} \exp(i\mathbf{q} \cdot \mathbf{r}) \sum_{j=1}^N \rho_j(\mathbf{r} - \mathbf{R}_j) \quad (3.25)$$

$$\stackrel{\mathbf{r}_j=\mathbf{r}-\mathbf{R}_j}{=} \sum_{j=1}^N \exp(i\mathbf{q} \cdot \mathbf{R}_j) \int d\mathbf{r}_j \exp(i\mathbf{q} \cdot \mathbf{r}_j) \rho_j(\mathbf{r}_j) \quad (3.26)$$

$$= \sum_{j=1}^N \exp(i\mathbf{q} \cdot \mathbf{R}_j) \cdot f_j(\mathbf{q}). \quad (3.27)$$

In the last calculation step, the form factor for the j -th particle is inserted, which was already introduced in Eq. (3.14). Finally, if Eq. (3.27) is inserted into Eq. (3.23)

$$I(\mathbf{q}) = \langle \sum_{j,k=1}^N f_j(\mathbf{q}) f_k^*(\mathbf{q}) \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)) \rangle \quad (3.28)$$

$$= \sum_{\substack{j=1 \\ j=k}}^N \langle f_j(\mathbf{q}) f_j^*(\mathbf{q}) \rangle + \sum_{\substack{j,k=1 \\ j \neq k}}^N \langle f_j(\mathbf{q}) f_k^*(\mathbf{q}) \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)) \rangle. \quad (3.29)$$

This equation is divided into two parts: the first part provides insights into the shape of the particles through the form factor, while the second part reveals information about the relative positions of the particles.

First, the focus lies on the first part of Eq. (3.29). Broken down to a single particle, the second part of Eq. (3.29) disappears. When considering a simple case

in which a single stationary particle gradually increases in size, a signal with constant intensity can be expected, provided it is normalized correctly. However, Eq. (3.29) is only valid for monodisperse particles which are not changing their shape in time. In later simulations, cylindrical (or elliptical) shaped islands are considered on a surface. However, the radius and, therefore, the form factor will change over time. Hence Eq. (3.28) has to be modified to

$$I(\mathbf{q}) = \sum_{j=1}^N \langle f(\mathbf{q}, \xi_j) f^*(\mathbf{q}, \xi_j) \rangle + \sum_{\substack{j,k=1 \\ j \neq k}}^N \langle f(\mathbf{q}, \xi_j) f^*(\mathbf{q}, \xi_k) \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)) \rangle, \quad (3.30)$$

where ξ stands for all possible changes in size and shape in time for particle j . The shape and the position of the particles can be correlated. Therefore, to correctly calculate Eq. (3.30) the relation

$$\langle \cdot \rangle_{R,\xi} = \langle \langle \cdots \rangle_{\xi_1} \cdots \rangle_{\xi_N} \rangle_R. \quad (3.31)$$

has to be used (similar as in [51, 52]). As a consequence, Eq. (3.30) can be written as

$$I(\mathbf{q}) = \sum_{j=1}^N \langle |f(\mathbf{q}, \xi_j)|^2 \rangle_{\xi_j} + \sum_{\substack{j,k=1 \\ j \neq k}}^N \langle f(\mathbf{q}, \xi_j) \rangle_{\xi_j} \langle f^*(\mathbf{q}, \xi_k) \rangle_{\xi_k} \langle \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)) \rangle_R \quad (3.32)$$

$$= N(\Delta\rho)^2 (P(\mathbf{q}, \xi) + F(\mathbf{q}, \xi) F^*(\mathbf{q}, \xi) (S(\mathbf{q}) - 1)). \quad (3.33)$$

In the second step the equation is simplified by

$$P(\mathbf{q}) = \frac{1}{(\Delta\rho)^2} \langle |f(\mathbf{q}, \xi)|^2 \rangle_{\xi}, \quad (3.34)$$

which is called shape factor and describes the mean shape of the particles. The factor $\Delta\rho$ ensures normalization. Furthermore, a quantity called the coherent scattering amplitude is introduced as

$$F(\mathbf{q}) = \frac{1}{(\Delta\rho)} \langle f(\mathbf{q}, \xi) \rangle_{\xi}, \quad (3.35)$$

which is the average scattering amplitude of one particle.

Finally, all the information about the spatial correlations and particle-particle

interactions is summed up in the structure factor

$$S(\mathbf{q}) = \frac{1}{N} \sum_{j,k=1}^N \langle \exp(i\mathbf{q} \cdot (\mathbf{R}_j - \mathbf{R}_k)) \rangle_R. \quad (3.36)$$

Eq. (3.33) can be modified to

$$\frac{I(\mathbf{q})}{N(\Delta\rho)^2} = \underbrace{P(\mathbf{q}) - F(\mathbf{q})^* F(\mathbf{q})}_{\text{incoherent scattering amplitude}} + \underbrace{F(\mathbf{q}) F^*(\mathbf{q}) S(\mathbf{q})}_{\text{coherent scattering amplitude}}. \quad (3.37)$$

This equation splits up into an incoherent part, which includes shape related quantities, i.e., kinetics, and a coherent part, which describes any spatial correlations, i.e., dynamics [53].

A calculation of the form factors for a sphere and a cylinder can be found in App. 13. The further discussion in the appendix will address how the latter calculation can be applied to determine the intensity correlation functions for a growing cylinder. The main idea is to provide a basic understanding of how the theoretical calculations can be used to interpret the experimental results presented in the results part in Chap. 9. The complexity introduced by the experimental geometry is explored in detail in Sec. 8.2.1. Despite the need for further calculations, this chapter provides a fundamental insight into the equations that form the basis for the simulations described in Sec. 8.2.2, which are used in this study, among other things, to interpret the experimental results.

3.4 Scattering on Surfaces

Since the central aspect of this work is the investigation of surfaces, the focus will be shifted to the subtleties and realization of their investigation using X-ray scattering.

If X-rays enter matter, the refractive index behaves as [46]

$$n = 1 - \delta + i\beta. \quad (3.38)$$

The values of δ and β appear due to dispersion and absorption effects, respectively. Both depend on the material properties and be calculated to [46]

$$\delta = \lambda^2 \frac{r_0 \rho_e}{2\pi}, \quad \beta = \lambda \frac{\mu}{4\pi}, \quad (3.39)$$

where μ is the absorption coefficient, and the electron density function is calculated to $\rho_e = \rho N_A Z / M_{\text{mol}}$, with the material density ρ , the Avogadro constant N_A , the atomic number Z and the molecular mass M_{mol} . Typical values are $\delta \approx 10^{-5} - 10^{-6}$ and $\beta \approx (1/10 - 1/100) \cdot \delta$. This leads to $n < 1$, which cor-

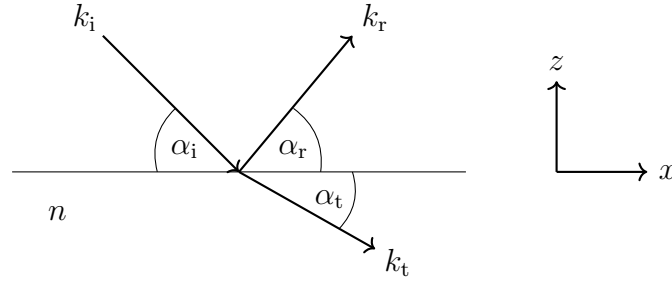


Figure 3.3: X-rays scattering on a material with refraction index n . The incident wave k_i encloses the angle α_i with the surface, and the reflected wave k_r the angle α_r . The angle between the surface and the transmitted wave k_t is denoted by α_t .

responds to phase velocities larger than the speed of light. However, there is no contradiction with the relativity concept because the information moves with the group velocity, which does not exceed this value.

The reflection and refraction of X-rays scattering on material are pictured in Fig. 3.3. A setup with an incoming X-ray beam is considered, characterized by k_i and enclosing an angle α_i with the surface. The X-rays come from the vacuum and scatter on a material with a refraction index of n . During this scattering process, the X-rays are reflected and refracted. The resulting radiation is denoted by k_r and k_t , respectively. Again, the corresponding angles from the X-rays to the surface are described by α with index r for reflected and t for transmitted. For simplicity, the restriction is applied to the xz -plane, i.e., specular reflection/transmission. Following, the wave vectors can be related to their angles via [54]

$$\begin{aligned} \mathbf{k}_i &= k_0(\cos \alpha_i \cdot \hat{\mathbf{e}}_x - \sin \alpha_i \cdot \hat{\mathbf{e}}_z) \\ \mathbf{k}_r &= k_0(\cos \alpha_r \cdot \hat{\mathbf{e}}_x + \sin \alpha_r \cdot \hat{\mathbf{e}}_z) \\ \mathbf{k}_t &= nk_0(\cos \alpha_t \cdot \hat{\mathbf{e}}_x - \sin \alpha_t \cdot \hat{\mathbf{e}}_z), \end{aligned} \tag{3.40}$$

with $k_0 = 2\pi/\lambda$. Due to the continuity of the electric field and its derivation on the surface ($z = 0$), the boundary conditions are given by

$$\begin{aligned} E_i(z=0) + E_r(z=0) &= E_t(z=0) \\ E_i(z=0) \cdot \mathbf{k}_i + E_r(z=0) \cdot \mathbf{k}_r &= E_t(z=0) \cdot \mathbf{k}_t \end{aligned} \tag{3.41}$$

with the initial, reflected and transmitted fields E with the corresponding denoted subscript of i , r , and t , respectively. Inserting Eq. (3.1), including the wave vectors

in Eq. (3.40) leads to

$$\begin{aligned}
& E_{0,i}e^{-k_0 \cos \alpha_i \cdot x} + E_{0,r}e^{-k_0 \cos \alpha_r \cdot x} = E_{0,t}e^{-k_0 n \cos \alpha_t \cdot x} \\
||: & E_{0,i} \cos \alpha_i e^{-k_0 \cos \alpha_i \cdot x} + E_{0,r} \cos \alpha_r e^{-k_0 \cos \alpha_r \cdot x} = E_{0,t} n \cos \alpha_t e^{-k_0 n \cos \alpha_t \cdot x} \\
\perp: & -E_{0,i} \sin \alpha_i e^{-k_0 \cos \alpha_i \cdot x} + E_{0,r} \sin \alpha_r e^{-k_0 \cos \alpha_r \cdot x} = -E_{0,t} n \sin \alpha_t e^{-k_0 n \cos \alpha_t \cdot x}.
\end{aligned} \tag{3.42}$$

The last two equations separate of a part parallel ($||$) and perpendicular ($\perp$) to the surface. Combining these equations results in Snells-Decartes law

$$\alpha_i = \alpha_r, \quad \cos \alpha_i = n \cos \alpha_t. \tag{3.43}$$

Searching for the angle where total external reflection appears leads to $\alpha_t = 0$. If we remember Eq. (3.38) and perform a Taylor expansion of the cosine, this critical angle is given by

$$\alpha_c \approx \sqrt{2\delta}. \tag{3.44}$$

Using typical physical values, α_c is in the range of mrad/0.1°. With angles close but below this critical angle, almost all of the incident radiation is reflected. The X-ray penetrates the material only as an evanescent wave of the form

$$E_t \propto e^{-z/\Lambda}. \tag{3.45}$$

This corresponds to a penetration depth of

$$\Lambda = \frac{\lambda}{4\pi \text{Im} \sqrt{\alpha_i^2 - 2\delta + 2i\beta}}, \tag{3.46}$$

which is typically 10 – 100 Å. Consequently, it is possible to investigate surfaces and interfaces almost without a contribution from the material below the surface.

Taking a closer look at the reflection and transmission, corresponding coefficients (Fresnel coefficients) can be defined according to [54]

$$\begin{aligned}
r &\equiv \frac{E_r}{E_i} = \frac{\sin \alpha_i - n \sin \alpha_t}{\sin \alpha_i + n \sin \alpha_t} = \frac{k_{i,z} - k_{t,z}}{k_{i,z} + k_{t,z}}, \\
t &\equiv \frac{E_t}{E_i} = \frac{2 \sin \alpha_i}{\sin \alpha_i + n \sin \alpha_t} = \frac{2k_{i,z}}{k_{i,z} + k_{t,z}}.
\end{aligned} \tag{3.47}$$

The intensity of the reflectivity and transmissivity can be calculated by squaring the amplitudes in Eq. (3.47), i.e. $R = |r|^2$ and $T = |t|^2$.

Chapter 4

Coherence in the Context of Scattering

This chapter introduces the central concept of this thesis and is characterized by the perspectives presented in [44, 46, 49].

Ideally, when considering X-rays, one imagines a completely monochromatic radiation with a clearly defined direction of propagation. However, reality deviates from this scenario. Therefore, the concept of coherence is introduced to determine whether and how long X-rays can be considered nearly monochromatic and parallel beams.

4.1 Interference

The traditional way of defining coherence is to link it to the interference property of radiation. Therefore, understanding the correlation between two wave fields, $\mathbf{E}_1(t)$ and $\mathbf{E}_2(t)$, is important. If they meet at a certain point, they add up according to the superposition principle to

$$\mathbf{E}(t) = \mathbf{E}_1(t) + \mathbf{E}_2(t). \quad (4.1)$$

The characteristic properties of waves are their amplitude and phase. In reality it is only possible to access these physical quantities by performing interference experiments. There, only the corresponding intensities that are related to the electric fields are measured. In an actual experiment, each detector averages over a certain space and time period. Therefore, a fixed phase relation between both waves in this time interval is needed to observe the contribution of the interference term. For simplicity, a short notation for the time average is introduced, given by

$$\langle f(t) \rangle = \lim_{t \rightarrow \infty} \frac{1}{t} \int_0^t f(t') dt'. \quad (4.2)$$

As a result, the measured intensity can be calculated to

$$I(t) \propto \langle |\mathbf{E}(t)|^2 \rangle = \underbrace{\langle |\mathbf{E}_1(t)|^2 \rangle}_{I_1} + \underbrace{\langle |\mathbf{E}_2(t)|^2 \rangle}_{I_2} + \underbrace{2\langle \text{Re}(\mathbf{E}_1(t) \cdot \mathbf{E}_2^*(t)) \rangle}_{\text{interference term}}, \quad (4.3)$$

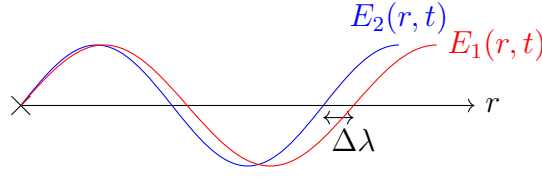


Figure 4.1: Two waves, $E_1(r, t)$ and $E_2(r, t)$, travel in the same direction but differ slightly in their wavelength, given by a difference of $\Delta\lambda$. At their source, they are exactly in phase.

with the complex conjugate denoted by $*$. The last term of this equation is responsible for interference effects, i.e., all interesting information about the correlation of the two wave fields is contained there. Consequently, a correlation function is defined that corresponds to

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2, t_1, t_2) = \langle \mathbf{E}_1(\mathbf{r}_1, t_1) \mathbf{E}_2^*(\mathbf{r}_2, t_2) \rangle. \quad (4.4)$$

In the most general case, this function can depend on different positions of the wave fields $\mathbf{r}_1$ and $\mathbf{r}_2$ and different times t_1 and t_2 . In the case of incoherent light, this correlation function vanishes and therefore no interference can be observed. With a fixed phase difference between both wave fields, as valid for coherent light, interference effects appear.

4.2 Temporal/Longitudinal Coherence

Firstly, the focus is on specific times in Eq. (4.4), i.e., the so-called temporal or longitudinal coherence. This means the ability of a wave field to interfere with a delayed version of itself has to be quantified.

The Michelson interferometer is an experiment to investigate this, where a light wave is split into two parts. After travelling different path lengths, both parts meet again, and the superposition of the fields is measured as a function of the path difference.

This analysis would be pretty simple for a perfectly monochromatic light source, as the phase relation between both wave parts for each path difference would always be known. However, considering an actual light source there is always a finite bandwidth, i.e., a range of wavelengths. To analyze the resulting consequences two plane waves are considered, $\mathbf{E}_1(r, t)$ and $\mathbf{E}_2(r, t)$, with wavelengths λ and $\lambda - \Delta\lambda$. Both are propagating in the same direction. They are exactly in phase at their origin ($r = 0$). After one wavelength, their travel distance to each other is given by $\Delta\lambda$. The scenario is sketched in Fig. 4.1. One wavelength is slightly larger than the other. Taking this scenario further, after a certain distance χ_l , both waves will be strictly out of phase, i.e., one wave crest will be at its maximum above the x-axis and the other below. Since this is a linear problem, both waves are in phase again after $2\chi_l$, but one of them has performed N wavelengths, while

the other one already covered $N + 1$. With this consideration, the characteristic length can be calculated to [46, 55]

$$2\chi_l = N\lambda_2 = (N + 1)(\lambda - \Delta\lambda) \Rightarrow \chi_l = \frac{1}{2} \frac{\lambda^2}{\Delta\lambda}, \quad (4.5)$$

which is called longitudinal coherence length, assuming that $\Delta\lambda$ is small compared to λ .

The consequence for the Michelson interferometer is that after a specific path difference the phase information between both waves will be lost and no interference pattern will be visible. For this scenario, Eq. (4.4) simplifies to

$$\Gamma(\mathbf{r}, \tau) = \langle \mathbf{E}(\mathbf{r}, t) \mathbf{E}^*(\mathbf{r}, t + \tau) \rangle, \quad (4.6)$$

with $t_1 = t$ and a time delay of τ between both waves. Typically, a normalized version of the correlation function is used, given by

$$\gamma(\mathbf{r}, \tau) = \frac{\Gamma(\mathbf{r}, \tau)}{\Gamma(\mathbf{r}, 0)}. \quad (4.7)$$

This function quantifies the complex degree of coherence and results in absolute values between zero and one. For $\tau = 0$, the highest correlation value is obtained, given by $\gamma(\mathbf{r}, 0) = 1$. This means that the wave field has only one wavelength, i.e., perfectly monochromatic waves are considered. If τ goes to infinity, the phase relation gets lost, and $\gamma(\mathbf{r}, \tau \rightarrow \infty) \rightarrow 0$. In reality, a fully incoherent wave field cannot exist.

To quantify the visibility of the interference pattern, the contrast function is introduced by

$$\beta = \frac{I_{\max} - I_{\min}}{I_{\max} + I_{\min}}. \quad (4.8)$$

The intensity $I_{\max}$ belongs to the highest, and $I_{\min}$ to the lowest intensity of the interference pattern. If $\beta = 0$, no interference pattern is visible, and therefore, it can be concluded that the waves are precisely incoherent. On the other hand, if $\beta = 1$, the contrast function reaches its maximum, and the waves are fully coherent. Every value in between is possible, i.e., $0 \leq \beta \leq 1$. In such cases, one speaks of partially coherent waves, a property that is inherent in reality.

4.3 Spatial/Transversal Coherence

After focusing on time differences, the attention now shifts to restricting considerations to different spatial positions, i.e., examining spatial or transversal coherence.

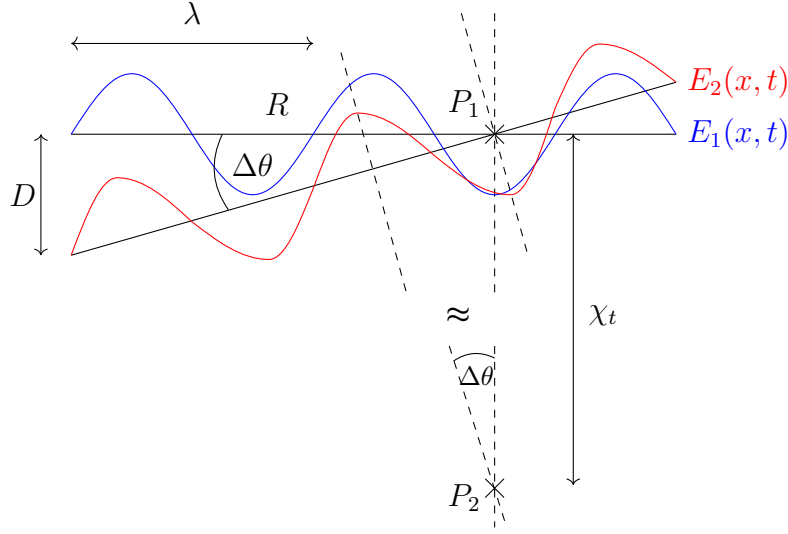


Figure 4.2: Two monochromatic waves, $E_1(x, t)$ and $E_2(x, t)$ with wavelength λ , are emitted from a source with length D . Both travel in slightly different directions, quantified by the angle $\Delta\theta$. They meet in phase after some distance R at a point P_1 and are out of phase after a distance χ_t at the point P_2 .

In this case, Eq. (4.4) is given as

$$\Gamma(\mathbf{r}_1, \mathbf{r}_2) = \langle \mathbf{E}(\mathbf{r}_1, t) \mathbf{E}^*(\mathbf{r}_2, t) \rangle. \quad (4.9)$$

The underlying experiment is Young's double-slit experiment. A light source can propagate through two different pin holes. A possible interference pattern can be analyzed on a screen behind them.

Instead of a double slit, one can also consider an extended light source of length D that emits light from both endpoints. Since only different spatial positions are considered and any time delays are neglected (i.e., slightly different wavelengths), the light is treated as monochromatic. The waves will propagate in slightly different directions and the interference will be analyzed in a given point. An angle $\Delta\theta$ can describe this diverging property. After some distance R , both waves meet at a point P in phase. After a characteristic transverse length χ_t , both waves are out of phase again. The geometry in Fig. 4.2 can be considered to calculate this length. There, the relations [46, 55]

$$\frac{D}{R} = \tan \Delta\theta \approx \Delta\theta \quad \text{and} \quad 2\chi_t \Delta\theta = \lambda \quad \Rightarrow \quad \chi_t = \frac{\lambda R}{2D}, \quad (4.10)$$

can be extracted. In the first equation, the angle $\Delta\theta$ is small. The resulting transversal coherence length χ_t will get larger for smaller light sources and larger observation distances.

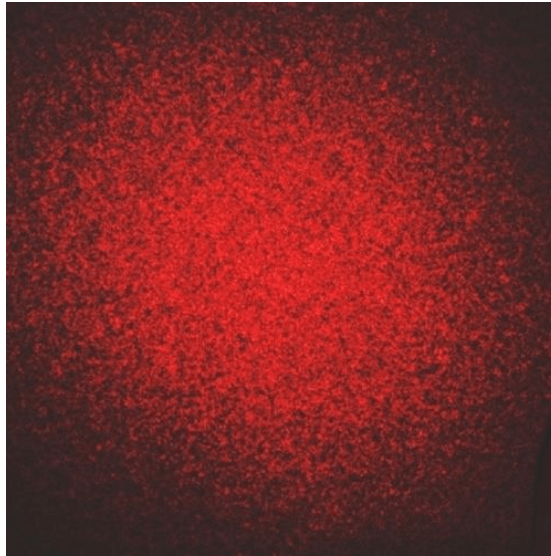


Figure 4.3: Observation of a speckle pattern created by radiating highly coherent laser light onto a rough surface from [60].

4.4 Speckle Pattern

If we radiate light with a high degree of coherence onto a rough surface, a grainy, blotchy structure can be observed [56–59]. In the case of laser light, which is almost coherent, the resulting image is depicted in Fig. 4.3. This speckle pattern results from unique coherence properties. Statistically distributed field strengths overlap at different points in space. As a result, each observer sees a different, spatially fixed pattern. The momentary positions of objects on the surface are encoded in this pattern.

If the scattering objects are moving, the speckle pattern will also change. Thus, the possibility arises to record several speckle patterns during a time period and, hence, measure tiny surface changes.

The size of the speckles depends on the wavelength and dimension of the light source. This is easy to understand by looking at the equation for the momentum transfer in Eq. (3.13). Larger q -values allow to look at smaller structures. Consequently, it is crucial to extend this value, which is done via the wavelength of the light source or the scattering angle. Since the latter is positioned in a sinus, the wavelength is more influential. In order to detect movements in the nanoscale regime, the X-ray facilities must be equipped with a sufficiently coherent X-ray beam.

Chapter 5

X-Ray Photon Correlation Spectroscopy

The method of XPCS is well explained in Ref. [12, 54, 61, 62], which this chapter is based on. The aim is to use coherent X-rays to measure nanoscale dynamics from intensity fluctuations.

The measurement of the speckle pattern during a time period gives access to intensity correlations in momentum space. These can be translated into fluctuations in real space by a Fourier transformation, providing information about the dynamics of the analyzed object.

5.1 Standard Analysis and Two-Time Correlation Function

Applying this method to surfaces is an area that has been little explored so far. For that, the grazing-incidence small-angle X-ray scattering (GISAXS) geometry has to be chosen, as specified in Sec. 3.4 and further detailed in Sec. 7.4.3. To get spatial and temporal information about the probe, the intensities are measured in dependence of the transfer vector and the time, denoted as $I(\mathbf{q}, t)$. With this input, an intensity auto-correlation function (g_2 function) can be calculated as

$$g_2(\mathbf{q}, t) = \frac{\langle I(\mathbf{q}, t)I(\mathbf{q}, t + \tau) \rangle_\tau}{\langle I(\mathbf{q}, \tau) \rangle_\tau^2} = 1 + \beta \cdot |\text{ISF}(\mathbf{q}, t)|^2. \quad (5.1)$$

The nominator quantifies how strongly the intensity at a given time correlates to itself after a short time period τ . The denominator normalizes this function.

In the second step, the function is reformulated and related to the electron density function via the normalized intermediate scattering function ISF ($\text{ISF}(\mathbf{q}, t) \propto \rho(\mathbf{q}, t)$). The unnormalized form of the ISF is represented by $g_1(\mathbf{q}, t)$, serving as a spatial Fourier transform of the van Hove function, as introduced in Eq. (3.19) (comparable to Eq. (3.20))

$$g_1(\mathbf{q}, t) = \frac{1}{N} \langle \rho(\mathbf{q}, 0) \rho(-\mathbf{q}, t) \rangle, \quad (5.2)$$

where the number of scatterers is denoted by N and $\langle \cdot \rangle$ represents an average of the possible configurations in the system. The prefactor β in Eq. (5.1) is the already known contrast factor from Eq. (4.8). Ideally, this factor is unity. In reality, due to a partially coherent beam this additional factor needs to be included, which ranges from $0 \leq \beta \leq 1$. It emphasizes the importance of finding a balance between reducing absolute beam intensity, which is influenced by factors such as monochromators to increase coherence and improve contrast, and maintaining a high counting rate to ensure robust statistical significance.

All the measured dynamics of the studied system are encoded in the normalized intermediate scattering function. Typically, this function can be expressed as an exponential function of the form [63–65]

$$\text{ISF}(\mathbf{q}, t) = \frac{g_1(\mathbf{q}, t)}{g_1(\mathbf{q}, t=0)} = \exp \left[- \left(\frac{t}{\tau} \right)^\gamma \right]. \quad (5.3)$$

The relaxation time τ describes the characteristic time scale of the system, and the stretching component γ indicates the type of dynamics (glassy, jammed, brownian, ballistic, etc).

To extract physical parameters from Eq. (5.3), a background and a scaling factor must be added to obtain a proper fit. Those additional parameters are mostly setup-related.

With $g_2(\mathbf{q}, t)$ it is only possible to learn something about the time-average fluctuations. If the investigated system is of non-equilibrium nature, for example, a system during a heating process or growth, the data can be analyzed with a two-time correlation (TTC) function, given by [12, 65, 66]

$$c(\mathbf{q}, t_1, t_2) = \frac{\langle I(\mathbf{q}, t_1) I(\mathbf{q}, t_2) \rangle}{\langle I(\mathbf{q}, t_1) \rangle \langle I(\mathbf{q}, t_2) \rangle}. \quad (5.4)$$

Unlike the other equations, the brackets in this equation indicate an average over the pixels. Averaging the TTC over the time t_1 , with $t = |t_2 - t_1|$, will result in Eq. (5.1) again, reaching from $1 < g_2(\mathbf{q}, t) < 2$.

It is also possible to not use a normalization via the mean intensity value, as in Eq. (5.4), but rather over the standard deviation [67, 68]

$$C(\mathbf{q}, t_1, t_2) = \frac{\langle (I(\mathbf{q}, t_1) - \bar{I}(\mathbf{q}, t_1))(I(\mathbf{q}, t_2) - \bar{I}(\mathbf{q}, t_2)) \rangle}{\sqrt{\langle (I(\mathbf{q}, t_1) - \bar{I}(\mathbf{q}, t_1))^2 \rangle} \cdot \sqrt{\langle (I(\mathbf{q}, t_2) - \bar{I}(\mathbf{q}, t_2))^2 \rangle}}. \quad (5.5)$$

For fully coherent radiation and an average constant intensity value, both TTC calculations are equivalent and can be translated into each other according to $C(\mathbf{q}, t_1, t_2) = c(\mathbf{q}, t_1, t_2) - 1$ [69]. But for partially coherent radiation, the contrast of a speckle pattern has to be taken into account, resulting in a relation of $C(\mathbf{q}, t_1, t_2) = 1/\beta \cdot (c(\mathbf{q}, t_1, t_2) - 1)$. Hence, breaking Eq. (5.5) down by aver-

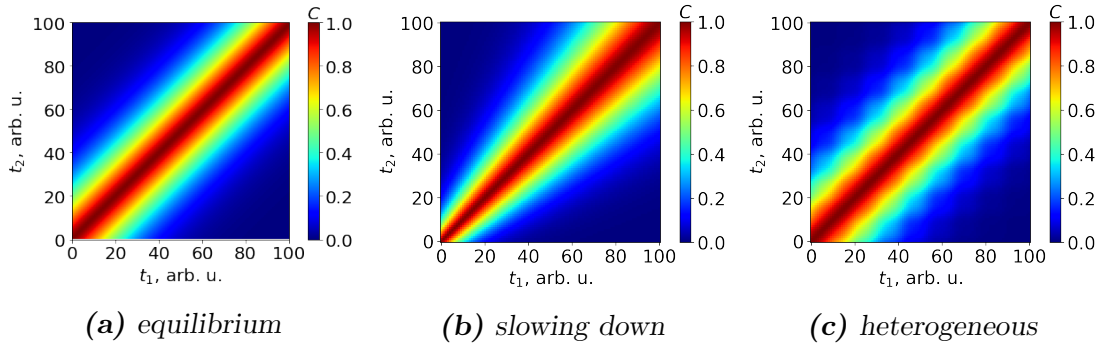


Figure 5.1: Examples of TTC functions calculated with Eq. (5.5). Fig. (a) shows an equilibrium, Fig. (b) a slowing down process and Fig. (c) a heterogeneous process.

aging over one time again results in a g_2 function ranging from zero to unity and is independent of β . As a consequence, this function is particularly well suited for systems that undergo dynamic and kinetic evolution. The intensity fluctuations in kinetic evolution can lead to changes in the speckle contrast, making Eq. (5.5) more suitable for such scenarios.

With the TTC function it is possible to probe ageing dynamics and get a time-resolved evolution of fluctuations. This function is typically represented in a 2D plot with t_1 and t_2 as axes, while the value C is represented via a color scheme. Toy examples are given in Fig. 5.1. As already mentioned, cutting lines perpendicular to the diagonal leads to the recovery of g_2 -functions as described in Eq. (5.1). The diagonal in a TTC always gives the highest value by construction. Depending on the normalization, this is either $\beta + 1$ (Eq. (5.4)) or unity (Eq. (5.5)). Moving away orthogonal from the diagonal, this value drops according to Eq. (5.1) in combination with Eq. (5.3). If we consider an equilibrium process in which the system remains stable and does not change over time (whereby all variables such as τ , γ , etc. are kept constant), the form of the TTC shown in Fig. 5.1 (a) results. As the system slows down, i.e., τ gets larger, the TTC will look similar to Fig. 5.1 (b). The increase of τ over time can be seen by the broadening of the diagonal. If, on the other hand, the system is accelerated, the diagonal would become smaller, and thus τ would decrease.

Another case is presented in Fig. 5.1 (c). This case shows a constant average relaxation rate accompanied by some fluctuations. These fluctuations of the relaxation time around some mean value indicate a heterogeneous behavior, which will be discussed in the following section.

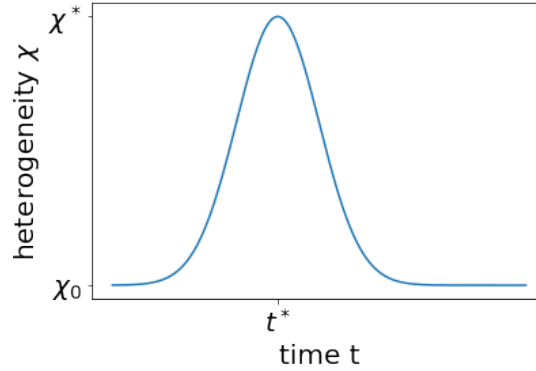


Figure 5.2: Ideal form of a fourth-order correlation function. Its minimum value is given by χ_0 , and a peak appears at the time t^* with height χ^* .

5.2 Fourth-Order Correlation Function

The process shown in Fig. 5.1 (c) is called a heterogeneous process. The TTC looks similar to the equilibrium, but τ fluctuates around a fixed value. Those kinds of TTCs are often observed in disordered structures with different local environments. As a consequence, the particles move differently with different relaxation rates and a distribution of τ will appear. This phenomenon is mostly observed in glass transitions, where the dynamics are slowing down [70, 71]. Analysing heterogeneous processes can be done by calculating the fourth-order correlation function

$$\chi(\mathbf{q}, t) = \frac{\langle C(\mathbf{q}, t_1, t)^2 \rangle_{t_1} - \langle C(\mathbf{q}, t_1, t) \rangle_{t_1}^2}{\langle C(\mathbf{q}, t_1, t=0) \rangle_{t_1}^2} \quad (5.6)$$

with

$$t = |t_2 - t_1|. \quad (5.7)$$

This equation for χ is identical to the standard deviation of the TTC in Eq. (5.5). A typical example of a fourth-order correlation function is presented in Fig. 5.2. Fluctuations around a mean value of τ appear. This distribution typically represents itself in a clear peak. A possible offset is considered in the minimum value χ_0 of the function. The maximal value at the position of t^* is denoted as χ^* . This value indicates the degree of heterogeneity of the system. In graphic terms, this describes the volume over which the structural relaxation processes are correlated. In heterogeneous systems, these values are extracted to gain insights into the molecular arrangements and movements within the system.

The benefits of those analyzes have been extended to other systems for some time. Jammed materials, which are systems that get stuck under increased density, can be found in the field of soft matter, with gels serving as an example [17]. The aim is to extend this analysis to surfaces as well.

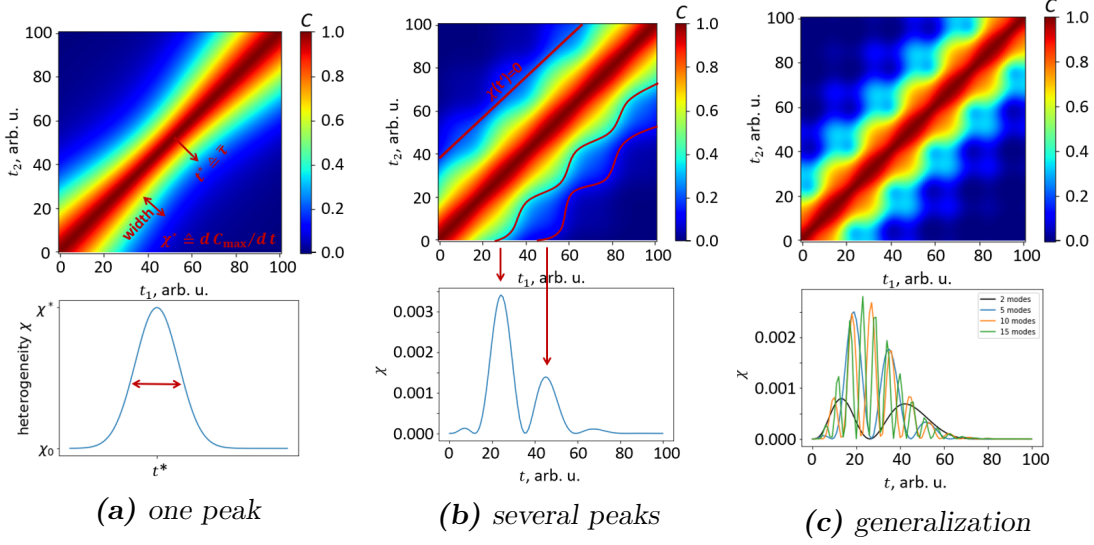


Figure 5.3: Examples of heterogeneous dynamics that lead to the occurrence of either one (a) or several (b) peaks in the corresponding fourth-order correlation function, which is shown below the TTC. This is generalized in (c), where an increasing number of modes (number of variations perpendicular to the diagonal) in the TTC leads to more peaks in the fourth-order correlation function. The TTC above represents the 5-mode example.

In the case of coherent scattering experiments on surfaces, it is very often observed that the calculation of the fourth-order correlation function reveals more than a single, distinct peak, as shown in Fig. 5.2. Rather, this analysis often reveals the presence of multiple peaks.

To understand the origin and significance of these multiple peaks, it is essential to further understand the mechanisms underlying this function and its relationship to conventional analyzes using g_2 functions and TTC calculations. Each data point within $\chi(t)$ indicates the changes along the diagonal (or the time difference t as defined in Eq. (5.7)). Accordingly, the height and position of the peak are given by the maximum rate of change, i.e., $\chi^* = dC_{\max}/dt$ (Fig. 5.3 (a)).

The width of this peak is related to the time period in which the changes unfold along the diagonal. Consequently, the first peak occurs at an average τ (which corresponds to the average relaxation rate). In cases where no further changes occur along a given diagonal at time t' , $\chi(t')$ is zero. However, subsequent changes at later time intervals lead to additional peaks in the function. The occurrence of multiple peaks can thus be attributed either to well-defined off-diagonal elements or 'alternating oscillations' along the diagonal, as visible in Fig. 5.3 (b). A further generalization of how the amount of several modes (number of variations perpendicular to the diagonal) influences the fourth-order correlation function is presented in Fig. 5.3 (c). The number of variations along the diagonal will only change the width of the heterogeneity peak but not the amount of peaks, while

the number of variations perpendicular to the diagonal will increase the number of peaks. The TTC on the top shows an example of five modes.

So far, this section has explained the math behind the fourth-order correlation function and provided a comprehensive understanding of how the TTC yields the corresponding fourth-order correlation function. The connection to physical processes will be discussed in more detail in the result sections, i.e., Chap. 9.

Part II

Materials & Methods

Chapter 6

Materials

This section serves as an introduction to the materials used in this study. Organic materials have recently been of high interest due to their processability, low cost, and flexibility. Anisotropic particle shapes bring an additional orientational degree of freedom and anisotropic interactions, which several studies address [37, 72–78]. These factors play a decisive role in influencing the structure and properties of thin films of these materials. As a result, for example, complex growth scenarios can arise in which the initial monolayers can either close completely and form a smooth film or, rapid unusual roughening can occur, depending on external conditions such as growth rate or substrate temperature [37, 72, 73]. Understanding the microscopic dynamics underlying the growth and annealing of organic materials is an essential prerequisite for the rational design of complex structures and morphologies with controlled properties. Such findings contribute to basic research and offer potential applications in optoelectronics, including OFETs, OSCs, and OLEDs [1–7].

6.1 Diindenoperylene

DIP ($C_{32}H_{16}$, Fig. 6.1 (a)) is a prototypical organic semiconductor characterized by its planar structure, in which two indeno-groups are attached to opposite sides of the perylene core. DIP is widely known and thin films of it are extensively characterized by conventional analytical techniques (Chap. 7). An established reference base in this field can be found for example in Ref. [72–74].

The main objective was to establish a protocol for analyzing the dynamics of such kind of materials using XPCS. Therefore, the growth mechanism and the annealing processes under coherent radiation were investigated. DIP was identified as a suitable candidate for that purpose as it exhibits a diverse growth mechanism at room temperature, including layer-by-layer growth and a roughening phase. The DIP used in this study was bought from abcr and had a purity of 95 %.

6.2 PTCDI-C8

PTCDI-C8 ($C_{40}H_{42}N_2O_4$, Fig. 6.1 (b)) is an organic semiconductor whose thin films naturally exhibit almost layer-by-layer growth. PTCDI-C8 is known for its applications in OFETs and OSCs [79–86], recent studies of thin films of this

material have already provided valuable insights into its growth process [87–91]. In particular, the annealing process holds the potential for further morphological optimization. Therefore, this study focuses on exploring surface modifications during annealing to uncover the underlying microscopic processes. For this study, PTCDI-C8 was obtained as a powder from Sigma Aldrich with a purity of 95 %.

6.3 Pentacene

Pentacene (PEN) ($C_{22}H_{14}$, Fig. 6.1 (c)) is one of the most extensively studied organic semiconductors, for which numerous theoretical and experimental investigations have been performed [92–98]. Its thin film growth behavior is well known [99–101]. This extensive research emphasizes the importance of PEN as a prototypical organic semiconductor and motivates its inclusion in the scope of this study.

PEN was purchased as a powder from Sigma Aldrich with a purity of 99 %.

6.4 Fullerene

Buckminsterfullerene (C_{60}) (Fig. 6.1 (d)) is a special type of fullerene. It consists of twenty hexagons and twelve pentagons, with each of the 60 carbon atoms connected to three neighbors. This gives it a characteristic cage-like, fused ring structure reminiscent of a truncated icosahedron, similar to a soccer ball. Studies on the structure of its thin films can be found in Ref. [102–104]. The isotropic nature of this material adds another aspect to the exploration of materials with different molecular shapes and led to its inclusion in this study on growth and annealing processes.

The used C_{60} , purchased as a powder from Sigma Aldrich, had a purity of 99.5 %.

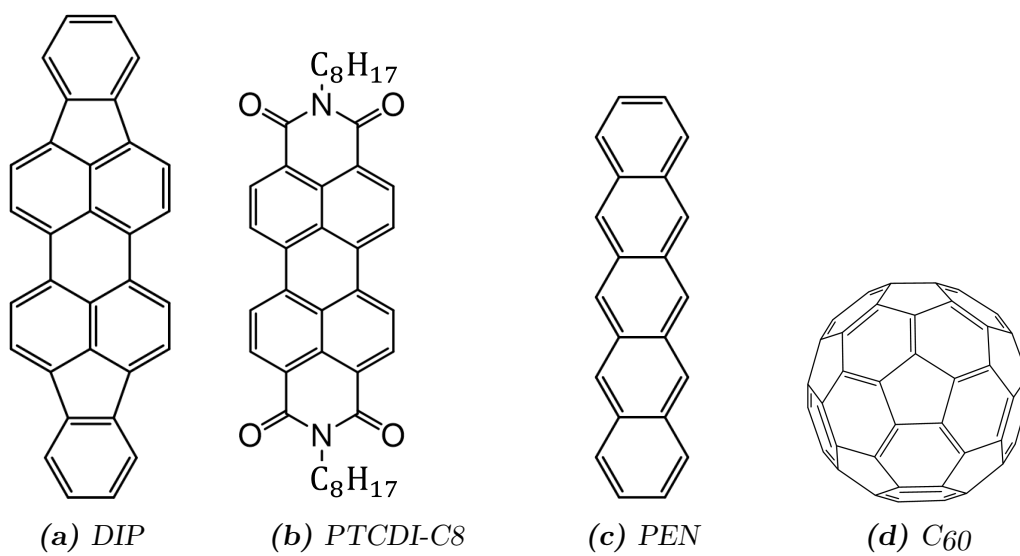


Figure 6.1: Chemical structures of all materials used in this work.

Chapter 7

Experimental Methods

Properties of thin films can be linked to their underlying characteristics, such as the crystalline order or the roughness of the surface, which in turn can be influenced by the methods used in production or processing. One well-known method for growing thin films is organic molecular beam deposition (OMBD) [31, 37, 105], which will be introduced in the next section.

This chapter will further present several surface analysis techniques that have proven to be valuable in revealing the structural order and morphology of thin films, aiming to enhance the understanding of intricate properties emerging during thin film growth or subsequent annealing processes. Atomic force microscopy (AFM) is an important tool in the analysis of thin films, as it provides a first insight into the morphology of the film by creating images of the surface in real space. However, to gain a deeper insight into the film properties, X-ray reflectivity (XRR) serves as a helpful analysis tool. It provides insight into both surface and internal structural properties.

Finally, the operation and use of synchrotrons are explained in more detail. In particular, the necessity of their usage for this study is elaborated and placed in context. By selecting the geometry of the experimental setup, the surface can be examined in a targeted manner. Therefore, GISAXS was used in the main experiments carried out at the synchrotrons, which will be explained in more detail at the end.

7.1 Organic Molecular Beam Deposition

In the context of this thesis OMBD was used to produce thin films. A sketch of an OMBD chamber with all the elements needed for film growth is given in Fig. 7.1. Molecules are vaporized in an evaporation cell, called Knudsen cell, by controlled heating. Changing the temperature in the evaporation cell allows the growth rate during film deposition to be changed later. A cell shutter allows the evaporation cell open and close to start or stop the growth process.

When the cell shutter is opened, a molecular vapor is released that is directed towards a substrate. Silicon substrates are used in this study. Upon contact with the substrate, the molecules are adsorbed, forming a thin film. The substrate temperature can be varied to study different growth conditions.

A quartz crystal microbalance (QCM) is used to monitor the thickness of the

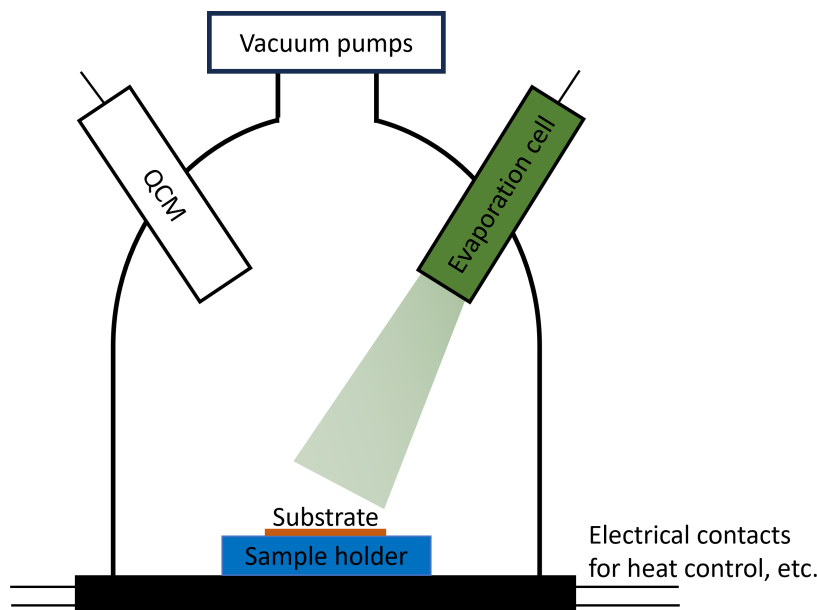


Figure 7.1: Sketch of an OMBD chamber used for thin film growth. A substrate is located on a sample holder, where molecules can be adsorbed from a molecular vapor origin from an evaporation cell. A QCM monitors the film thickness. The volume of the chamber is vacuumed.

thin film and is positioned close to the evaporation cell [106]. The vibration frequency of the QCM changes depending on the amount of material attached to its surface. This means that it has to be calibrated before the thickness of thin films is determined. This requires the production of a test film, which is then analyzed using methods such as XRR (see Sec. 7.3) to determine its actual thickness. By that calibration, the geometry of the entire setup is also taken into account, i.e., the positioning of the QCM relative to the evaporation cell. With the knowledge of the real film thickness of the test film, the QCM can be calibrated for that specific material and geometry and subsequently used to monitor the film thickness of similar films.

To ensure the purity of the resulting thin films, the whole volume of the chamber works under ultra-high vacuum conditions. In this work, the thin films that were produced and analyzed were grown under a pressure of about $p \approx 10^{-8}$ mbar.

7.2 Atomic Force Microscopy

AFM is a crucial technique that makes it possible to scan and, consequently, image surface structures [107–112].

A sketch of the setup is depicted in Fig. 7.2. There, a cantilever moves over the surface of a sample with its sharp tip moving just above it. This cantilever can be used in different scanning modes, depending on the material to be examined.

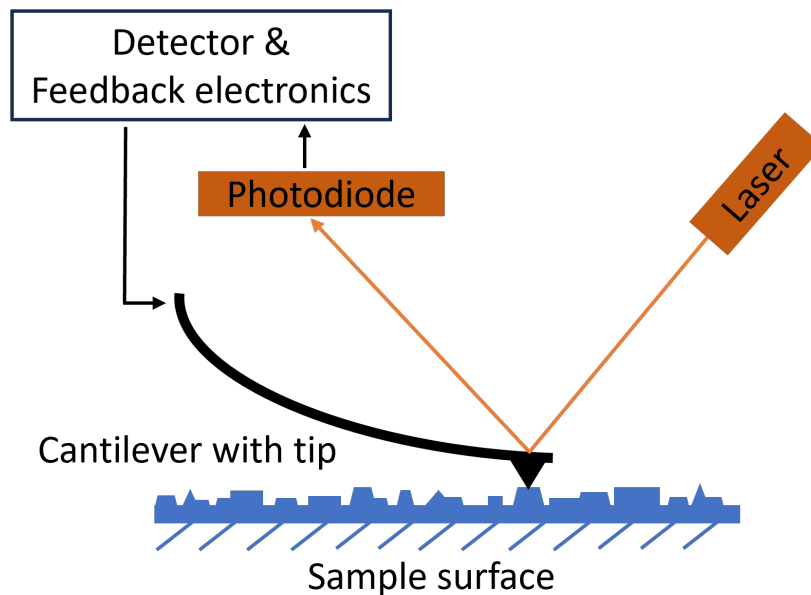


Figure 7.2: Schematic structure of the most crucial parts of an AFM. The tip of a cantilever moves over a surface. Surface changes lead to different signals of a reflected laser light on a photodiode, which leads to the construction of a real space image of the sample surface.

For soft materials, the intermittent contact mode is a common choice. This mode proves to be advantageous when working with sensitive materials as it prevents damage while ensuring high sensitivity for surface characterization. In this mode, the cantilever oscillates at a specific frequency. Its deflection alternates between the attractive and repulsive forces emerging when the tip approaches the surface. To compensate for these vibrations a compensation voltage is generated, the magnitude of which can be translated into the surface profile. As a final result, a representation of the sample surface is created.

For most soft matter materials, a range of several micrometers is usually measured in both spatial directions to get a reasonable representation of the surface morphology. Moreover, with the technology described above, it is possible to achieve a resolution in the height profile in the range of nanometers.

The analysis of the AFM data is done with the software Gwyddion [113]. The program considers the height h_i (with mean value h_{mean}) of all pixels N and calculates the roughness according to

$$\sigma^2 = \frac{1}{N} \sum_i r_i^2. \quad (7.1)$$

with the mean value of $r_i = h_i - h_{mean}$ expected to be zero. Consequently, the roughness is calculated in units of nanometers, i.e. $[\sigma] = \text{nm}$.

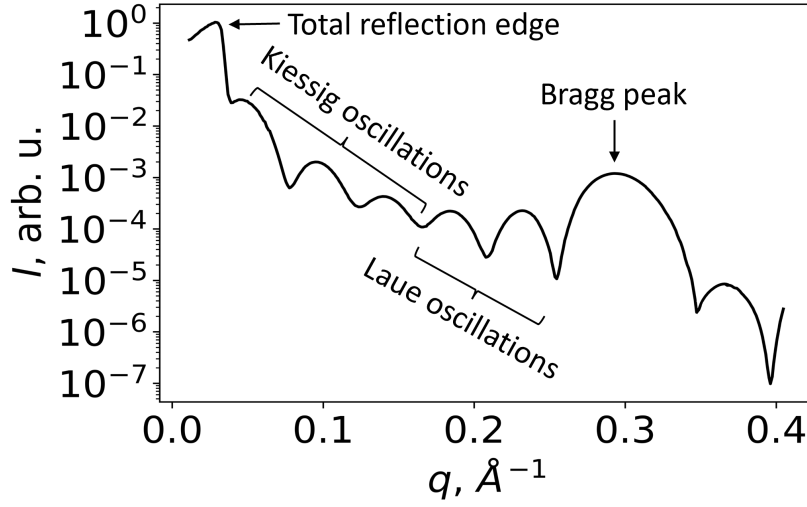


Figure 7.3: XRR curve of a 10 nm PTCDI-C8 film grown on silicon at room temperature. The features relevant for film characterization are marked in the plot.

7.3 X-ray Reflectivity

The analysis of thin films, can be performed with XRR [54, 114]. In this technique, an X-ray beam is directed onto the surface of a thin film. For this thesis $\text{CuK}\alpha$ radiation was used, characterized by a wavelength of $1.541 \text{ \AA}$. The resulting reflected intensity is detected with a 1D detector (here: Meteor 1D XRD Eigenmann) in the specular direction. This results in an intensity spectrum that depends on either the angle of incidence or the momentum transfer q , from which a variety of properties of thin films can be derived. Fig. 7.3 shows an exemplary intensity pattern of a 10 nm PTCDI-C8 film grown on silicon at room temperature. The relevant features for characterizing the film are marked in the diagram and will be explained in more detail below.

The first characteristic feature in the intensity pattern is the total external reflection edge. At this specific angle (or q -value), the X-ray beam undergoes total external reflection, aligning with the critical angle associated with the thin film material (see Sec. 3.4). In the range of small q -values, the interference between X-rays origin from the interface between the substrate and the film and those directly coming from the surface of the film leads to oscillations in the intensity spectrum, called Kiessig oscillations. The period of these oscillations is a direct indicator of the thickness of the thin film, while the amount of damping within the oscillations provides additional information, i.e., the surface roughness. Thus, parameters such as the film thickness, the surface roughness and even the electron density can be determined by a fit of the experimental data. For that, the machine learning algorithms 'mlreflect' are used [115].

Analysing the data at higher q -values reveals information about the inner structure

of the thin film. Mainly, Bragg peaks can be observed in the intensity spectrum of crystalline thin films. These peaks appear due to the underlying layer spacing within the crystal lattice and provide information about the film's structural arrangement. Laue oscillations may be visible around a Bragg peak, providing additional information about the size of the crystalline domains within the film. More information on the interpretation of XRR data can be found in Ref. [46, 116, 117].

7.4 X-Ray Sources

Over time, synchrotron sources, which provide X-ray beams and X-ray detection, have developed considerably. These advances offer the possibility to perform scattering experiments with sufficiently coherent X-ray beams to study dynamic effects of samples [118].

This section explains the necessity of using synchrotrons in this study, examines the inherent limitations, and provides insight into the geometric design of the underlying experiment.

7.4.1 Synchrotron Measurements

A synchrotron is a particle accelerator in which charged particles (for example electrons) move on a circular path with the help of magnets. As these charged particles move along their curved path, they experience a change in direction, causing them to lose energy. The lost energy is emitted through high-intensity X-rays called synchrotron radiation, which can be used for scattering experiments. Achieving high resolution in scattering experiments, especially when studying particles in the $\mu\text{m} - \text{nm}$ range, is a significant challenge and requires the right choice of wavelength, i.e. X-ray energy. This relationship between the size of the particles to be examined and the energy (or wavelength) is described in Eq. (3.13). The connection between resolution and energy or wavelength plays a crucial role in the design and analysis of experiments.

To achieve the small wavelengths required for the type of experiments in this work, synchrotron facilities capable of delivering wavelengths down to 0.1 nm, are needed. In current XPCS experiments, the q -values studied range from $(10^{-3} - 1) \text{ nm}^{-1}$ [12], which resolves in length scales of $\mu\text{m} - \text{nm}$.

Fig. 7.4 brings XPCS into the context of measuring techniques regarding the frequency-wave vector space. The measurement of larger objects leads, for example, to the field of photon correlation spectroscopy, and the increase in radiation energy leads to methods such as inelastic X-ray scattering through to scattering with neutron sources.

For further reading about synchrotrons and their applications it is referred to [119].

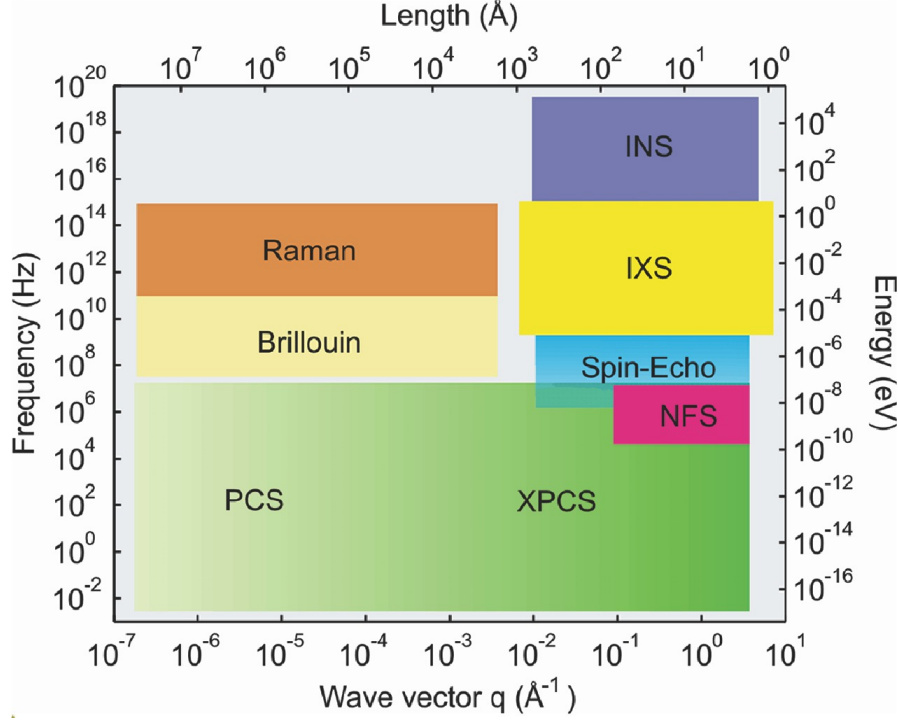


Figure 7.4: Overview on different measurement techniques covering several areas in the frequency-wave vector space, such as Inelastic Neutron Scattering (INS), Inelastic X-Ray Scattering (IXS), Nuclear Forward Scattering (NFS), Photon Correlation Spectroscopy (PCS), and X-ray Photon Correlation Spectroscopy (XPCS) [12].

7.4.2 Limitations

As described in Eq. (4.10) and (4.5), the coherence length is proportional to the wavelength of the radiation. Since X-rays have a short wavelength (typical hard X-ray wavelength: $\lambda_{\text{x-ray}} \approx 1 \text{ \AA}$), the coherence length is correspondingly small. This highlights the difficulty of developing experiments using coherent X-rays. Of course, coherence is not a discrete concept. In reality, only partially coherent radiation is always present. The aim in the context of these measurements is to increase the degree of coherence as much as possible.

Looking again at the Eqs. (4.10) and (4.5), it becomes clear that technical improvements can extend the coherence length. A small X-ray source can already increase the coherence of the beam. Additional slits would improve the transversal coherence, while the longitudinal coherence can be increased with monochromators. However, both improvements have the additional side effect of causing the beam to lose flux. That is why the development of stronger synchrotron sources in this context is so important. The longitudinal coherence length for the experiments performed in the context of this work is around $\chi_l \approx 0.025 \mu\text{m}$.

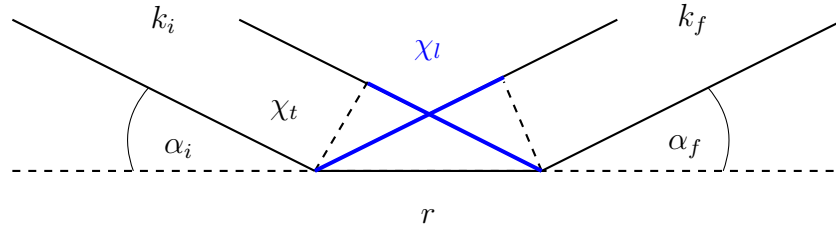


Figure 7.5: Geometry of X-rays scattering on a surface. The initial (final) beam is denoted as k_i (k_f) with the corresponding initial (final) angle α_i (α_f). Two points with distance r scatter coherently for a light source with the corresponding longitudinal coherence length χ_l and transversal coherence length χ_t .

Another way to influence the coherence is to adapt the geometry of the setup. The geometry of an X-ray beam scattering onto a surface is sketched in Fig. 7.5. The initial beam is denoted as k_i with the corresponding initial angle α_i . The final beam and angle have a corresponding subscript f . Two points at distance r to each other are considered. The scattered waves at those points are considered to be coherent if both conditions

$$\chi_t > r \cdot \sin \alpha_i \quad (7.2)$$

$$\chi_l > r \cdot (\cos \alpha_i - \cos \alpha_f) \quad (7.3)$$

are satisfied. The first condition demands a small incident angle, while the second requires almost specular surface scattering. Achieving coherent scattering is, therefore, easier for scattering under grazing incidence, i.e., surface scattering. Of course, the geometry is not limited to one dimension. According to Eq. (4.10) the transversal coherence length at a synchrotron can be calculated in both directions in which the beam is expanded. Hence, D can either be the expansion in x -direction σ_x or in y -direction σ_y . With this information, the coherence volume can be calculated. If it is larger than the investigated volume the X-rays are considered to be coherent.

In the experiments carried out as part of this work, the transversal coherence length is approximately $\chi_t \approx 35 \mu\text{m}$. Consequently, it is assumed that at an angle of incidence of $\alpha_i = 0.15^\circ$, two points separated by a distance of $r \approx 13 \text{ mm}$ scatter coherently. This distance is of the same order of magnitude as the footprint of the beam on the sample in the direction parallel to the beam, which is approximately 5 mm at the same angle of incidence. This indicates that the degree of coherence is sufficient for the experiments.

If, in this sense, coherent radiation scatters onto a rough surface, a speckle pattern can be observed. The measurement of the speckle pattern for different time periods allows access to intensity correlations in momentum space. These can be translated into fluctuations in real space by a Fourier transformation and gives

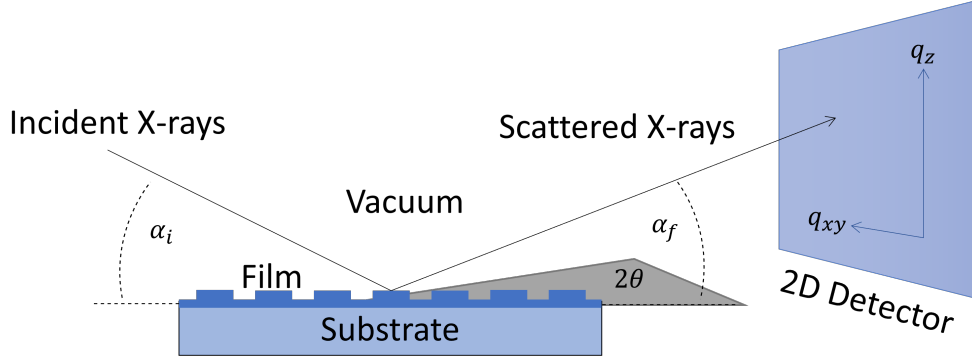


Figure 7.6: Sketch of a typical XPCS setup: When molecules cover the substrate, X-rays are scattered on it with an incidence (final) angle α_i (α_f) and an angle in off-specular direction 2θ . The intensity spectrum is detected on a 2D detector as a function of the momentum transfer q . It is split into a component parallel (q_{xy}) and orthogonal (q_z) to the surface.

information about the dynamics of the analyzed object. For this, it is not enough to provide a sufficiently coherent X-ray beam to observe tiny surface changes, it is also necessary to have the hardware to detect them. Hence, the recent development of faster detectors is a crucial step in the investigation of surface dynamics. At present, it is possible to measure time scales of $\mu\text{sec} - 1000\text{ sec}$.

7.4.3 Grazing Incidence Small Angle X-ray Scattering

The experimental geometry significantly influences the targeted measurements. As already mentioned, the emphasis of this work is on surfaces. In order to be sensitive to these, an incidence angle below the critical angle is chosen, which leads to a total reflection of the X-rays. This technique is called GISAXS [54, 64, 120–123]. With this geometry, information about the surface dynamics of nanoscale objects is obtained, for example, the island formation during a growth process.

A typical geometry of a GISAXS experiment is shown in Fig. 7.6. There, an incoming beam k_i is considered, that is falling on a sample under an angle α_i . The outgoing wave k_f can have an angle of 2θ parallel and an angle α_f perpendicular to the surface. Since the speckle pattern is measured in momentum space, the angles are transformed into momentum-transfer vectors. This results in

$$q_x = k_0 \cdot (\cos 2\theta \cos \alpha_f - \cos \alpha_i) \quad (7.4)$$

$$q_y = k_0 \cdot (\sin 2\theta \cos \alpha_f) \quad (7.5)$$

$$q_z = k_0 \cdot (\sin \alpha_f + \sin \alpha_i). \quad (7.6)$$

Due to the 2-dimensionality of the detectors, it is not possible to distinguish between the q value in the x - and y -direction, which is why a combination of both

is used

$$q_{xy} = q_x^2 + q_y^2 = k_0 \cdot \sqrt{\cos^2 \alpha_i + \cos^2 \alpha_f - 2 \cos \alpha_i \cos \alpha_f \cos 2\theta}. \quad (7.7)$$

In this case, q_z belongs to the q -component perpendicular to the probe surface, and q_{xy} to the one parallel to it, i.e.,

$$q_{||} = q_{xy} \quad (7.8)$$

$$q_{\perp} = q_z. \quad (7.9)$$

This measurement geometry is the foundation for all the synchrotron experiments presented in the results section.

The 2D diffraction pattern in this geometry provides valuable information about the surface properties. For ideally flat surfaces, only the specular reflection appears. Any deviation from flatness leads to intensity signals in the non-specular direction, referred to as diffuse scattering. These diffuse scattering signals can contain important lateral information.

In cases where an island landscape has formed on the surface, two symmetric peaks may appear in the off-spectacular intensity pattern, known as correlation peaks. As described in Sub. 3.3.3, in first order, the intensity is proportional to the form factor and the structure factor (Eq. (3.37)). This equation results from the Fourier transform of the particle shape and the van Hove function, which defines the probability that two islands are separated by a certain distance. From this, a connection between the peak positions and the average distance between islands denoted as D , can be derived [124–126]

$$\Delta q_{||} \approx \pm 2\pi/D, \quad (7.10)$$

where $\Delta q_{||}$ is the distance from $q_{||} = 0$ to the position of the peak.

Chapter 8

Simulations

The simulation of the experiment can be split up into two parts: First, the simulation of the real space is described. There are several possibilities to achieve that, which will be discussed in the following section, i.e. Sec. 8.1.

The second part of the simulation plays a more significant role in the context of this thesis. The scattering process and, therefore, phenomena in the Fourier space will be reproduced there. Due to the use of the experimental geometry, this simulation is rather challenging and will be introduced in Sec. 8.2.

8.1 Real Space Simulation

It will first be focused on the parametrization of the surface in real space to simulate the entire experimental process. This will be broken down in the first chapter, where various surface representations will be introduced to suit different growth modes.

8.1.1 Pixel Representation

To create a sufficiently large surface in real space while keeping the computational costs low, it is possible to use effective theories. In the following subsections the phase field theory and kinetic Monte Carlo simulations are introduced. Both simulations produce a model of a film surface consisting of rectangular pixels. In general, any method that produces a reasonable pixelated surface representation can be used as input to simulate the scattering process, which is the main focus of this work.

Phase Field Theory

To simulate structural surface changes in the micrometer range over several minutes to hours, effective theories are useful. Examples can be found in Ref. [127–129].

One possibility to produce a parametrized surface is the phase field theory, following the model and equations in Ref. [34, 130–133]. In the phase field theory, a diffusion equation $u(r, t)$ is used to describe the concentration of a mobile species

at position $\mathbf{r}$ and time t . The differential equation

$$\frac{du(\mathbf{r}, t)}{dt} = \nabla(D(\mathbf{r}, t)\nabla u(\mathbf{r}, t)) - \frac{d\Phi}{dt} + \text{random deposition}(\mathbf{r}', t') \quad (8.1)$$

describes the density of diffusing solitary particles. This quantity includes the contributions of the spatially varying diffusion constant $D(\mathbf{r})$, as described in Chap. 2 in Eq. (2.2) at surface step edges and Eq. (2.1) elsewhere.

A further differential term, $d\Phi/dt$, is introduced, which captures the solidification process to an immobile covering. The equation includes several factors, such as a penalty term for the formation of steps, the tendency of Φ to assume integer values corresponding to terraces, the diffusion-mediated development of step edges, and the formation of islands.

The final term in Eq.(8.1) describes the influx of molecules during growth, putting them on a random location $\mathbf{r}'$ at time t' .

For the realization of the creation of quantitative growth simulations according to the introduced theory, a Java code, developed in the context of another PhD thesis is used [134]. To avoid instabilities, numerical aspects are taken into account and the parameter space is explored to find reasonable constants that are not experimentally accessible or based on physical principles. As a result, a 100×100 pixel surface is constructed, where the height of each pixel varies with the simulated deposition time.

Kinetic Monte Carlo Simulations

Furthermore, a surface can be constructed using kinetic Monte Carlo simulations. Examples can be found in Ref. [78, 124, 135, 136]. The following will rely on the work in Ref. [78]. The simulation is performed within the framework of a cubic lattice, initially developed to simulate film growth at the molecular level. The simulations involve anisotropic nearest-neighbor interactions that mimic Van-der-Waals attraction between particles. However, for the specific purpose of this work, the anisotropy of shape and interaction is not required.

The entire simulation framework was developed in the context of another PhD thesis [137] and is here reused for macroscopic surface structures. The resolution is fixed to 256×256 pixels for the surface size, with periodic boundary conditions. Due to this low resolution, not every pixel corresponds to a single molecule. However, the size of a pixel can be determined by comparison with experimental data, such as AFM data of the material of interest.

The time course is measured by the number of particles per filled layer. In the simulations used here, 500 time steps are produced, corresponding to about 100 time steps per layer.

The general control parameters in film growth that govern the development of roughness, including temperature, growth rate and substrate conditions. Various

simulation parameters come into play in the simulation, including:

- particle-particle interaction: $\epsilon \in [2, 6]$
- interaction anisotropy: η
- substrate-particle interaction: ϵ_s
- lateral diffusion: $D \in [10^3, 10^5]$
- rotational diffusion: $D_{\text{rot}} \in [10, 10^4]$
- growth rate: F
- Ehrlich-Schwoebel barrier: ΔE_{ES}

It should be noted that these values can deviate from the experimental values, which makes direct comparisons difficult.

New particles are randomly inserted into the simulation at a rate of F without forming overhangs. The particles can jump to neighboring locations at a rate of D (surface diffusion coefficient) and rotate at a rate of D_{rot} . Two models are considered: Model B, where all particles can rotate, and Model S, where only the surface particles can rotate. The latter model is used because the rotation of the particles is not crucial for the purpose presented here, and it reduces the computation time.

Four growth modes can be achieved, depending on the input parameters: layer-by-layer growth, islanding to layer-by-layer growth, islanding to 3D growth and 3D growth. Over long periods of time, however, all films become rough. This study introduces a distinction between island growth and 3D growth using the roughness parameter as a key metric. A roughness parameter σ that oscillates with increasing film thickness (total layer coverage) Θ indicates layer-by-layer growth, while a rapid increase indicates island formation ($\sigma \propto \Theta^n$ with $n > 1/2$) and a monotonic increase indicates 3D growth ($\sigma \propto \sqrt{\Theta}$, see Sec. 2.1). 3D growth essentially means strong island dynamics without subsequent coalescence, as appearing in systems investigated in Ref. [92, 138–141].

8.1.2 Cylinder Representation

In the later growth phase of many soft matter materials a transition from layer-by-layer growth to 3D island formation occurs. Therefore, this section will focus on the evolution of islands. This provides an opportunity to improve the space-time resolution by representing the islands on the surface as cylinders. Consequently, these cylinders can change in radius and height to simulate island growth.

With this, a $10 \times 10 \mu\text{m}^2$ area with cylinders representing the islands can be constructed. Subsequently, some surface changes can be applied by changing the size

of the cylinders. An annealing process could be best represented by implementing a cylinder with increasing radius and decreasing height. In addition to the change in cylinder size, it is also possible to investigate some movement, for example some drift (constant movement in a fixed direction) or a random walk of the center of mass (COM). Examples of both the change in size and the movement of cylinders are discussed in the results section and adapted to the experimental data.

The choice of cylinder size is motivated by translating the position of correlation peaks to the real space. As a first approximation, the typical distance between the islands can be approximated by the typical island size, i.e., the cylinder size.

Considering the AFM data the materials introduced in Chap. 6, a dense island population is expected. However, implementing island overlap in the simulation is challenging. In order to avoid overlapping particles in this area, a total of only 50 cylinders are distributed randomly.

It is important to note that even if the real space simulation does not match the surface of the actual film precisely, for example the island density in the simulation may differ from the experimental one, the results still offer representative insights into the effects on the surface and the resulting structures in the TTCs.

8.2 Scattering Simulation

After the simulation of the surface in real space, this chapter will focus on the scattering process and the simulation of the resulting detector image. The aim is to reproduce measurements in the GISAXS geometry. To achieve this goal, the distorted wave Born approximation (DWBA) must be considered [54, 142], explained in the first section.

It is important to note that constructing a scattering simulation including the DWBA is beyond the scope of this thesis. Therefore, the existing BornAgain (BA) software will be relied upon to perform the simulations. It can be used to generate intensity patterns of growing and moving islands. Then, analogous to the analysis of the experimental data, the XPCS calculation can be applied to compute TTCs and other relevant parameters.

8.2.1 Distorted Wave Born Approximation

In classical electrodynamics, a monochromatic electromagnetic wave can be characterized by the wave vector $|\mathbf{k}| = 2\pi/\lambda$. The propagation of the electromagnetic wave in a non-uniform media with the refractive index $n(\mathbf{r})$ can be described by the Helmholtz equation

$$(\nabla^2 + n^2(\mathbf{r})\mathbf{k}^2)\mathbf{E}(\mathbf{r}) = 0, \quad (8.2)$$

which describes the electric field $\mathbf{E}(\mathbf{r})$ of the electromagnetic wave. A similar equation can be established for the magnetic field of the electromagnetic wave. Consequently, it is sufficient to focus only on the electric field when investigating wave propagation.

Perturbation expansion is often used to solve Eq. (8.2), with the Born approximation serving as the first approximation. This approach proves to be particularly efficient for single scattering scenarios, where the influence of multiple scattering can be neglected, and the interaction between X-rays and matter is weak. However, in the case of surface scattering, even small differences in the refractive index can cause substantial refraction and reflection, making multiple scattering a crucial factor to consider. As a consequence, Eq. (8.2) has to be calculated using the DWBA. The deeper treatment of this topic can be found in several textbooks, such as in Ref. [143, 144].

The initial focus is on the Born approximation, which essentially considers the non-uniform index of refraction $n(\mathbf{r})$ as a perturbation to the vacuum condition, for which the solution of Eq. (8.2) is well-known. In vacuum (i.e., $n = 1$), the solution for Eq. (8.2) is expressed as

$$\mathbf{E}_0(\mathbf{r}) = \mathbf{E}_0 \cdot \exp(i\mathbf{k} \cdot \mathbf{r}). \quad (8.3)$$

If we consider the interaction with some material (for example a surface) with some effective optical potential $V(\mathbf{r}) = \mathbf{k}^2(1 + n^2(\mathbf{r}))$ decaying faster than $1/|\mathbf{r}|$, Eq. (8.2) can be reformulated as

$$(\nabla^2 + n^2(\mathbf{r}))\mathbf{E}(\mathbf{r}) = V(\mathbf{r})\mathbf{E}(\mathbf{r}). \quad (8.4)$$

A solution utilizing the Green's function $G(\mathbf{r}, \mathbf{r}')$ can be produced as

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}')V(\mathbf{r}')\mathbf{E}(\mathbf{r}')d\mathbf{r}'. \quad (8.5)$$

The different orders of the Born Approximation emerge by solving Eq. (8.5) iteratively. This series converges for weak $V(\mathbf{r})$, but as the potential increases, convergence becomes problematic.

For scenarios involving large potentials, an improved version, such as the DWBA, is necessary. In DWBA, a small distortion $\Delta V(\mathbf{r})$ is added to the potential, given by

$$V(\mathbf{r}) = V_0(\mathbf{r}) + \Delta V(\mathbf{r}), \quad (8.6)$$

where $V_0(\mathbf{r})$ is the undistorted potential, for which the solution is known from above (Eq. (8.5)). If this is inserted into Eq. (8.4), similar considerations apply as for the Born approximation in order to find a solution. Utilizing the Green function and the solution for the undisturbed potential, the DWBA expression is

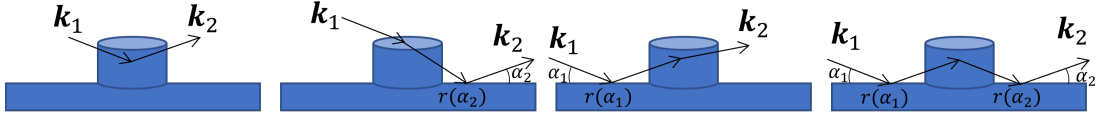


Figure 8.1: Sketch of the DWBA scattering contributions.

given by

$$\mathbf{E}(\mathbf{r}) = \mathbf{E}_0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') \Delta V(\mathbf{r}') \mathbf{E}(\mathbf{r}') d\mathbf{r}' = \mathbf{E}_0(\mathbf{r}) + \delta \mathbf{E}(\mathbf{r}), \quad (8.7)$$

where the solution is decomposed into a reference field $\mathbf{E}_0(\mathbf{r})$ and a perturbation field $\delta \mathbf{E}(\mathbf{r})$.

Examining applications of these calculations, particularly concerning surfaces, one ideal scenario is an absolutely flat surface characterized by $V_0(\mathbf{r})$. In this case, an exact solution exists, described in terms of the Fresnel coefficients (see Eq. (3.47)). If a graded or rough surface is considered, any deviations from the flat surface can be regarded as small distortions [145–150].

To approach the topics discussed in this thesis, these calculations can be applied to scattering processes with particles such as nanoparticles [151] or islands on a surface, as shown in Fig. 8.1. During the scattering process, various scattering events occur due to the reflection of the incident and final beam. Each reflection is weighted with the corresponding Fresnel coefficient, and the final waves interfere coherently to create an effective form factor. However, simulating this process is challenging. Therefore, an already existing software is utilized, which is described in more detail in the following section.

8.2.2 Software BornAgain

An existing software called BA is used to simulate the scattering process. BA is a free and open source C++/Python software for simulating and fitting small angle scattering by grazing incidence [152]. The incoming X-ray beam is assumed to be perfectly monochromatic and collimated. In addition, a desired wavelength can be selected.

Furthermore, different types of samples can be chosen. For example, the simulated surface can either consist of an arbitrary number of layers or represent a rough interface. In addition, a more specific surface can be constructed from simple and composite particles.

Unfortunately, BA is not constructed to simulate speckle patterns. The only possibility to use coherent scattering without averaging is to remain within one particle layout in the same layer. A summary of all possible particle layouts is given in Fig. 8.2. When different particle layouts are combined, the intensity pat-

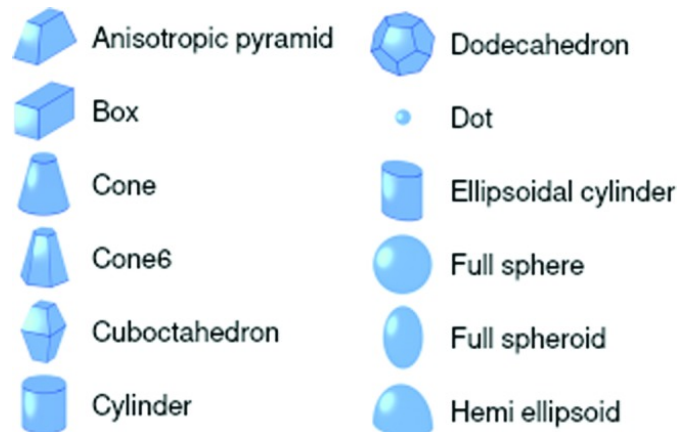


Figure 8.2: Summary of all possible particle layouts available in BA [152].

Table 8.1: Definition of the material in the simulation using the refractive index, including dispersion (δ) and absorption effects (β) from Eq. (8.8).

Material	δ	β
DIP	$4.23 \cdot 10^{-6}$	$5.39 \cdot 10^{-9}$
PTCDI-C8	$3.55 \cdot 10^{-6}$	$5.28 \cdot 10^{-9}$
silicon	$6.49 \cdot 10^{-6}$	$1.28 \cdot 10^{-7}$
vacuum	0	0

tern is computed as an incoherent average. At first glance, this severely limits the options to construct a complex surface with multiple monolayers. However, both the surface construction with the pixel representation as well as with the cylinder representation allow the use of only one particle layout per layer. For this purpose, boxes or cylinders with various heights (and also radii for the latter) are used. Surfaces obtained from the previous section serve as input for the BA software. The software specializes in generating intensity patterns on a two-dimensional detector based on the surface information provided.

The material is defined by its refractive index, expressed as

$$n = 1 - \delta + i\beta, \quad (8.8)$$

where δ and β appear due to dispersion and absorption effects, respectively. The specific values for the materials in the experiment are summarized in Tab. 8.1.

To introduce motion or changes in particle properties during the simulation, appropriate functions are implemented, including changes in particle coordinates (COM motion), radius, and height. BA is then used to generate intensity patterns for each time step, incorporating the changes in particle properties due to the implemented functions.

Once the simulated data is available, it is analyzed in the same manner as the experimental data, e.g., an XPCS analysis is applied to calculate TTCs and other relevant parameters.

Part III

Results

Chapter 9

Analyzing Island Dynamics during DIP Thin Film Growth

This chapter addresses the dynamic analysis using XPCS during the growth of a DIP thin film.

Growth of thin films is a classic example of a statistical non-equilibrium process [153]. The resulting morphology, structure, and properties of the film are closely related to the dynamics and kinetics of the growth [41]. The complexity of thin film growth can be further enhanced by the possible anisotropy of organic molecules, which involves both, orientational degrees of freedom and anisotropic interactions [37, 73–78, 154]. These factors contribute to different growth scenarios that affect the structure and properties of the film. Accordingly, MLs can either close completely or roughen rapidly in the initial phase, which can also be influenced by external conditions such as the growth rate or substrate temperature [37, 73, 154]. In order to understand the underlying microscopic processes that can lead to the different growth scenarios, it is necessary not only to perform post-growth characterizations but also to investigate the growth process in situ. Coherent X-ray diffraction proves to be a powerful tool to study growth dynamics. This method provides insight into the arrangement of the film surface throughout the growth process and provides information on the adsorption of molecules on the substrate and the subsequent formation, rearrangement, and diffusion of molecular islands.

In this context, DIP serves as a prototype organic semiconductor and provides a platform for exploring and understanding the nuances of thin film growth in the field of organic materials. The focus of this study lies in the comparison of experimental data with simulations, which is a crucial step towards understanding the dynamics and kinetics involved in the formation of the film. This comparative approach will provide valuable insights into the complicated processes that determine the growth of DIP thin films. The basis of this chapter is closely rooted in the content presented in Ref. [155].

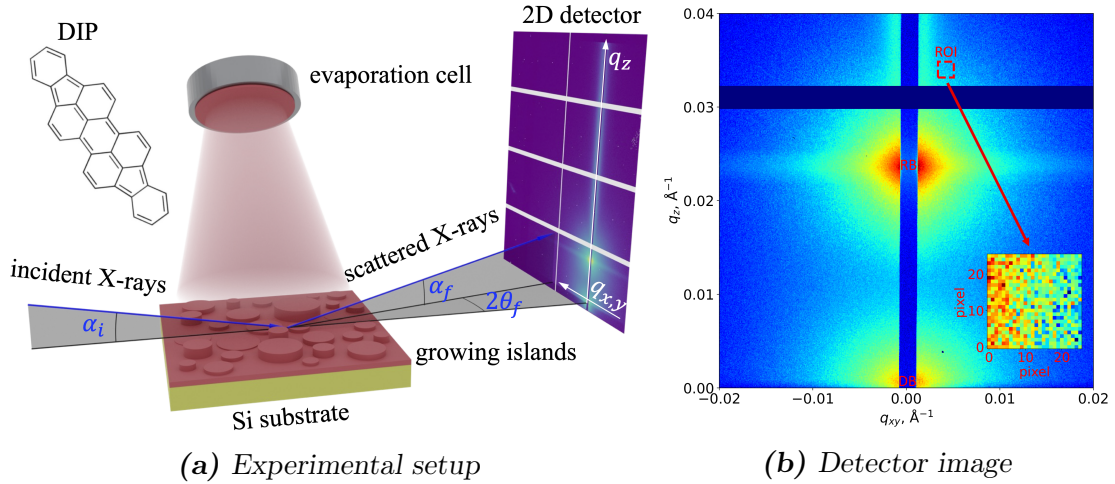


Figure 9.1: a) Sketch of the experimental setup at the synchrotron during DIP thin film growth. While a silicon surface is covered with molecules from an evaporation cell, X-rays scatter with an incidence (final) angle α_i (α_f) and an angle in horizontal direction $2\theta_f$. The scattered intensity is detected with a 2D detector as a function of the scattering vector $\mathbf{q}$, which is divided into a component parallel (q_{xy}) and orthogonal (q_z) to the surface. b) Detector image at deposition time $t_{\text{dep}} = 3800$ sec in q -space. The positions of the direct beam and reflected beam are marked as 'DB' and 'RB', respectively. To improve visibility, the analyzed region (ROI) is enlarged and inserted into the lower right corner of the image [155].

9.1 Experimental Results

First, the experimental setup and fundamental aspects of DIP thin film growth will be explored. Following this, a conventional analysis of the DIP thin film is executed and assessed to acquire insights into its evolution. This analysis serves as a foundation for uncovering additional knowledge through XPCS. To achieve this, comparisons with XRR and AFM results are performed.

9.1.1 Setup & Basics

The growth of DIP films prepared by organic molecular beam deposition [37, 74, 156] on Si substrates at a slightly elevated temperature ($T_{\text{sub}} \approx 40^\circ\text{C}$) is investigated. The films were prepared in a portable ultra-high vacuum chamber [157] at a rate of 0.1 nm/min, to a final thickness of approximately 10 nm. The primary experiment was performed at the coherence applications beamline P10 at PETRA III (Deutsches Elektronen-Synchrotron (DESY), Hamburg) using an X-ray beam focused to $8\ \mu\text{m} \times 5\ \mu\text{m}$ (hor. $\times$ vert.) with a photon energy of $E = 8.7\ \text{keV}$.

To capture the speckles present in the scattered X-ray intensity, a 2D detector (Eiger X 4M, pixel size $75\ \mu\text{m} \times 75\ \mu\text{m}$) was positioned 5 meters downstream from the sample. The setup is illustrated in Fig.9.1 (a). To ensure sensitivity to surface

changes and suppress substrate contributions, the measurements are performed in the GISAXS geometry (see Sec. 7.4.3). For this purpose, an incidence angle of $\alpha_i = 0.15^\circ$ was chosen, which is slightly below the critical angle of DIP ($\alpha_c = 0.17^\circ$) at the specified X-ray energy [54]. Fig. 9.1 (b) demonstrates an example of a detector image at a specific time, $t_{\text{dep}} = 3800$ sec in q -space, during the growth phase. Both, the direct beam and reflected beam are covered by a beamstop. At this point, correlation peaks are already visible, and the speckles are apparent. The speckle contrast for the measured diffraction patterns during the experiment was approximately $\langle I^2 \rangle / \langle I \rangle^2 - 1 \approx 0.12$. To enhance speckle visibility, an enlarged image of the region of interest (ROI) with a size of 25×25 pixels is inserted in the lower right corner of Fig. 9.1 (b).

In an earlier investigation of the sensitivity of organic materials to potential radiation-induced damage, in particular DIP, films were irradiated under constant conditions (see also App. 14). This meant that a constant room temperature was maintained at which dynamic changes visible in the TTCs were not expected, as the film morphology had already been allowed to relax over several days. The analysis focused on examining signals, particularly TTC changes, to detect possible radiation damage. The DIP films showed a stable signal over about 900 seconds. Consequently, this 900 second irradiation duration was chosen for the in situ growth measurements performed in the main experiment. As a result, the DIP thin film growth run was split into three scans, each lasting 1800 seconds, with one-second exposure time followed by one second of dark time. In between these scans, the position of the X-ray spot was shifted.

9.1.2 Complementary Analysis

The growth of DIP thin films has been the subject of extensive investigation in the scientific community. Those interested in a thorough investigation of this topic can find insights in a number of exemplary references available at [72–74, 154, 158–162].

In order to provide additional support for the validation of the XPCS findings, the ex situ surface morphology of a DIP thin film grown under the same conditions as the film investigated and measured at the synchrotron was investigated. Fig. 9.2 (a) presents an AFM image illustrating the surface. The height distribution, extracted from this data and depicted in Fig. 9.2 (b), reveals three distinct peaks. The separation between these peaks corresponds to the height of a single DIP layer [154]. Consequently, it can be inferred that these peaks represent three open layers on the surface. Therefore, it is reasonable to anticipate the development of around three layers at this film height for films grown under the same conditions as well.

The post-growth XRR data for the same DIP film is presented in Fig. 9.3 (a). A recognizable Bragg peak occurs at about $0.38 \text{ \AA}^{-1}$, which indicates some degree

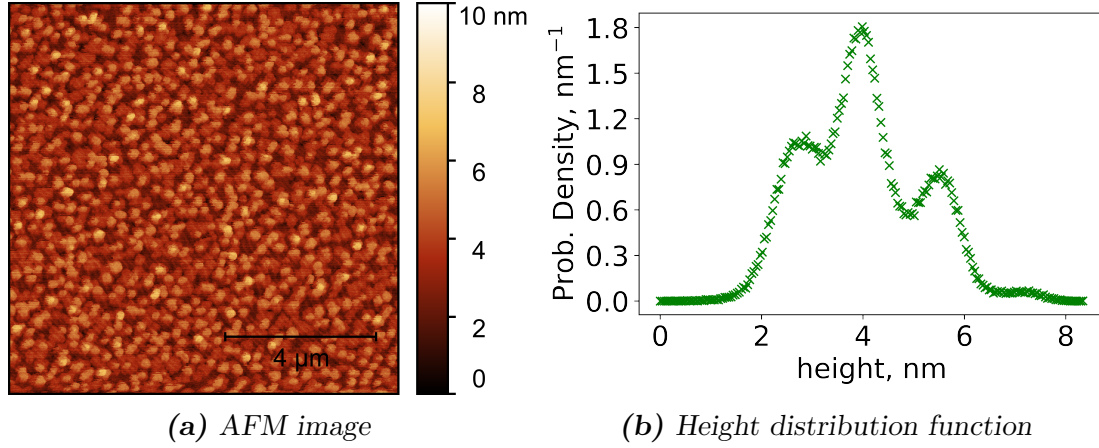


Figure 9.2: a) AFM image of a DIP film grown under the same conditions as the films measured at the synchrotron. b) The corresponding height distribution function shows three distinct peaks corresponding to three open layers [155].

of crystallinity in the film. This peak corresponds to a layer spacing of 1.65 nm, which is consistent with the findings from the literature [154].

In addition, Kiessig oscillations can be observed, which offer the possibility of determining key parameters such as the thickness and roughness of the film. Employing a machine learning tool introduced in Ref.[115], the data was fitted, as demonstrated in Fig. 9.3 (b). The fitting process estimated a thickness of $d = 8.0$ nm and a roughness of $\sigma_{RMS} = 1.2$ nm for this specific thin film.

9.1.3 XPCS Analysis

At room temperature, the growth of DIP begins in a layer-by-layer fashion. After a few layers, molecular islands are formed, which leads to rapid roughening [37, 73, 154]. By analysing the diffuse scattering signal, it becomes possible to distinguish between these two regimes and track the formation of initially formed MLs and the roughening process.

The diffuse scattering signal is plotted well above the critical angle ($q_z \approx 0.09 \text{ \AA}^{-1}$) in Fig. 9.4 (a). The absence of a diffuse scattering signal indicates a smooth film surface with no open layers [25, 124]. Conversely, the presence of a diffuse scattering signal suggests a rough surface with islands. Further, the q_{xy} -position of the signal allows the extraction of average distances between islands. Converting this into a length scale corresponds to the average in-plane size of the surface roughness [145]. As a valid approximation, it can be applicable to the typical island size on the surface, serving as a starting point for the simulations introduced in the next section.

For the investigated film grown at the synchrotron (Fig. 9.4 (a)), it is observable that the first two layers open and close completely. Subsequently, the surface becomes rough. The plot marks the total coverage Θ in units of MLs, with one

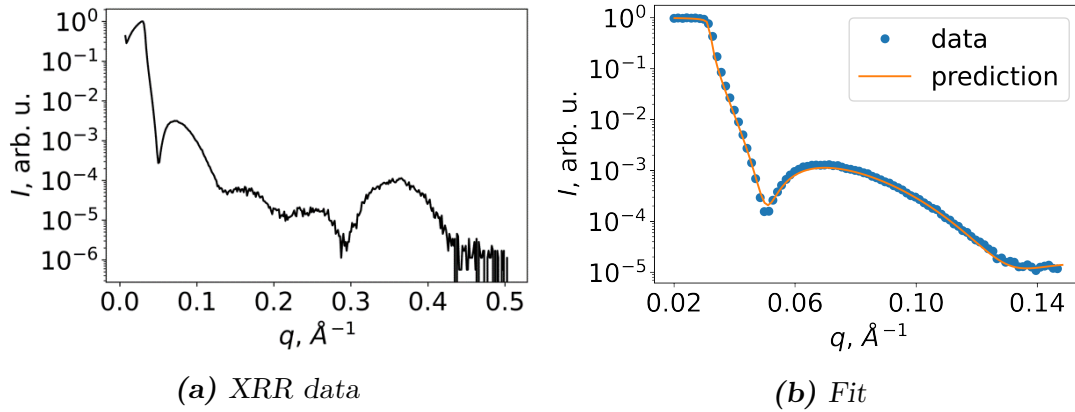


Figure 9.3: a) post-growth XRR data of a DIP thin film grown on silicon at room temperature. b) Fit to the XRR data using [115], resulting in a thickness of $d = 8.0$ nm and a roughness of $\sigma_{RMS} = 1.2$ nm.

ML expected to be 1.6 nm, as extracted from the XRR results in Subsec. 9.1.2. Furthermore, the maximum of the diffuse scattering shifts to smaller q_{xy} -values, indicating that the surface correlation length initially increases during growth until stabilizing at the third ML at $l_{\text{corr}} \propto 2\pi/q_{xy} \approx 450$ nm.

In Fig. 9.4 (b), the XPCS results are presented, manifested in the calculation of TTCs using Eq. (5.5), depending on the deposition time $t_{\text{dep}} = (t_1 + t_2)/2$. The analysis is confined to a ROI, where the intensity of the diffuse scattering is sufficiently high to ensure reliable results, as marked in red in Fig. 9.1 (b). This ROI corresponds to a 25×25 pixel region at $q_z = 0.034 \text{ \AA}^{-1}$ and $q_{xy} = 4.22 \times 10^{-3} \text{ \AA}^{-1}$. Transforming these q -values into real space yields length scales of $l_z \approx 15$ nm and $l_{xy} \approx 150$ nm, corresponding to the size of molecular islands. Consequently, the XPCS analysis is sensitive to the motion of these islands.

Upon closer examination of the results, a broadening perpendicular to the diagonal (i.e., with an increase in t_{dep}) is evident, indicating an overall slowdown during growth. Additionally, irregularities along the diagonal are observed, suggesting non-monotonic behavior – successive slowing down followed by acceleration, commonly referred to as dynamic heterogeneity [17, 64, 65]. Previous studies have associated similar features with layer closing and opening [25], which might hold true for the presented data, especially for growth times $t_{\text{dep}} \leq 2600$ sec. Surprisingly, these features persist even at later growth stages when the film becomes rougher, and no layers close anymore ($t_{\text{dep}} \approx 2000$ sec). In this later growth regime, the average intensity saturates at a constant value. Therefore no information on dynamics can be extracted from the analysis of the average intensity. However, the TTCs continue to exhibit intriguing patterns. This underscores that the exploration of this hidden insight into the roughening process can only be effectively investigated through the use of XPCS.

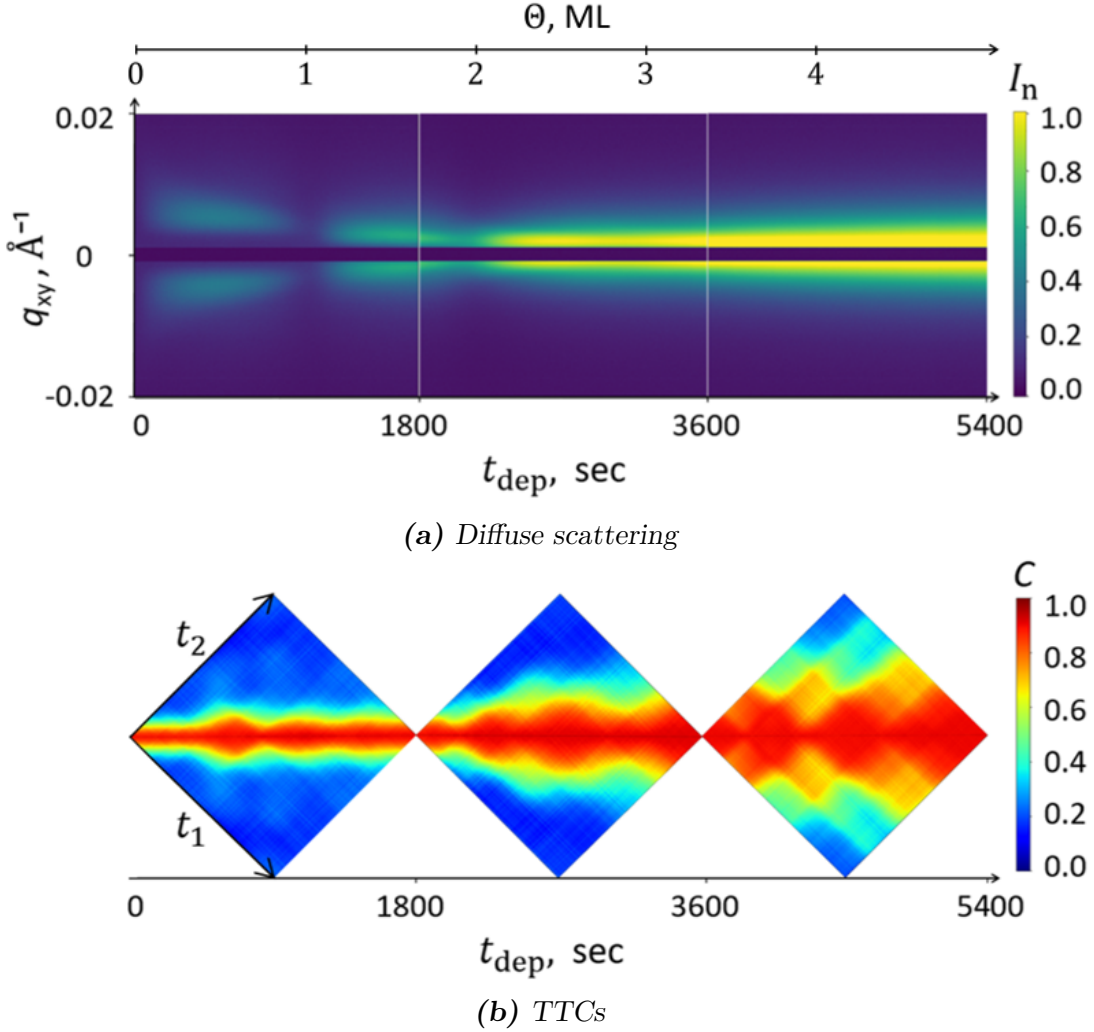


Figure 9.4: XPCS analysis during the growth of a DIP film at room temperature [155]. a) Diffuse scattering signal, calculated at $q_z \approx 0.09 \text{ \AA}^{-1}$, to follow the formation of initial layers up to the subsequent roughening process supported by the total layer coverage Θ for better orientation. b) TTCs in dependence of the deposition time $t_{\text{dep}} = (t_1 + t_2)/2$. After 1800 sec, the radiation spot was changed to avoid radiation damage, resulting in three scans for the whole growth process. The analysis was performed at a 25×25 pixel region at $q_z = 0.034 \text{ \AA}^{-1}$ and $q_{xy} = 4.22 \times 10^{-3} \text{ \AA}^{-1}$.

The investigation of the TTCs reveals a crucial aspect – the heterogeneous behavior. For a more precise quantification, the fourth-order correlation function is calculated using Eq. (5.6). The results obtained are presented in Fig. 9.5, which shows the calculation for the first two layers separately (layer 1: $t_{\text{dep}} = 100 - 1000$ sec, layer 2: $t_{\text{dep}} = 1000 - 1800$ sec). The roughening of the film is then examined from layer 3 onwards.

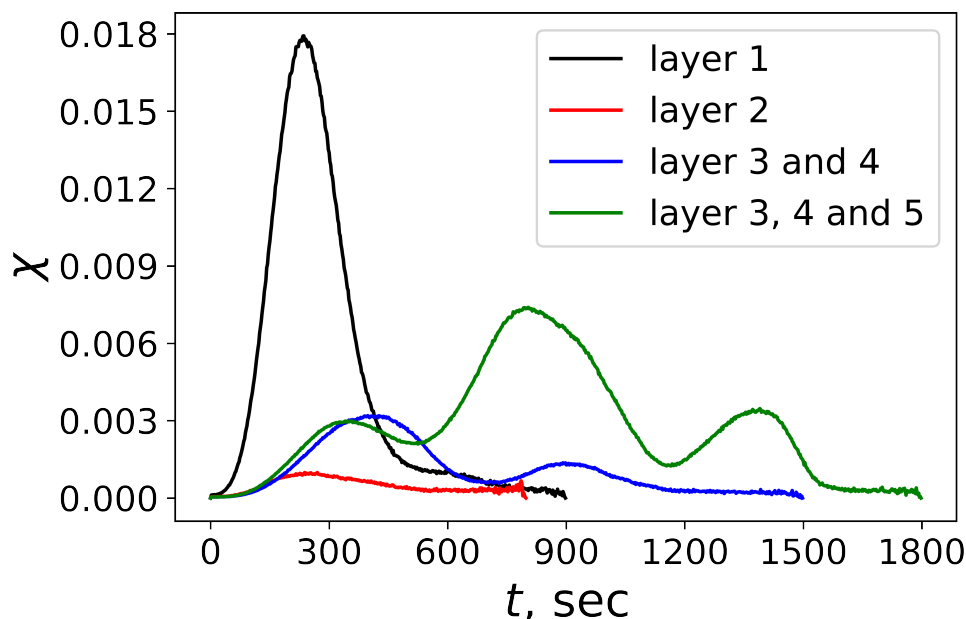


Figure 9.5: Fourth-order correlation function extracted from the TTCs in Fig. 9.4 [155]. The calculation of the first two layers (layer 1: $t_{\text{dep}} = 100 - 1000$ sec, layer 2: $t_{\text{dep}} = 1000 - 1800$ sec) was separated from the roughening part starting from layer 3 ($t_{\text{dep}} > 2100$ sec).

As described in Sec. 5.2, this function typically has a single peak at the position t^* , which corresponds to the characteristic time of the system, and a height χ^* , which represents the degree of heterogeneity. However, with increasing roughening of the film, Fig. 9.5 shows the appearance of multiple peaks. The results of this phenomenon are examined using simulations in Sec 9.2 to understand the reason for this phenomenon.

As already mentioned, thin film growth is a non-equilibrium process. To estimate characteristic time scales for the underlying physical processes during growth, a g_2 -analysis can be conducted using Eq. (5.1). The g_2 -curves are extracted from each TTC in Fig. 9.4 (b), and the results are presented in Fig. 9.6.

There, a non-monotonic decay is evident, originating from the heterogeneous behavior of the TTCs. Further investigation of this behavior will be addressed later, utilizing simulations to trace back physical processes on the surface from these features (Sec. 9.2). Averaging over each TTC results in the loss of information about the time evolution. Nevertheless, an averaged time scale is obtained during each growth stage. The extraction of average quantities can be done using an exponential fit, as described in Eq. (5.3). For that, the relaxation rate τ becomes crucial as it offers a characteristic time scale of the underlying physical process. This parameter is of primary interest, but the fit also encompasses a background and magnitude to consider the finite contrast of the experimental data. Addi-

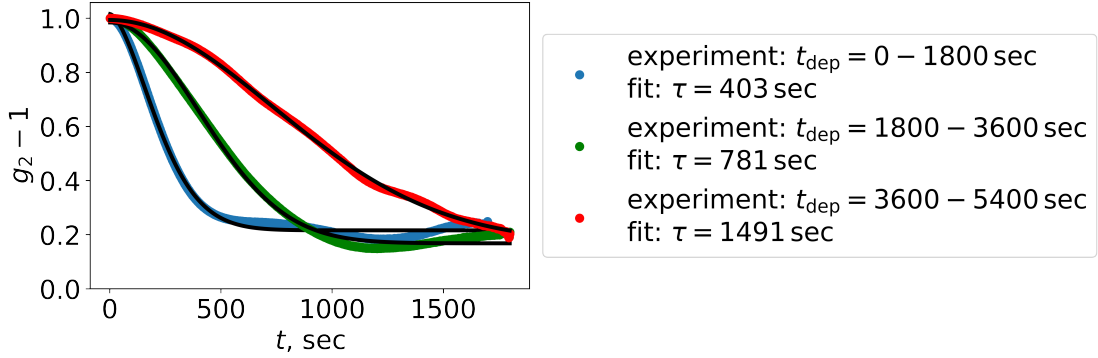


Figure 9.6: g_2 -function for each TTC in Fig. 9.4 (b). Using an exponential fit, given in black, physical quantities can be extracted. The resulting relaxation rates τ are incorporated in the legend [155].

tionally, the stretching exponent accommodates non-Brownian dynamics of the islands. The results of the relaxation rate are incorporated in Fig. 9.6. Typical time scales appear to be around hundred seconds for the underlying surface changes. An additional upward trend in the relaxation rate over deposition time is also evident, quantifying the previously observed slowing down process during growth.

Finding a direct translation of these time scales to specific physical processes is not trivial. For spatial correlations in the XPCS data and, specifically, to understand and interpret the heterogeneous behavior, simulations will be necessary and applied in the following section.

9.2 Simulations

Connecting the XPCS results to physical processes involves the use of simulations as a helpful tool. The infrastructure of the simulations employed in this work is explained in Chap. 8. This chapter utilizes this framework to distinguish between dynamics, representing the actual movement of islands, and kinetics, denoting the pure growth of islands. Additionally, various growth scenarios are explored using the phase field theory.

9.2.1 Real Space Simulations

As mentioned in Sec. 8.1, there are several possibilities to simulate the surface in real space. In the following, different possibilities along with their advantages and disadvantages, are presented to reproduce the DIP growth.

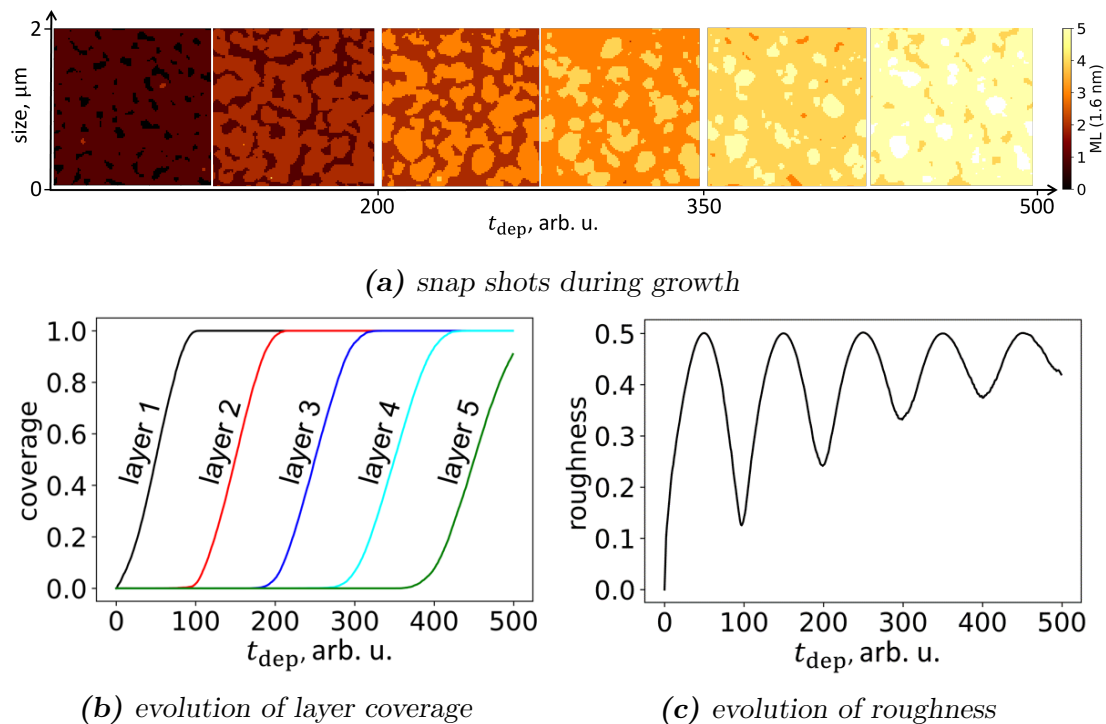


Figure 9.7: (a) Six snap shots during the change in surface morphology in dependence of deposition time during simulated film growth, using [134]. The size and height are found by comparison to the AFM data of DIP from Ref. [74]. (b) Extracted Layer coverage and (c) roughness evolution of the same simulated film growth.

Phase Field Theory

In an attempt to replicate a real space similar to the observed DIP growth, a surface was constructed based on the phase field theory used in Ref. [134]. Fig. 9.7 (a) shows six snapshots of the surface evolution and aims to replicate the observed DIP growth as closely as possible. As in the experimental data (see Fig. 9.4), the first and second layers close, and starting from the third layer, the film becomes rough, with the evolution of layers overlapping. Comparing the simulation results to the AFM data from Ref. [74] results in some reasonable length scales, represented in the surface area and height.

Using this simulation, some surface quantities, like the evolution of the single layers and the roughness (see Eq. (2.7)), can be extracted. Both are shown in Fig. 9.7 (b) and (c), respectively. Initially, the layers still close almost completely, but as the deposition time progresses, the developments of the layers overlap. Furthermore, the roughness of the surface increases with time.

These simulations are a powerful tool for modelling surface changes as accurately as possible. However, achieving computational efficiency at the desired length scales is a major challenge. Consequently, modelling individual molecular diffusion

Table 9.1: Parameters for recreating macroscopic surface changes using Monte Carlo simulations, according to [78].

ϵ	η	ϵ_s	D	D_{rot}	F	ΔE_{ES}
-5	1	-6	10^5	10	1	0

processes becomes computationally expensive. To overcome this, it is switched to simulations of the collective motion of molecular assemblies, which, however, entails limitations in terms of temporal and spatial resolution.

Kinetic Monte Carlo Simulations

Using kinetic Monte Carlo simulations based on the PhD Thesis of Ref. [137], a 256×256 pixels surface area can be constructed. In this setup, each pixel corresponds to a size of 20×20 nm. This size was determined by comparison to AFM images of DIP [74].

To be as close as possible to the DIP growth data, the focus in this work is primarily on the layer-by-layer growth, in particular, the study of the development of five layers with 100 time steps per layer.

To achieve this, the seven parameters introduced in Sec. 8.1.1 can be adapted. The values of these parameters, which lead to the closest match between the simulation results and experimental observations, are given in Tab. 9.1. These values were chosen to promote strong particle-substrate and particle-particle interactions while maximizing the diffusion parameter to achieve layer-by-layer growth. The rotation parameter is set to the smallest possible value. This means that the rotation of the particles is neglected, as no molecules are considered anyway, but rather collections of molecules, and the calculation time can thus be minimized. Six snap shots of the resulting surface are shown in Fig. 9.8 (a) in dependence of the deposition time. Again, the length scales in the simulations were selected in a way that the simulated results match the AFM data of DIP from Ref. [74]. From those simulations it is possible to extract some surface quantities. The evolution of each single layer and the roughness of the whole surface over the simulation time are depicted in Fig. 9.8 (b) and (c). In the course of the simulation, the overlapping of the layers starts to increase, and the overall roughness increases. Hence, the simulation is constructed in such a way as the DIP growth is expected to happen.

Cylinder Representation

The cylinder representation is used to show the later growth phase of the DIP, in which islands are formed. This offers a better spatial and temporal resolution, as the real space is no longer pixelated. A $10 \times 10 \mu\text{m}^2$ surface area is constructed, with cylinders representing the islands. The cylinder size is justified by converting

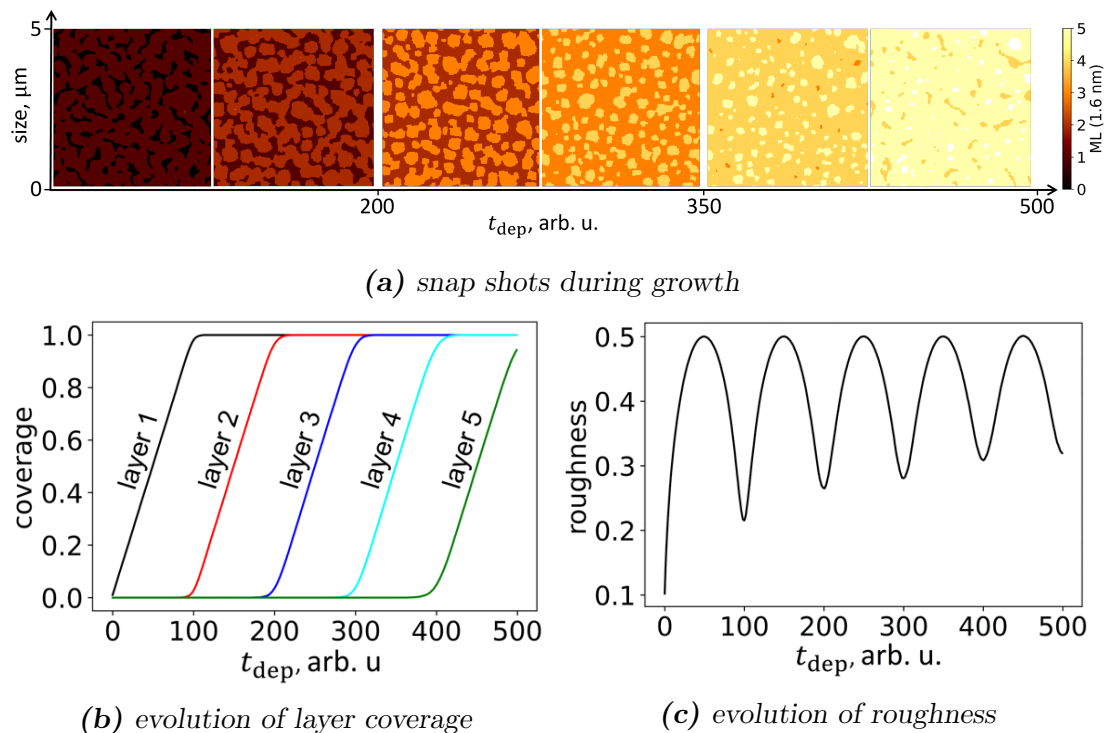


Figure 9.8: (a) Six snap shots during the change in surface morphology in dependence of deposition time during simulated film growth, using Monte Carlo Simulations [78]. The size and height are found by comparison to some AFM data of DIP from Ref. [74]. (b) Extracted Layer coverage and (c) roughness evolution of the same simulated film growth.

the position of correlation peaks in Fig. 9.4 (a) to the real space (as explained in Sec. 7.4.3), selecting a radius of approximately 200 nm. Fig. 9.9 (a) focused on the pure growth of cylinders, while Fig. 9.9 (b) also includes a random walk of the cylinder COM.

9.2.2 Dynamics vs. Kinetics

In the following, the diffraction patterns of different kind of surface changes are modelled, leading to the determination of the simulated TTCs.

To create a basis for consistency, a surface without any movement or dynamic effects is modelled first, and the corresponding TTC is calculated. Subsequently, the focus will shift towards exploring pure dynamics (investigation of the COM movement) and growth kinetics separately. This separation allows to gain insight into how each of these factors individually affects the TTC patterns.

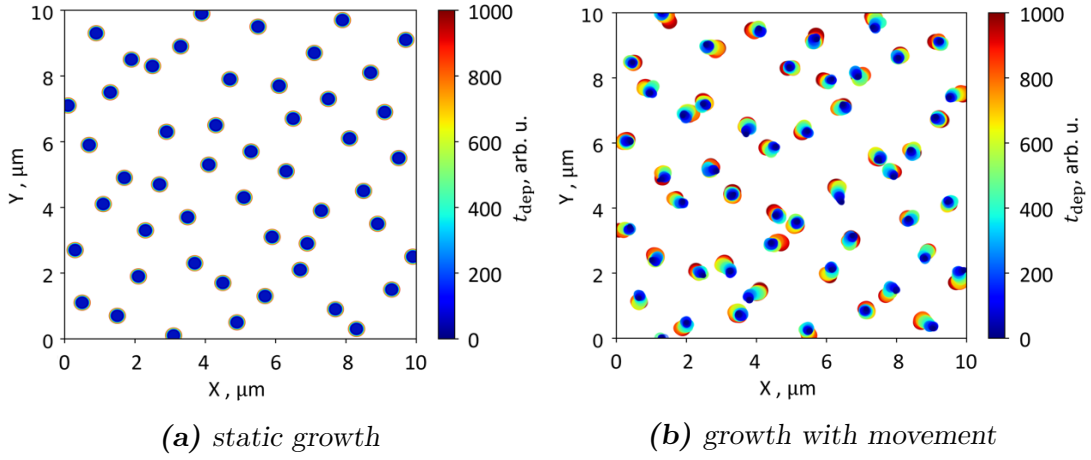


Figure 9.9: Cylinders representing islands on a $10 \times 10 \mu\text{m}^2$ surface. a) shows the growth of cylinders with a non-changing COM. The change of the radius over the deposition time t_{dep} is encoded in the color scheme. b) contains an additional motion (random walk) to the growth.

No Movement

To cross check if the simulation gives access to dynamics, the static case is considered first, i.e., a surface containing cylinders is constructed, which are neither growing nor moving.

In particular, 50 cylinders with an average radius of 200 nm and an average height of 20 nm over a simulated time of 1500 time steps are created. Furthermore, a small size distribution for both, the radius and the height is chosen, multiplying both with a random factor between 0.9 – 1.1. Fig. 9.10 (a) shows the simulated real space. The corresponding TTC in Fig. 9.10 (b) shows a constant intensity correlation over the whole time period. Since there is no motion happening on the surface and the intensity does not change with time, this result is expected.

Dynamics

Using the cylinder representation, it is possible to separate the kinetics, i.e. pure island growth, from the dynamics and the movement of islands.

On the one hand, cylinders with a fixed radius and fixed height can be considered, which move on the surface at a constant speed in the direction orthogonal to the beam. The TTCs with effective drift velocities of 1 nm/arb. u. and 5 nm/arb. u. are shown in Fig. 9.11 (a) and (b). This effective drift velocity is characterized by the total displacement of the COM per time unit. A slight fluctuation of the relaxation rate is visible in both TTCs, possibly due to the random distribution and changing number of particles (some of them move out of the investigated surface area), different radii, and heights. Nevertheless, both TTCs show a straight diagonal to a good approximation, indicating constant motion. With increasing

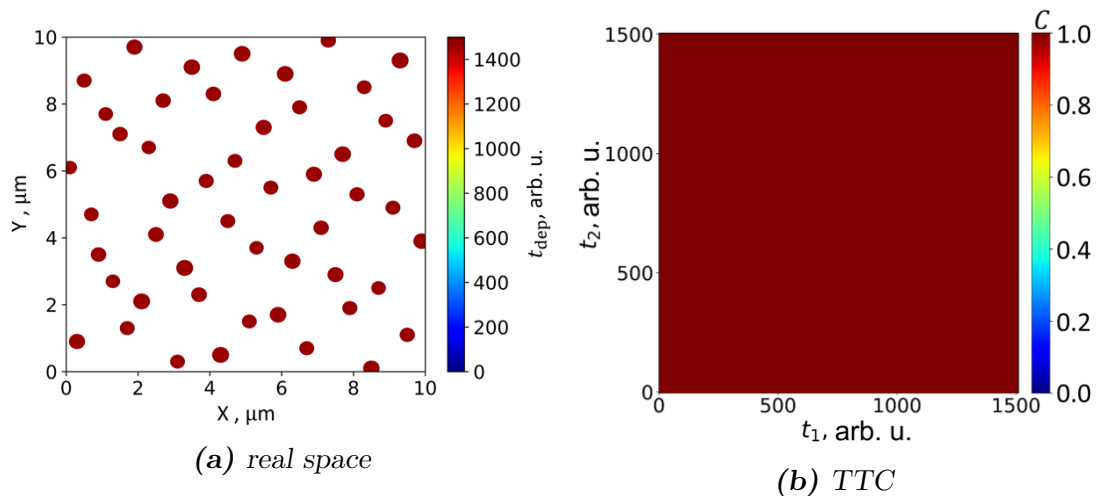


Figure 9.10: Simulation using the cylinder representation for 50 static cylinders with a radius of 200 nm and height of 20 nm multiplied with an additional random distribution factor between 0.9 – 1.1. a) Real space image of the static process. b) The corresponding TTC shows no movement.

effective drift velocity, the diagonal is getting narrower. This is a reasonable result since the characteristic time of the system is decreasing.

On the other hand, the COM can be fixed and the islands only grow. This result is presented in Fig. 9.11 (c). There, the heterogeneity is a key feature, which will be further discussed in the next section dedicated to the kinetics.

To understand how both effects are mixing, growth and drift will be combined. Again, a movement with a constant step size could be chosen. But to be closer to the physical effect on the surface, a random walk for the COM will be considered according to a normal distribution, given by

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\frac{x^2}{2\sigma^2}\right). \quad (9.1)$$

In this scenario, the step size of the COM is distributed around zero with a variance of σ^2 . The latter one can either be chosen to be constant or it can decrease according to the decrease in radius change (the calculation of the radius will be discussed in more detail in the next section). Since a constant material flux is considered in the experiment, a decreasing σ^2 will fit better.

To investigate the interplay between dynamics and kinetics, a TTC is simulated for different effective drift velocities. This translates into different values of σ^2 in terms of the difference in radius after each time step Δr . To obtain those different strengths the change in radius is multiplied by different integers, the chosen ones are summed up in Fig. 9.12. The resulting TTCs can be seen in Fig. 9.13.

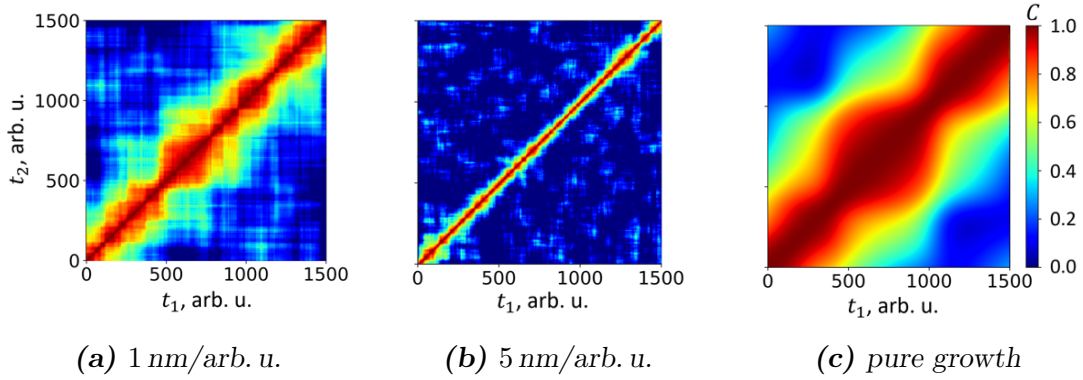


Figure 9.11: Comparison of pure movement and growth. a) 50 cylinders (radius $r = 200$ nm, height $h = 100$ nm) move with an effective drift velocity of 1 nm/arb. u. b) Same cylinders with an effective drift velocity of 5 nm/arb. u. (c) Pure growth of 50 cylinders from $r = (175 - 205)$ nm and $h = (66 - 80)$ nm.

To have a better understanding how that looks in real space, the movement of a single island is shown below each TTC. It can be seen that for an increasing COM motion, the TTC structure appearing from this motion competes with the structure formed from growth.

Comparing these TTCs with their counterparts derived from real data gives an approximate average effective drift velocity of 0.25 nm/sec. From this it can be deduced that the changes in the coherent diffraction patterns are primarily due to the growth of the islands, while their motion only has a minor influence on the TTC structure.

Kinetics

In the previous section, it was shown that the structure of the TTCs appears mainly due to kinetic effects. As a consequence, the investigation shifts towards a more intricate exploration of how the growth of islands contributes to the heterogeneous behavior observed in the TTCs.

For this purpose, cylinders representing islands on a surface, need to grow. Since it is physically reasonable to maintain a constant material flow, the volume of the islands is expected to grow linearly. To achieve this, the radius (and height) of the cylinders are varied according to

$$r(t_{\text{dep}}) = r_0 + r_s \cdot t_{\text{dep}}^{1/3}, \quad (9.2)$$

where r_0 is the initial radius, r_s is a scaling factor, and t_{dep} corresponds to the deposition time in the real experiment. The parameters are selected so that the simulation matches the data as closely as possible, using AFM images and correlation lengths as reference values, given in Fig. 9.2 (a) and Fig. 9.4 (a), respectively. One example of a TTC matching a part of the experimental data of the DIP

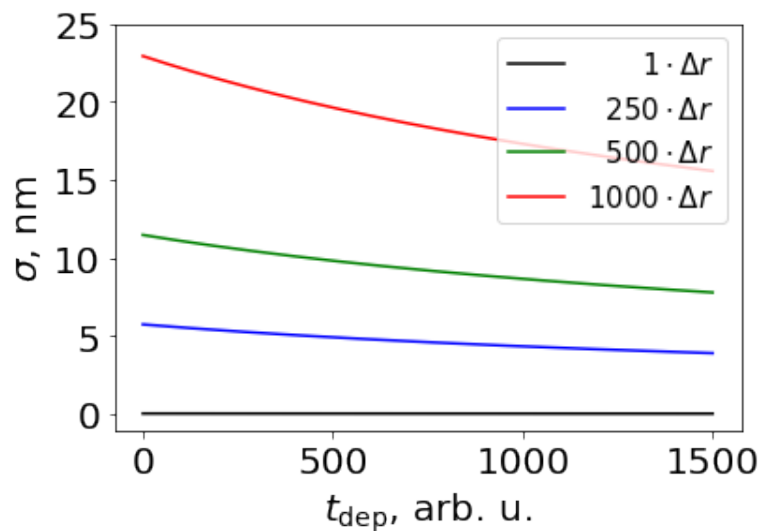


Figure 9.12: Change in variance corresponding to the increase in radius size (Δr) during the simulation time t_{dep} . Different colors denote different strengths, realized by multiplying by an integer [155].

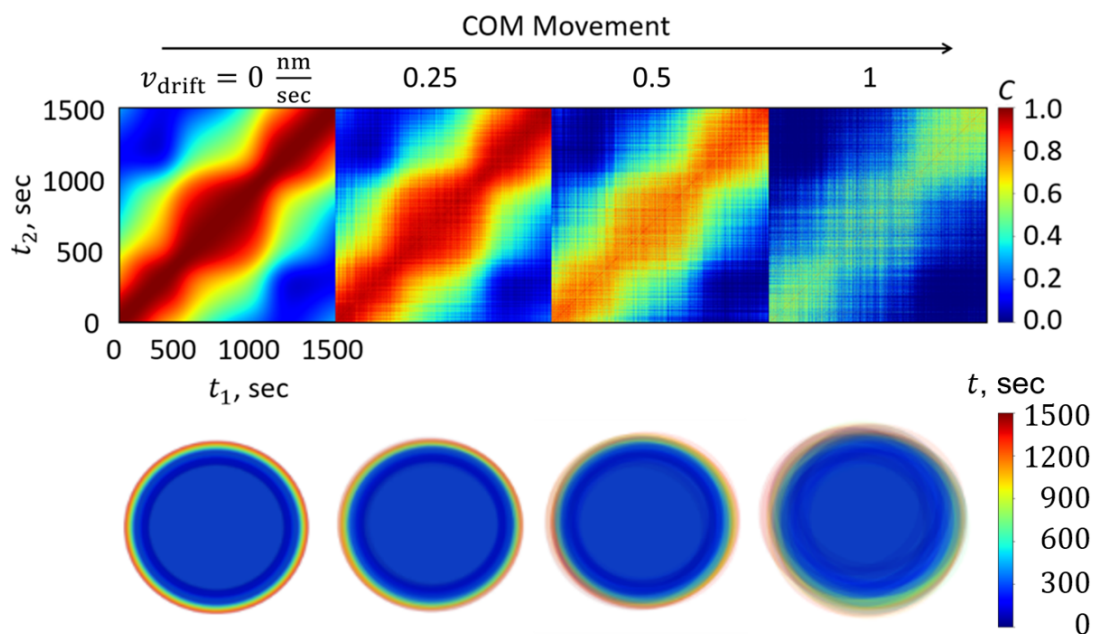


Figure 9.13: Influence of pure island growth (kinetics) in combination with movement (dynamics) on the TTC structure. With increasing COM movement, given by the effective drift velocity, the TTC structure originating from growth got suppressed by the one from motion (nearly constant decrease on smaller time scales). The real space image of a single island with a radius of around 200 nm is shown below each TTC [155].

growth shown in Fig. 9.4 (b) is given in Fig. 9.11 (c). As mentioned before, the key feature here is the heterogeneous behavior, i.e., the alternating accelerations and slow downs in the system.

To better understand the origin of the heterogeneous behavior, a larger area of the 2D detector is simulated. A pixel area of 250×1000 pixels is sufficient to understand the pattern on the detector but also does not increase the computation time too much.

First, the growth in radius and height of only one cylinder is investigated. One detector image of this process is shown in Fig. 9.14 (a), which should represent the form factor of a cylinder. Due to a shallow incidence angle, the cylinder effectively looks like a rectangle so that the width of the vertical and horizontal strikes can be estimated as $\Delta q = 2\pi/L$, where L is either the height or diameter of the cylinder. For orientation, the position of the direct and reflected beam is marked as 'DB' and 'RB', respectively. The intensity pattern shows vertical stripes whose position is determined by the size of the radius. In the same way, the height is responsible for the horizontal streaks. With increasing radius and height, the streaks will move closer to each other.

Performing the XPCS analysis within the ROI results in the TTC in the lower right corner of the detector image. While the horizontal and vertical intensity streaks will shift due to the growth of the cylinder, the intensity minima and maxima will move through the ROI. This results in a correlation between the n th minima at time t_1 and the $(n + 1)$ th minima at time t_2 , where $t_2 > t_1$, resulting in the heterogeneous behavior observed in the TTC (similar results were found in [163]). Accordingly, a higher growth rate leads to faster time scales.

In the second step, the number of particles in the simulation will be increased to 50, which are all growing with the same speed. The resulting intensity pattern is shown in Fig. 9.14 (b). Increasing the number of particles does not change the structure of the intensity pattern, but does lead to the appearance of speckles, as expected.

The random positions of the particles with respect to each other have only a minor influence accordingly, the basic structure of the TTC does not change.

Lastly, some growth distribution will be added, so that not all 50 particles grow with the same speed. To achieve this, the radius and height are multiplied with a random factor between 0.5 – 1.5. The resulting intensity pattern, visible in Fig. 9.14 (c), shows washed out minima and maxima. This result is reasonable since the distribution in radii and height does not lead to defined minima and maxima anymore. As a consequence, the heterogeneous behavior in the TTC will decrease (also similar to [163]).

With this knowledge, general information from the TTCs can be derived. This includes the extracted time scales being related to the rate of island growth and the extent of heterogeneity being related to the distribution of island sizes, i.e., the roughness of the surface.

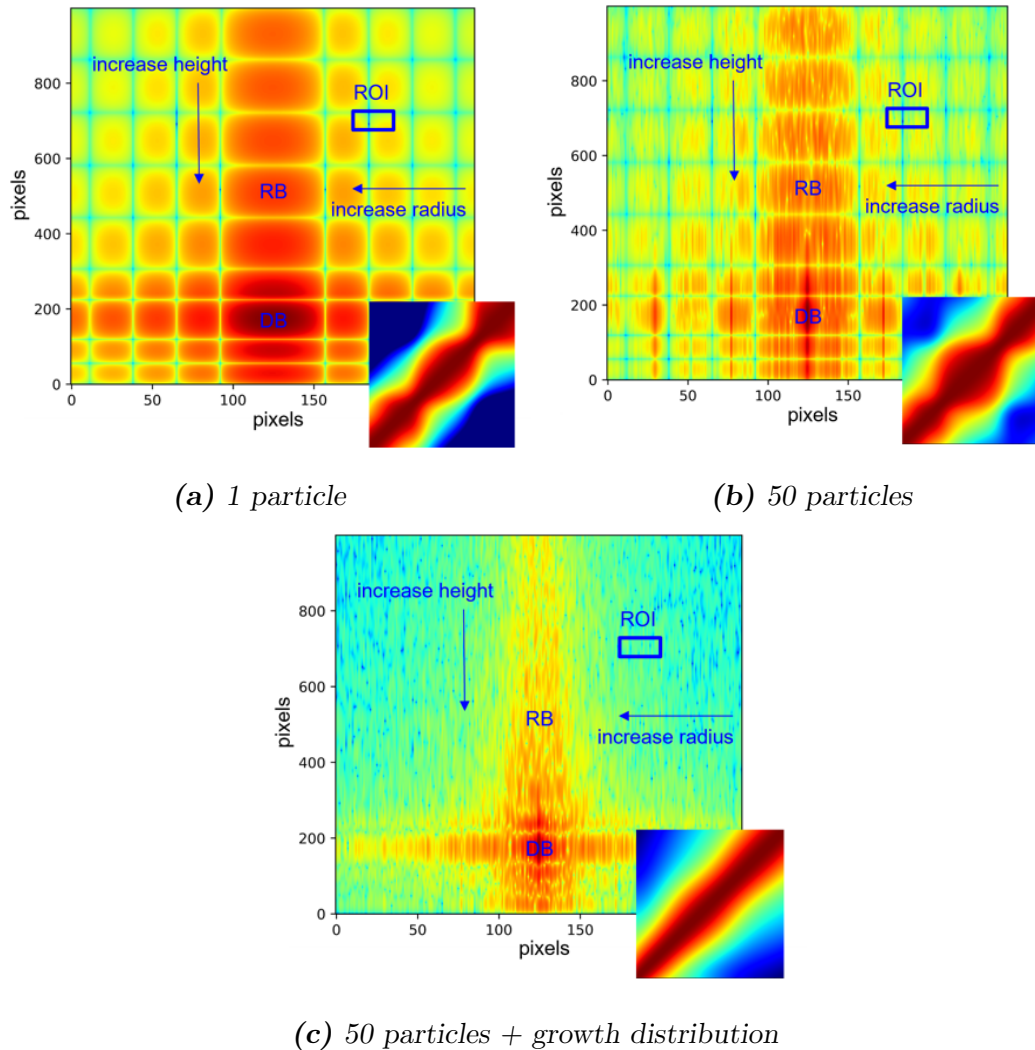


Figure 9.14: Simulated detector image produced with BA for a single cylinder (a), for 50 identical cylinders (b), and 50 cylinders with different sizes (c). The positions of the direct beam and reflected beam are marked as 'DB' and 'RB', respectively. With increasing radius ($r = (175 - 205) \text{ nm}$) and height ($h = (66 - 80) \text{ nm}$), the intensity streaks will move closer to each other. Performing the XPCS analysis on the ROI results in the TTC in the lower right corner of the detector image [155].

9.2.3 Realization of Different Growth Scenarios

The pixel representation is used in the following section to study different growth scenarios in multilayer systems. For this purpose, different cases are examined, starting with the growth of a single layer. Then, gradually, more complex scenarios are considered, such as layer-by-layer growth and islanding, as well as an intermixing between them.

Through the XPCS analysis of the simulated data, TTCs and fourth-order correlation functions are calculated. The results can be compared to the experimental data, providing insights into realistic growth scenarios. In addition, the challenges associated with pure islanding from the beginning or with rough growth will be closer looked into. This ultimately shows the limitations of the methodology used in this work and, thus, the difficulties of characterizing very rough growth scenarios.

Layer-by-Layer Growth

In the beginning, the simplest case is considered, which is the growth of a single layer (Frank-van-der-Merwe growth, see Sec. 2). Fig. 9.15 shows in part (a) a snapshot of the development of the layer in real space and in part (b) the corresponding TTC of the entire growth process. To get rid of the noise, which appears due to the insufficient space resolution at the beginning and end of the growth, about five time steps of the data are cut out. Both the simulated TTC agrees well with the experimental data, and the real-time figure agrees well with the AFM data in Fig. 9.2 (a).

Expanding upon the single-layer growth scenario, the layer-by-layer growth process can be explored in multilayer systems. Not only calculating the TTC but also the fourth-order correlation function for the single layer from above and the evolution of four layers results in the functions shown in Fig. 9.15 (c) and (d), respectively. Again, a few time steps at the beginning and end of the growth are cut out, to reduce noise.

The evolution of one layer reveals only one heterogeneity peak, while the evolution of four layers undergoing layer-by-layer growth results in four distinct peaks. This supports the assumption that each layer is represented by one heterogeneity peak. Comparing Fig. 9.15 (d) with the real space data of the simulation leads to several assumptions that can be extracted from the fourth-order correlation function. With ongoing layer, the heterogeneity peak shifts to higher times t^* , since the growth process of the individual layer slows down. Furthermore, also the χ^* value decreases, which can be related to the increasing roughness of the surface. Hence, by the position and height of the heterogeneity peak, it is possible to extract quantities of a single layer, such as the characteristic time of layer growth and roughness.

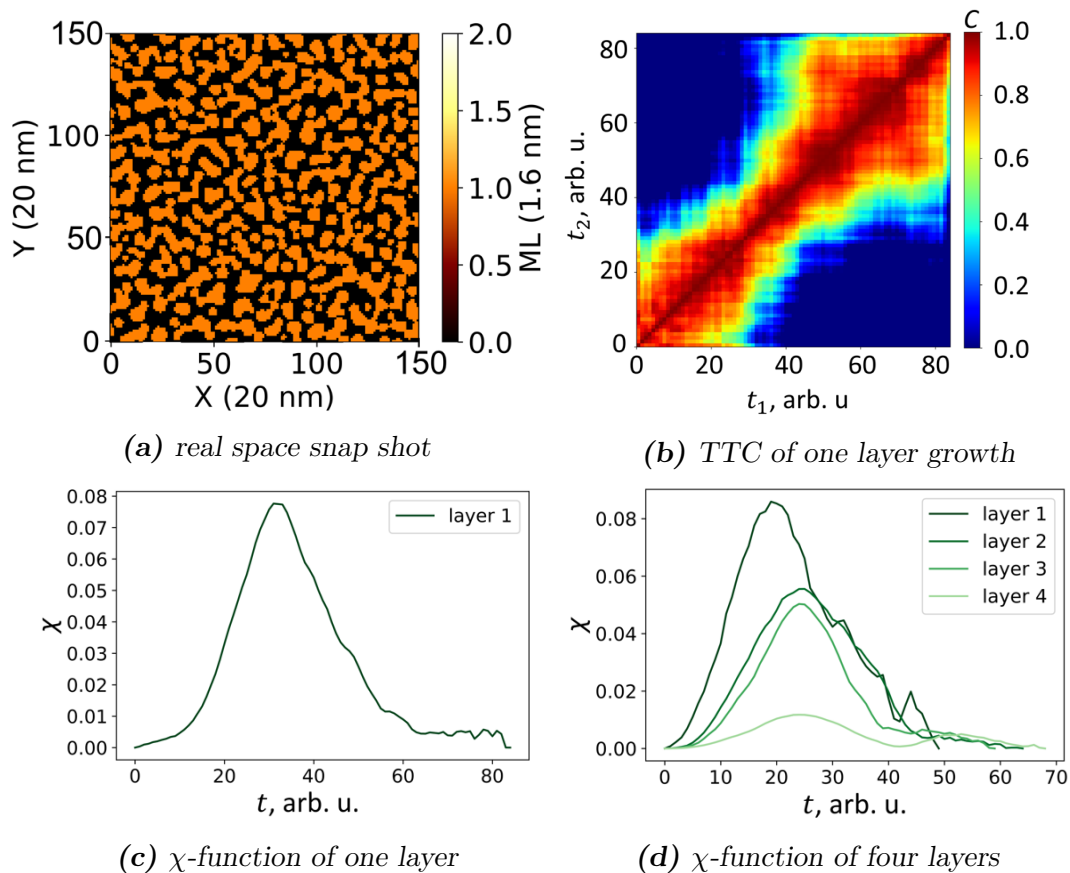


Figure 9.15: Simulation of the layer-by-layer growth. a) Snap shot of the real space image after half of the growth process. b) TTC of the whole growth process. c) Fourth-order correlation function of the corresponding layer [155]. d) The same function of four layers.

3D Island Growth

The opposite case of pure islanding (Vollmer-Weber growth, see Sec. 2) should be investigated. There, several layers grow simultaneously right from the start, as in Fig. 9.16 (a). These growth scenarios result in overdetailed TTCs (see Fig. 9.16 (b)), making it challenging to extract meaningful information. Consequently, characterizing such growth scenarios requires the development of novel analytical techniques to extract any quantitative results. This limits the generalization of the analysis using the fourth-order correlation function to get access to individual layer evolution quantities to material, which grows not too rough.

Transition from Layer-by-Layer to 3D Island Growth

To mirror real-world growth scenarios, the transition from the layer-by-layer growth to the 3D island growth will be investigated (Stranski-Krastanov growth, see Sec. 2), using kinetic Monte Carlo Simulations as introduced in Sec. 9.2. This

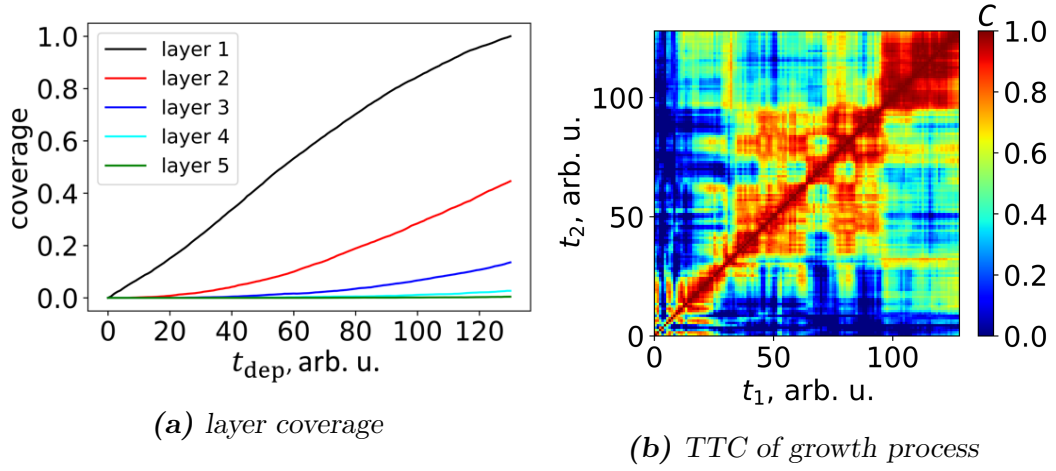


Figure 9.16: Simulation of 3D island growth. a) The layer coverage shows the evolution of several layers simultaneously. b) Resulting TTC of the whole growth process.

should best reflect the experimental data. A setup for a suitable simulation is already discussed in Sec. 8.1.1, and characteristics of the resulting surface are summed up in Fig. 9.8. For that specific growth scenario the TTC is shown in Fig. 9.17 (a). It shows the expected heterogeneous behavior along the diagonal, along with distinct pinching points that occur when the layers close. To gain a better understanding of the structure, the TTC will be split into specific growth intervals: the first layer ($t_{\text{dep}} \approx 0 - 95$ sec), the second layer ($t_{\text{dep}} \approx 100 - 195$ sec), the third and fourth layers ($t_{\text{dep}} \approx 200 - 300$ sec), and the evolution of the last three layers ($t_{\text{dep}} \approx 285 - 450$ sec). Fig. 9.8 (b) shows the corresponding evolution of the layers.

Those intervals serve as input for the calculation of the fourth-order correlation function, which is presented in Fig. 9.17 (b). Similar to the result for the layer-by-layer growth, the number of heterogeneity peaks matches the number of open layers.

Conclusively, parameters of the layer growth can be extracted from the position and height of the correlation peaks. In more detail, the increasing peak position (t^*) indicates that the growth process slows down during the deposition time. This is especially true for the simultaneous evolution of several layers. At the same time, the decrease of the peak height (χ^*) after the first layer indicates that the size distribution of the islands (i.e., the surface roughness) increases with deposition time.

The results of this analysis technique of the simulated data are subsequently compared with those of the experimental data presented in Sec. 9.1.3. This comparative analysis, specifically using the fourth-order correlation function, provides a comprehensive understanding of the transition process from layer-by-layer growth to islanding and offers insights into the multilayer system.

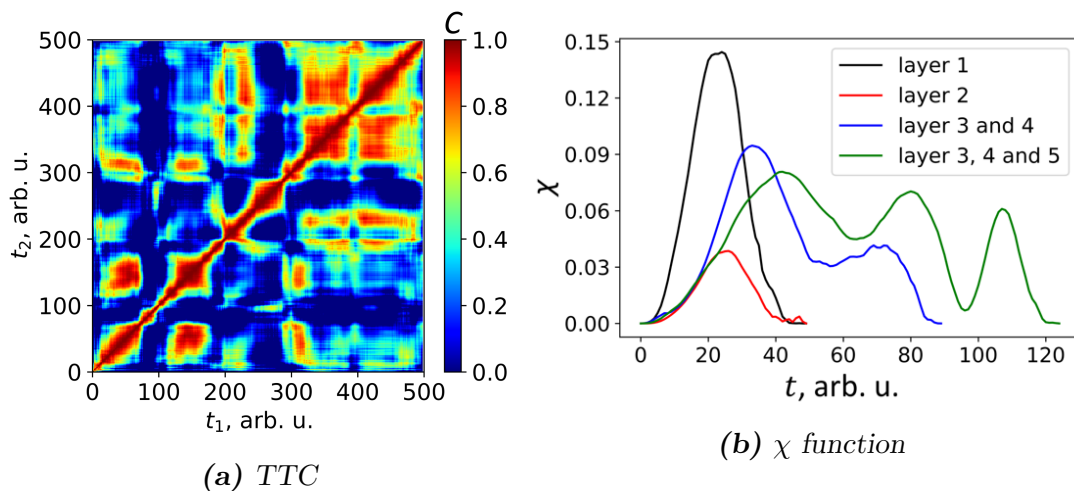


Figure 9.17: Simulation of the transition from layer-by-layer growth to 3D island growth [155]. a) TTC of the growth process shown in Fig. 9.7. b) Corresponding fourth-order correlation function.

Stability of the Simulation

The TTC in Fig. 9.17 (a) exhibits similar structures along the diagonal as the experimental data. Nevertheless, many off-diagonal elements can also be observed, which are not present in the experimental data. An explanation to that will be discussed in the following.

Since the simulation of the real space is based on a statistical process, the stability of the simulated TTCs has to be evaluated. By simulating ten times the same growth process ($5 \times 5 \mu\text{m}^2$ area for 500 time steps), it is examined which structures are statistically significant and which correspond to a specific realization of the growth simulation and, therefore will cancel out on the averaged TTC. Subsequently, the resulting TTCs are compared with each other. To eliminate the statistically conditioned structures, an average of all TTCs is calculated, resulting in Fig. 9.18 (a). Comparing the averaged TTC with that from a single simulation (Fig. 9.17 (a)), the main difference is the disappearance of the off-diagonal elements. The structures along the diagonal, in particular the pinching points corresponding to the closure of the layers, remain clearly visible. From that, it is possible to conclude that these structures are related to fundamental features of the growth process and do not depend on specific microscopic distribution of islands in a given realization of the simulation.

Fig. 9.18 (b) shows the averaged fourth-order correlation function for the same ten simulations. The assumption that the number of peaks gives access to the individual layers also fits the results here. Hence, the conclusions from the previous section remain unchanged.

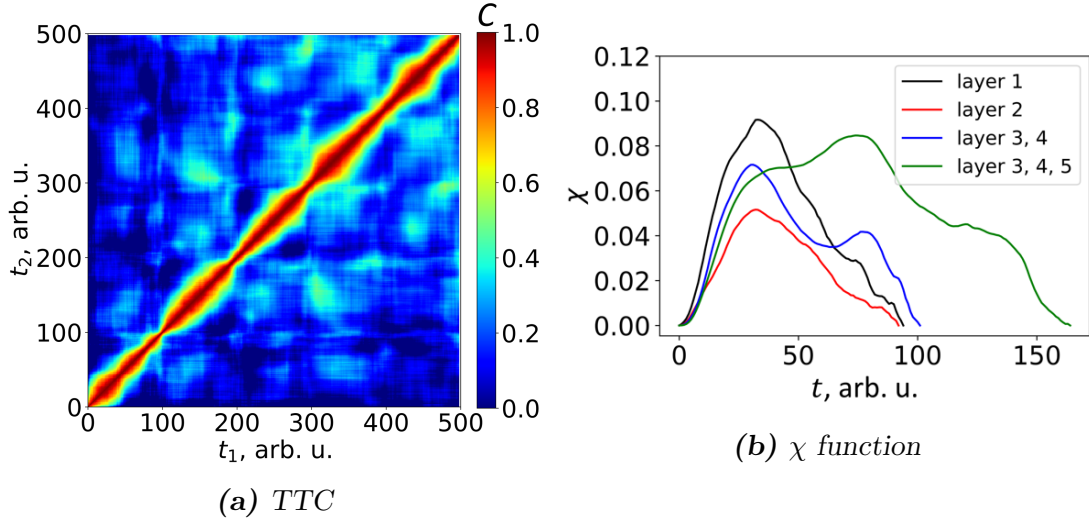


Figure 9.18: Averaged simulations of the transition from layer-by-layer growth to 3D island growth [155]. a) Averaged TTC for ten similar surface growth simulations, including the one from Fig. 9.17. b) Averaged fourth-order correlation function for the same ten simulations

9.3 Conclusions

The XPCS analysis of a DIP film during growth was successfully performed. It was possible to characterize layer-by-layer growth and identify the transition to islanding, resulting in film roughening. Even during the roughening stage, meaningful information about surface evolution could be extracted using the XPCS analysis. This method made it possible to study the growth process, in particular, the growth and movement of island structures on the surface.

The presented TTCs exhibited a notable heterogeneous behavior and revealed time scales of surface changes in the range of several hundred seconds, extracted through a conventional g_2 -analysis. Numerical simulations attributed the TTC structure to kinetic effects, suggesting an approximately static evolution of the islands. Additionally, it is demonstrated that the heterogeneity arises not only from the opening and closing of layers but also from the growth of the islands.

For quantification, the fourth-order correlation function is calculated, allowing the translation of the number of peaks to the number of open layers. The simulations indicated that layer evolution quantities can be extracted from the fourth-order correlation function, specifically the height and position of the correlation peaks. It was shown that the height and position of each peak can be related to the roughness and speed of the individual layer evolution, respectively.

This approach is applicable more generally to other materials as well to understand the microscopic dynamics underlying structure formation, as long as they do not grow too rough.

Chapter 10

Structural Surface Changes during the Annealing of PTCDI-C8

Thin film annealing provides an opportunity to explore microscopic surface dynamics such as surface diffusion and cluster formation. An in-depth understanding of these processes also has significant implications for understanding thin film growth. This complicated process takes place in a non-equilibrium environment and is influenced by a multitude of factors [73, 164–166]. One step to unravel this complexity is to focus on a comparatively simple scenario, namely the thin film annealing of deposited organic materials. This method not only proves to be more manageable than thin film deposition itself, as it maintains a constant total amount of deposited material and requires fewer experimental parameters but it also allows the transition of structure and morphology to an equilibrium state.

For that purpose, the main focus is on the material PTCDI-C8. The growth of PTCDI-C8 closely follows the layer-by-layer regime during OMBD [87–91]. Consequently, the films investigated here have only a few open ML, which further simplifies the interpretation of the data. In addition, the material is of particular interest to the industry due to its existing applications in OFETs and OSCs [79–86] (as mentioned in Chap. 6). In this context, thermal annealing of PTCDI-C8 films can enable further structural optimization.

The dynamic analysis of the experimental data reveals notable features during the annealing process of PTCDI-C8. However, at the end of the experimental section it is shown that the results go beyond PTCDI-C8, and similar patterns occur for other molecules.

The difficult task of interpreting dynamic analyzes using XPCS for surface diffusion processes leads to resorting to simulations to shed light on the underlying dynamic processes.

This entire chapter is closely related to the work presented in Ref. [167].

10.1 Experimental Results

This section focuses on the experimental results, starting with a description of the setup and the experimental parameters. The standard analysis techniques (described in Chap. 7) were used for film characterization to get an impression of how the PTCDI-C8 films have changed after growth and after each individual annealing process. The XPCS results are then presented, which provide insight into the surface dynamics induced by heating.

To show that these findings can also be transferred to other materials, the XPCS analysis for thin films of other molecules is presented at the end of this section.

10.1.1 Setup & Experimental Parameters

The films were deposited in a portable ultra-high vacuum chamber on silicon substrates at a growth temperature (T_{gr}) of 35 °C and a pressure of around $5 \cdot 10^{-8}$ mbar. The deposition rate was approximately 0.16 nm/min, resulting in a final thickness of about 16 nm, which corresponds to the deposition of eight layers of PTCDI-C8.

The subsequent annealing was carried out on an Anton Paar hot stage in a vacuum, close to the evaporation temperature of PTCDI-C8 ($T_{\text{ev}} \approx 200$ °C). The Annealing was carried out at temperatures (T_{an}) of 100, 150, and 190 °C. After reaching each temperature, in situ XRR and ex situ AFM were performed.

The coherent in situ experiment during annealing was performed at the Coherent Scattering Beamline ID10 at the European Synchrotron Radiation Facility (ESRF). The X-ray beam with a photon energy of 8.7 keV and a focus size of $8 \mu\text{m} \times 5 \mu\text{m}$ (hor. $\times$ vert.) was sent onto the sample under GISAXS geometry to be sensitive to surface changes (as explained in Sec 3.4). This was done with an angle of incidence (α_i) of 0.15°. The specular scattering signal was reflected at an angle α_f , while the diffuse scattering signal was detected at the angle $2\Theta_f$.

The Detection was performed with a 2D Eiger X 4M detector with a pixel size of $75 \mu\text{m} \times 75 \mu\text{m}$ positioned 6770 mm downstream from the sample. The diffraction patterns were recorded in specular (q_z) and off-specular (q_{xy}) directions. The entire setup is shown in Fig. 10.1. For the annealing scans, the film was kept at a constant temperature and measured for 2200 seconds, alternating between one second of radiation and one second of waiting time.

These measurement times have proven their effectiveness in capturing the expected characteristic time scales (validated by measurements on similar organic materials) without damaging the sample by radiation. Additionally, to improve the protective measures, absorbers were also used, which in particular attenuated the intensity of the incident beam by 3.5 times through four 80 micrometer thick silicon membranes. Further, the diffraction signal was recorded at a new position on the sample for each temperature measurement.

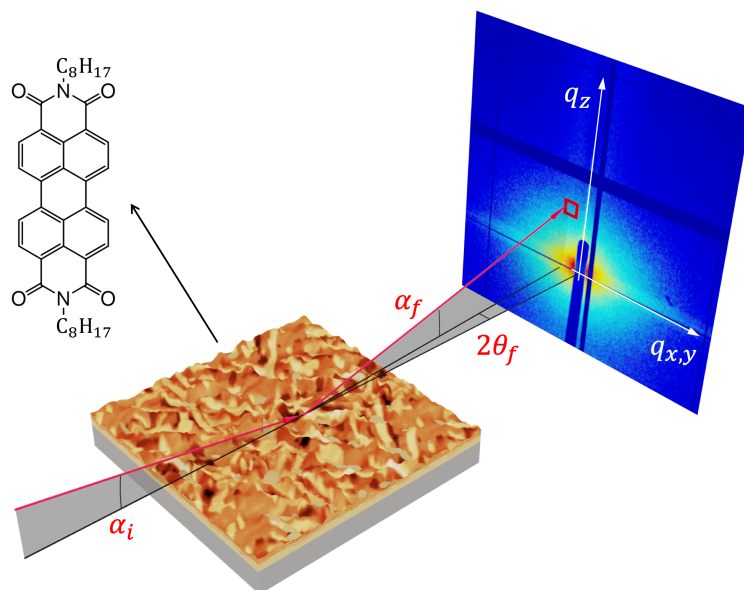


Figure 10.1: Sketch of the setup at the synchrotron during the annealing of a PTCDI-C8 thin film [167]. The initial beam scatters on the surface under an angle α_i and moves towards the detector in specular direction under an angle α_f and diffuse direction $2\theta_f$. An exemplary detector image is given in q -space, the ROI is marked in red. The chemical formula is incorporated above the thin film.

10.1.2 Film Characterization using Standard Techniques

The exploration of PTCDI-C8 films using conventional analytical techniques serves as an important foundation that provides initial insight into how the film changes through annealing. This initial understanding serves as a starting point that enables a more informed and insightful interpretation of the subsequent dynamic analyzes. The synergy between these two phases contributes to a seamless alignment and enables a comprehensive understanding of the film's composition and behavior.

AFM analysis

The AFM analysis gives access to the film surface in real space after growth and after each annealing step, shown in Fig. 10.2 a). The Gwyddion software is used for the analysis. On the surface, islands can be seen that are approximately one ML above the average surface and visible holes correspond to a depth of one ML below the average surface. As the annealing temperature increases, the film surface becomes smoother, as evidenced by a decrease in the root-mean-square roughness: from 1.2 nm at 35 °C and 100 °C, to 1.1 nm at 150 °C and further to 0.8 nm at 190 °C.

Some islands and holes show growth or shrinkage during annealing. Another

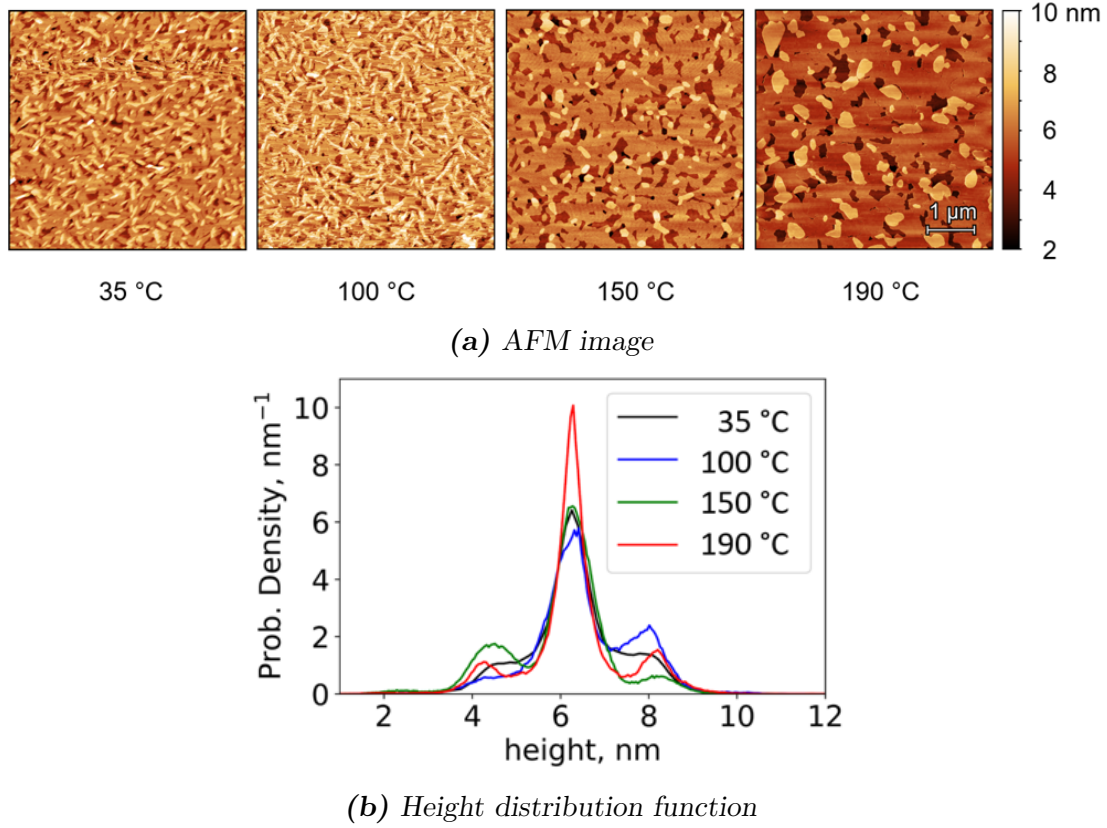


Figure 10.2: AFM analysis of a PTCDI-C8 film after growth ($T_{gr} = 35^\circ\text{C}$) and three different annealing steps ($T_{an} = 100, 150, 190^\circ\text{C}$) [167]. a) shows the real space images from which the height distribution function in b) can be extracted.

striking structural transformation takes place between 100°C and 150°C , where needle-like structures of islands and holes transform into cylindrical shapes. The material redistribution between the MLs during annealing is effectively illustrated by the height distribution function extracted from the AFM data, as shown in Fig. 10.2 b). Three open MLs can be observed at all temperatures. In addition, the size of the central peak increases significantly at 190°C , indicating a smoothing of the surface.

XRR analysis

The XRR analysis included the ex situ analysis after growth and the in situ analysis immediately after the annealing processes. Each scan lasted for 30 minutes and began after the target temperature was reached. Kiessig fringes can be observed in the scattered intensity in Fig. 10.3, which could be used to extract the thickness and roughness of the film with the machine learning tool *mlreflect* [115]. The fits for the different temperatures are shown in Fig. 10.4 a)-d) and show a decrease in roughness from 1.3 nm ($T_{gr} = 35^\circ\text{C}$ and $T_{an} = 100^\circ\text{C}$) to 0.9 nm

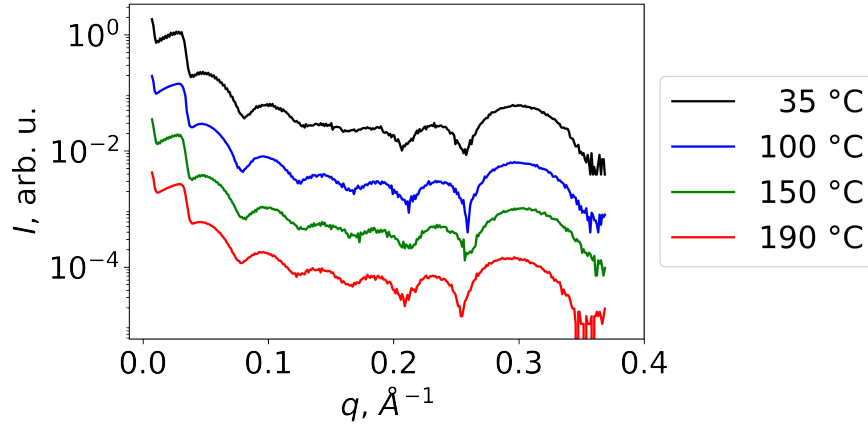


Figure 10.3: XRR analysis of a PTCDI-C8 film after growth ($T_{gr} = 35^\circ\text{C}$) and three different annealing steps ($T_{an} = 100, 150, 190^\circ\text{C}$).

($T_{an} = 150$ and 190°C). These results are consistent with the AFM data.

Furthermore, the XRR data in Fig. 10.3 show a shift of the Bragg peak to smaller values: $q_B = 0.300$ to $0.295 \text{ \AA}^{-1}$ for 35°C to 190°C . There is also a slight increase in film thickness from 12.0 to 12.7 nm at the same temperatures, both indicating thermal expansion, as described in Ref. [168].

Investigation of correlation peaks

Performing in situ synchrotron X-ray scattering experiments provides insights into the structural changes during the annealing process. The gradual changes in the scattering intensity reflect the material redistribution within the molecular layers of the film. Hence, the investigation of correlation peaks provides an insight into the distribution of the islands on the surface. For this purpose, the intensity profiles are examined at large q -values, in particular at $q_z = 0.05 \text{ \AA}^{-1}$. To increase the statistical reliability, averaging is performed over a range with a width of $\Delta q_z = 0.01 \text{ \AA}^{-1}$. The development of the correlation peaks for all annealing temperatures is shown in Fig. 10.5 a). The derivation of the in-plane correlation length from the peak positions is an approximation of the average island size in the layer. With increasing time and varying temperature, a recognizable shift towards smaller q -values and higher intensities of the correlation peaks can be observed.

Fig. 10.5 b) and c) show how the peak position and height shifts by extracting the peak information using Lorentzian fit. The position moves from $q_{xy}^{\text{peak}} = 2.0$ to $0.2 \cdot 10^{-3} \text{ \AA}^{-1}$ – indicating an increase in island size. The calculation of the average island size using $l_{\text{corr}} = 2\pi/q_{xy}^{\text{peak}}$ shows variations from $0.3 \mu\text{m}$ to $3.1 \mu\text{m}$ during the annealing process. The increasing intensity indicates a smoothing of the surface of the film.

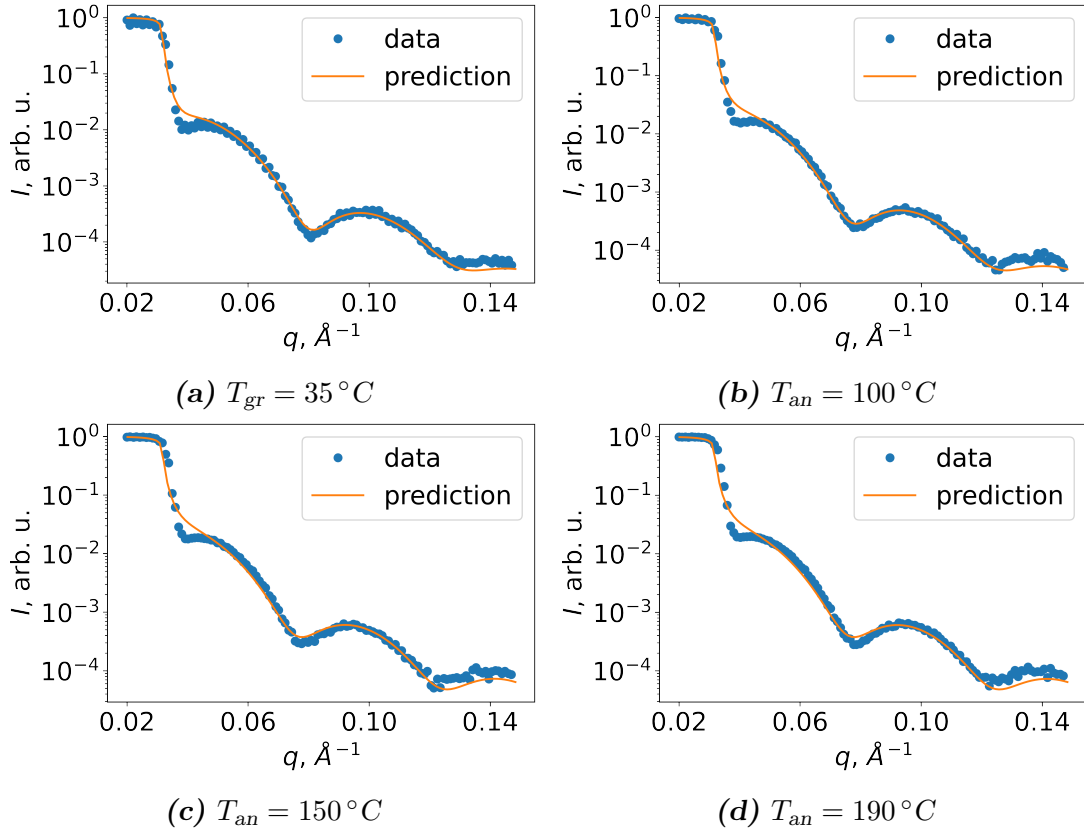


Figure 10.4: XRR fits of a PTCDI-C8 film (a) after growth ($T_{gr} = 35^\circ\text{C}$) and (b)-(d) three different annealing steps ($T_{an} = 100, 150, 190^\circ\text{C}$) [167] using the machine learning tool *mlreflect* [115].

10.1.3 XPCS Analysis

The dynamical processes are investigated using XPCS at certain q_z and q_{xy} values, using Eq. (5.5) to calculate the TTCs. The resulting g_2 functions are extracted by averaging over the time t_1 . The translation of the q -values into real space results in length scales of $l_z \approx 20\text{ nm}$ and $l_{xy} \approx 450\text{ nm}$. These dimensions indicate an observations of the dynamics of relatively large molecular islands during annealing. Fig. 10.6 a)-c) shows the results.

A general slowdown can be observed in the first 15 minutes, indicating that the reorganization process is complete and the surface has reached equilibrium. Hence, it will be further focused on the initial 15 minutes. In addition to the frequently observed drop in the intensity correlation, the spots and stripe-like structures in the outer region of the TTCs are very striking. The interpretation of these features is not straight forward and will further be investigated with simulations in the following section, linking them to molecular movement within a layer or between different layers.

Characterizing time scales of the system involves the extraction of g_2 functions at

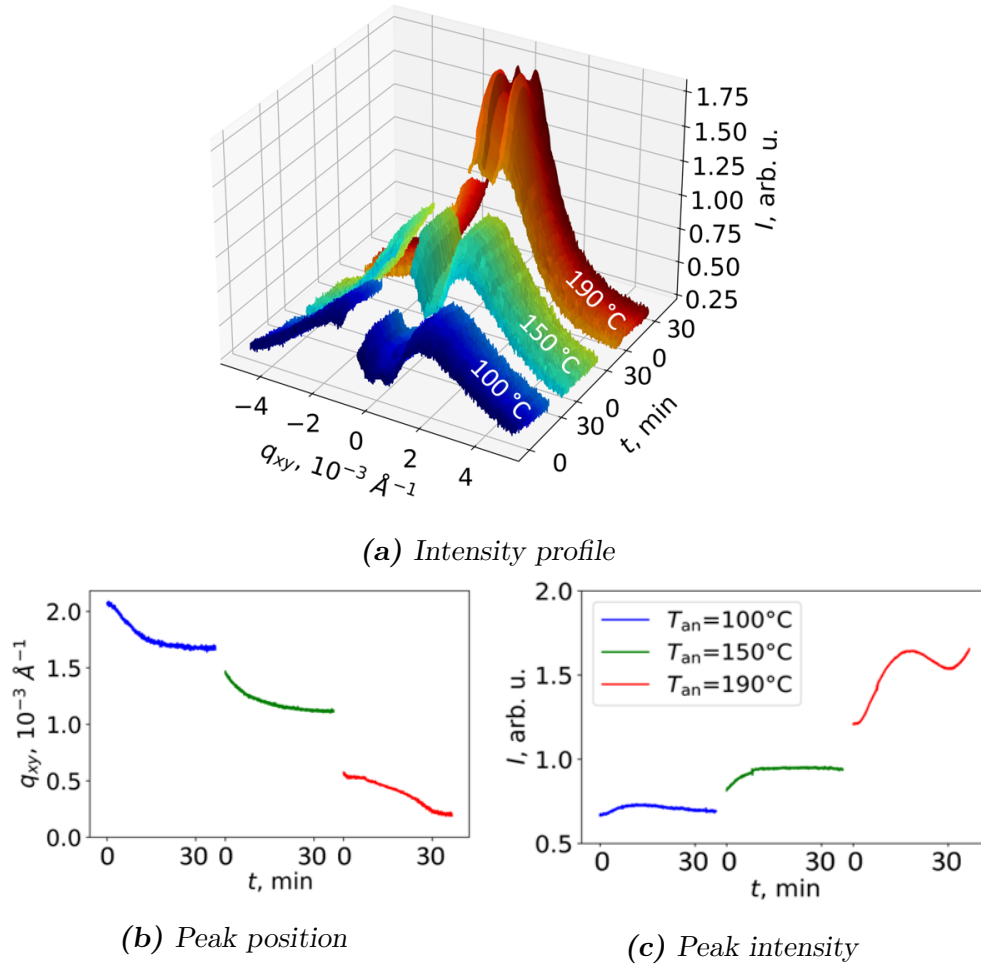


Figure 10.5: Time evolution of the correlation peaks of a PTCDI-C8 film for three different annealing temperatures [167]. a) Intensity profile at $q_z = 0.05 \text{ \AA}^{-1}$, averaged over a width of $\Delta q_z = 0.01 \text{ \AA}^{-1}$. Time evolution of the correlation peak position (b) and height (c) at positive q -values, extracted with a Lorentzian fit.

a specific time during reorganization (5 minutes after reaching the temperature are chosen). Due to the TTC structure the g_2 functions do not only show the common initial decay, but also subsequent oscillations caused by the off-diagonal elements are visible. With increasing annealing temperature, the system slows down, and the oscillations smooth out. Fitting according to Eq. (5.3) allows the extraction of the relaxation rate τ , ranging from approximately 65 sec to 140 sec with increasing temperature, while the stretching exponent γ remains constant at 1.8.

Comparing these results with the AFM data in Fig. 10.2 a), a correlation between the reorganization of the surface and the structural changes observed in the TTC data (transition from point to stripe features) can be surmised. This

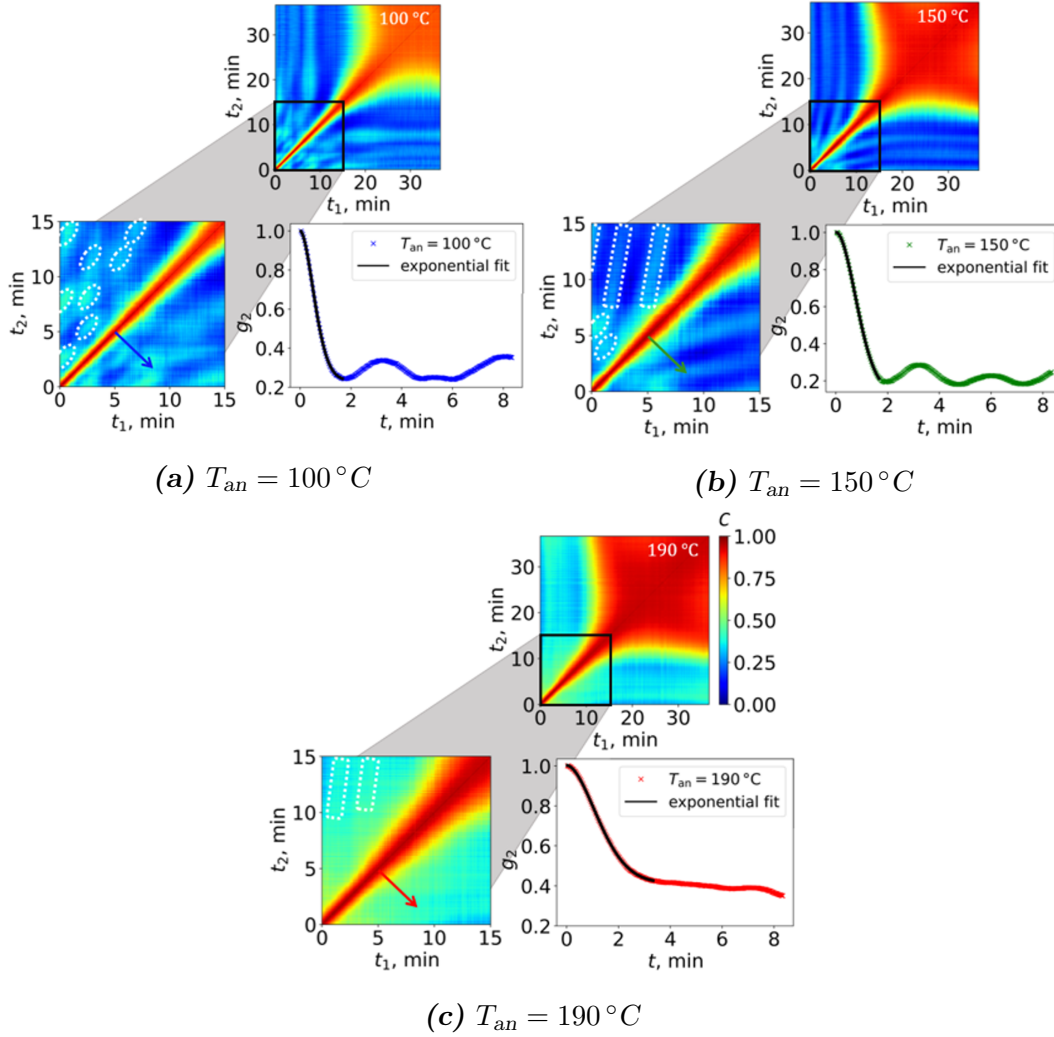
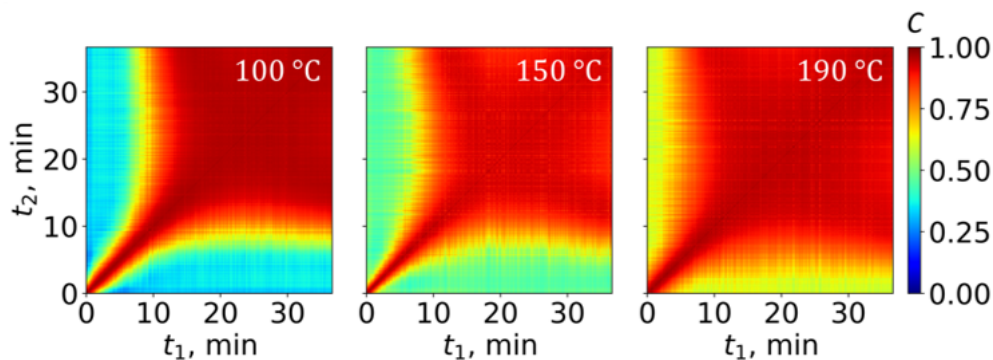
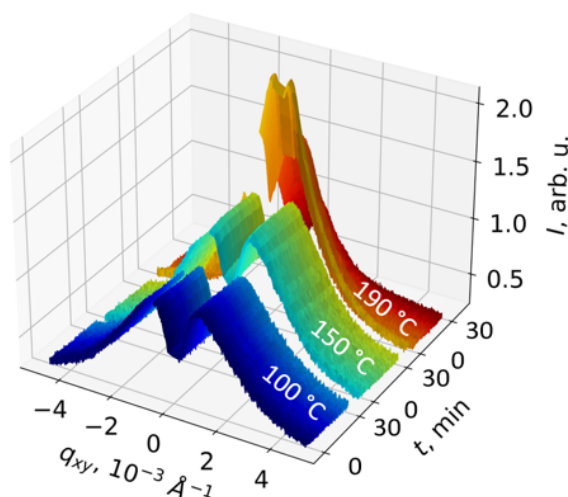


Figure 10.6: XPCS analysis during the different in situ annealing processes [167]. The focus is on the TTC function (Eq. (5.5)) calculated for an area of 25×25 pixels at $q_z = 0.028 \text{ \AA}^{-1}$ and $q_{xy} = 1.46 \cdot 10^{-3} \text{ \AA}^{-1}$. The concentrated examination of the first 15 minutes of the data shows the occurrence of circular and striped maxima. Approximately 5 minutes after heating, a diagonal cut is performed, indicated by an arrow in the TTCs. The data is then averaged over a 100-second interval and the g_2 function is calculated. The fitting is performed with Eq. (5.3) (represented by a black line), focusing on the initial decay.

transition becomes clear at $T_{an} = 150^{\circ}C$. In addition, the restructuring of the surface seems to contribute significantly to a very heterogeneous behavior, especially at this temperature. To improve the understanding of the microscopic dynamic processes related to these TTC structures, simulations are performed in the following section.



(a) XPCS analysis



(b) Intensity profile

Figure 10.7: Annealing results for a PTCDI-C8 film grown at $T_{\text{gr}} = 70^\circ\text{C}$ [167]. a) TTCs for three different annealing processes. b) Evolution of the correlation peaks after each annealing step.

To put the experimental results into context, a comparative analysis is carried out for a film grown at an elevated temperature ($T_{\text{gr}} = 70^\circ\text{C}$). The corresponding TTCs after each annealing step and the development of the correlation peaks are shown in Fig. 10.7 a) and b), respectively.

Similar to the film grown at $T_{\text{gr}} = 35^\circ\text{C}$, the TTCs show a general slowdown after 15 minutes. However, the reorganization process seems to have longer relaxation times at higher temperatures, about three times as long. In addition, the atypical features in the off-diagonal region of the TTCs are less pronounced, as only at $T_{\text{gr}} = 100^\circ\text{C}$ does the corresponding TTC exhibit a weak parallel stripe.

This observed behavior can be attributed to the already larger island size that is reached during growth at higher temperatures [87]. The molecules seem to tend to form islands during growth at elevated temperatures, which are already close

to an equilibrium state before evaporation. Consequently, the smoothness may increase only slightly during annealing, but the island size changes only minimally. This is confirmed by the almost stationary peak position of the correlation peaks in Fig. 10.7 b).

10.1.4 Extension to other Materials

To investigate whether the untypical off-diagonal features associated with the annealing of PTCDI-C8 occur only for this specific film and molecule, coherent measurements and XPCS analyzes are repeated on other films and molecules. For that, a PTCDI-C8 film grown at low temperatures (LT: $T_{\text{gr}} = -120^\circ\text{C}$) as also materials, in particular C_{60} and DIP were used and annealing scans were performed just before their evaporation temperatures. Fig. 10.8 shows the resulting TTCs for the thin film annealing processes of the three different films. All TTCs show a similar pattern, with an initial drop in the intensity correlation followed by circular-or striped-shaped maxima in the off-diagonal region. Over time, there is an overall slowdown, indicating surface relaxation. Although the time scales and expression of off-diagonal features may vary, possibly due to factors such as different initial growth scenarios or molecule-specific Ehrlich-Schwoebel barrier values that influence molecular motion, a consistent trend emerges. This means that structural surface changes near the evaporation temperature of the material lead to unique off-diagonal features in the TTCs. This suggests the possibility of generalizing the analysis and subsequent simulations to unravel the mystery of these unknown features.

10.2 Coarse-Grained Simulations

The meaning of the untypical off-diagonal features in the experimental TTCs, characterized by distinct patches and streaks, is a complex task. To establish a potential link to the real space, simulations prove to be a valuable tool, in line with the current trend in the interpretation of TTC features, as described in Ref. [163]. First, we address the structure of the simulation. Then, attention can be drawn to diffusion processes that show patterns similar to those of the experimental data. Finally, our findings can be adapted for the interpretation of the experimental data.

10.2.1 Simulation Structure

The modeling of the XPCS signal requires the simulation of surfaces that are subject to different dynamic processes. Guided by the AFM results in Fig. 10.2 b), which mainly show three open MLs, a flat PTCDI-C8 surface is constructed that exhibits deviations from the average surface height in the form of islands and holes. The islands are approximately 1 ML (about 2 nm) above the average

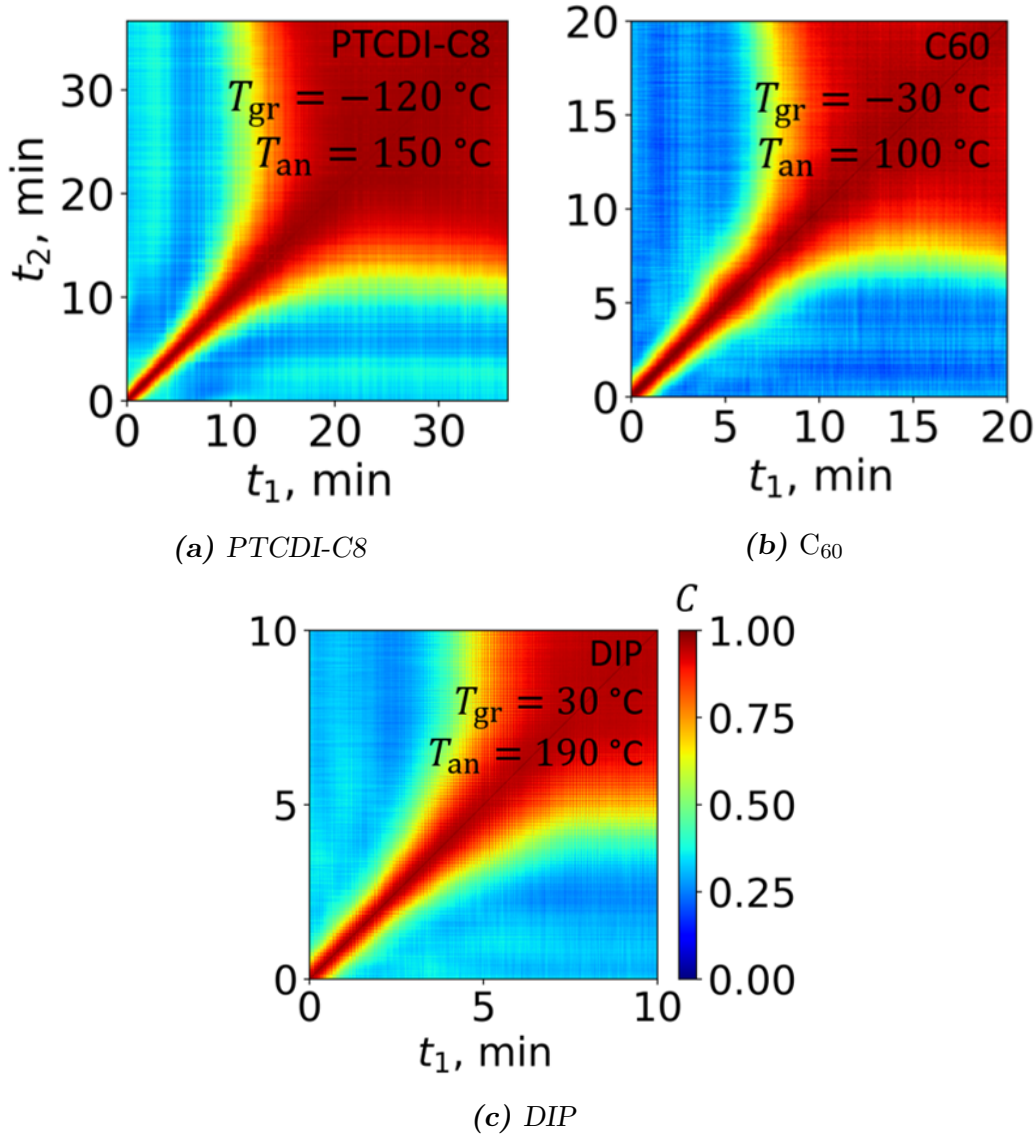


Figure 10.8: Observation of similar TTC features in data sets with other thin film [167]s. The growth and annealing temperatures are noted in each figure. a) TTC of a PTCDI-C8 film. b) TTC of a C₆₀ film. c) TTC of a DIP film.

surface height, while the holes are 1 MLs below, resulting in three open MLs. In particular, 25 islands and 25 holes are constructed, which are uniformly distributed on a $10 \times 10 \mu\text{m}^2$ area, excluding contact.

In the dynamic processes, the size and shape of islands and holes are expected to change over time while their COM coordinates remain fixed. This approach focuses on the contribution of size change and material redistribution on the surface and not on the relative positions of islands and holes to each other. In addition, no movements of the islands and holes are considered, as only minimal movement is

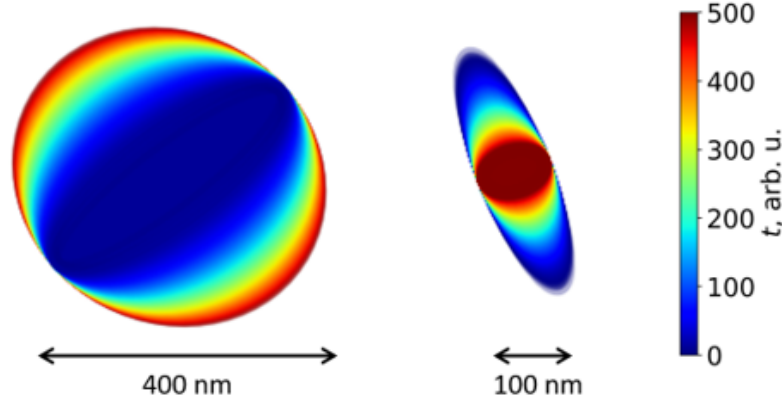


Figure 10.9: An expanding island is sketched on the left and a shrinking island on the right, each with a random orientation. The color scheme shows the development of their size over time.

expected on the investigated length scale [155]. The shape of the islands and holes can change from an ellipse to a cylinder by changing only one axis, which reflects the observations in the AFM data during annealing (Fig. 10.2 a)). As a consequence, each island or hole can have a different orientation, which was randomly chosen between 0 and 180 degrees with respect to the beam direction. However, due to the flat angle of incidence, the diffraction pattern is mainly sensitive to the dimension perpendicular to the incident beam. Hence, the effects of the orientation and size distribution have a comparable influence on the diffraction pattern, since the decisive factor is exclusively the growth in the direction perpendicular to the incident beam.

The following study focuses on the growth and shrinkage process of islands and holes. The radii for growth ($r_{\text{long}} = 400 \text{ nm}$) or shrinkage ($r_{\text{short}} = 100 \text{ nm}$) remain constant for one axis, while the other axis changes according to

$$r_{g,s}(t_{\text{sim}}) = r_0^{g,s} \pm r_s \cdot t_{\text{sim}}^{1/2}, \quad (10.1)$$

where t_{sim} are the simulated time steps. The initial radii are 50 nm for growth and 400 nm for shrinkage, where the scaling factor r_s is determined as $(r_0^s - r_0^g)/t_{\text{max}}^{1/2}$. The selected quantities were influenced by the AFM and correlation peak studies (Fig. 10.2 a) and Fig. 10.5). For visualization, an example of a growing and shrinking island is shown in Fig. 10.9.

In addition, a size distribution of the axes is incorporated by randomly multiplying the radius at each time step with an integer chosen from a distribution around unity. The functions representing the growing and shrinking radii can be found in Fig. 10.10. To achieve physically meaningful results, all negative radii are set to zero, which corresponds to the disappearance of an island or hole.

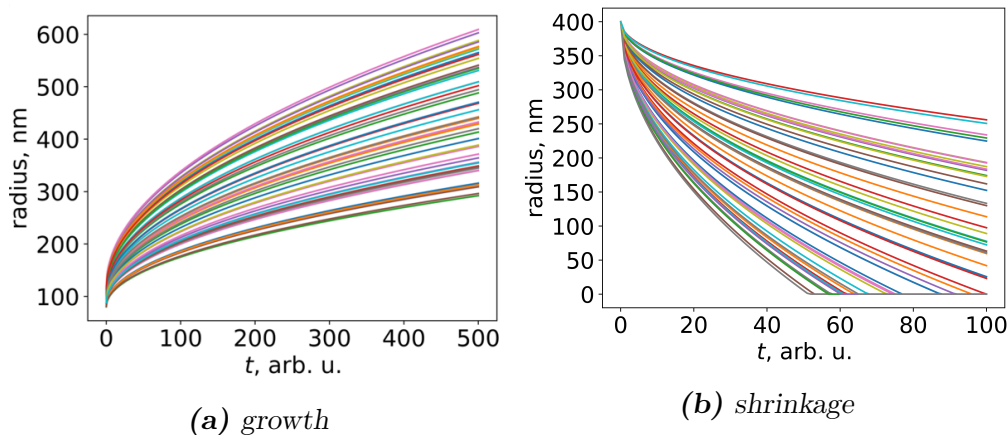


Figure 10.10: Growth (a) and shrinkage (b) of the radii of 25 islands and holes, characterized by a size distribution generated by multiplying Eq. (10.1) by a random integer in the range 0.6 – 1.4. To ensure physical relevance, all negative radii are set to zero [167].

To simulate the scattering process, the software BA [169] is used again, as described in Chap. 8. The resulting diffraction pattern is subjected to an analysis that mirrors the approach of the experimental data (same averaging and q -region), which ensures a reliable comparison between simulation and experiment.

10.2.2 Molecular Diffusion

During the annealing of thin films, two different material redistribution effects can occur on the surface: Molecules can either remain in their original layer and move within it (intralayer diffusion) or, depending on the height of the Ehrlich-Schwobel barrier, move between the layers (interlayer diffusion). Both effects are studied separately to understand their influence on specific features in the XPCS analysis.

Both diffusion scenarios have the effect that islands or holes either grow or shrink. In order to better understand the influence of growing or shrinking islands or holes, this effect is first examined separately. From Ref. [155] it can already be adapted that the speed in the size change is linked to the characteristic time scales. Furthermore, the expression of the characteristics is related to the size distribution. To extract the effect of pure growth or shrinkage, 50 islands or holes are considered, which grow or shrink with the same speed from 50 to 400 nm (or vice versa) in one ellipse axis. Furthermore, the positions and orientations are fixed for an appropriate comparison between growth and shrinkage. The resulting TTCs are shown in Fig. 10.11. There, it can be observed that circular maxima occur in the off-diagonal region of the TTCs during the growth of islands and holes (top

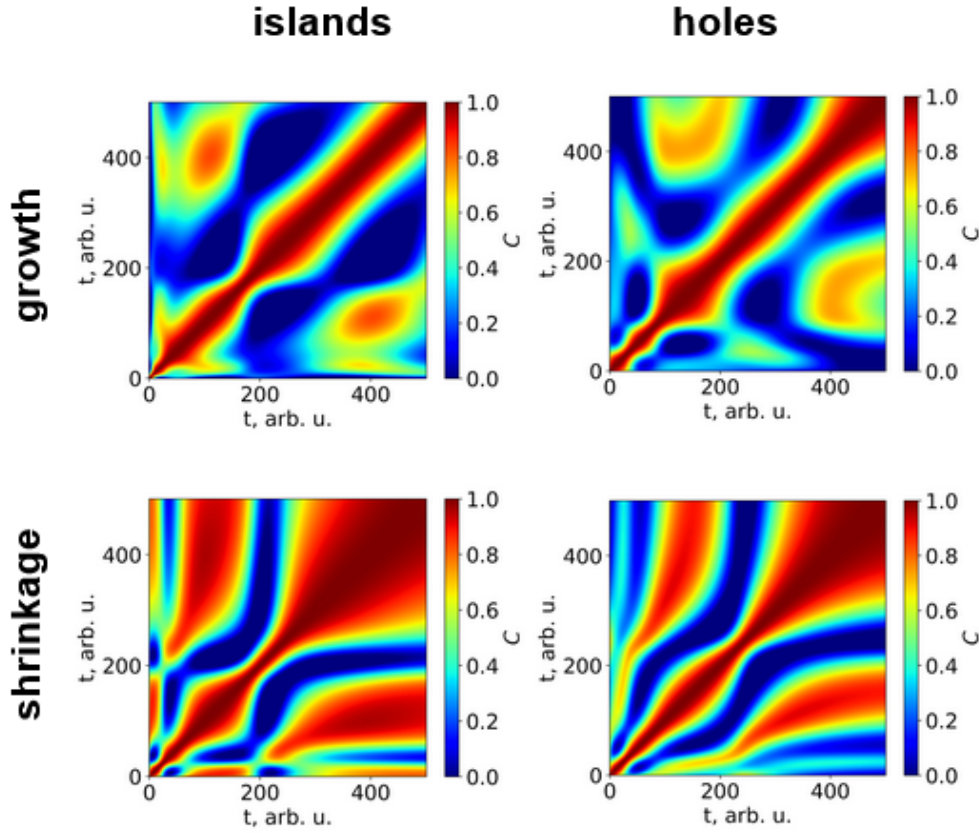


Figure 10.11: Tabular view of the separated growth or shrinking TTC features of islands and holes [167]. In the underlying simulation, 50 islands or holes with a fixed orientation and position grow or shrink with the same speed to extract the influence of the single processes of pure growth or shrinkage.

row). On the other hand, the shrinkage of islands and holes leads to streaks in the outer region of the TTCs (bottom row). In summary, these observations lead to the assumption that on these length scales, the growth of islands or holes leads to distinct spots, and the shrinkage of islands and holes leads to parallel streaks in the outer region of the TTCs.

With these findings, it will be returned to the investigation of physically plausible processes, i.e., the two diffusion types. Since annealing processes are considered, the amount of material should remain constant throughout the measurement or simulation time. The transport between the layers is relatively simple as the material flows between the layers, causing islands and holes to shrink at a similar rate. To this end, it is hypothesized that the islands and holes are all shrinking because as the annealing temperature increases, most of the molecules diffuse from the top layer to the lower layers, resulting in a smoothing of the surface, and consequently a reduction in the size of all islands and holes.

The challenge during the simulation of interlayer transport is to maintain a constant flow of material within a single ML. In order to explain how this can be achieved, the layer with islands will first be discussed. Eq. (10.1) describes the change in size of an elliptical axis, whereby the same size is assumed for all islands for the sake of simplicity (in any case, the effect of the size distribution will cancel itself out in the end). To ensure a constant amount of material over time, the total area of the islands A must remain constant during the entire simulation time, which is given by

$$A(t_{\text{sim}} = 0) = x \cdot r_{\text{short}} \cdot r_{\text{long}} + y \cdot r_{\text{long}} \cdot r_0^g \quad (10.2)$$

$$A(t_{\text{sim}}) = x \cdot r_{\text{short}} \cdot r_s(t_{\text{sim}}) + y \cdot r_{\text{long}} \cdot r_g(t_{\text{sim}}). \quad (10.3)$$

This leads to the determination of 5 growing islands ($x = 5$) and 20 shrinking islands ($y = 20$), which also applies to the layer of holes.

The results of modeling both diffusion processes are shown in Fig. 10.12 a) and b), with the simulated real space on the left and the resulting TTC on the right. In the off-diagonal region, patterns similar to those in the experimental data can be recognized. Dominant streak-like features characterize the diffusion between the layers, while distinct spots can be seen in the diffusion within the layers.

In interlayer diffusion, only islands and holes shrink, which is reflected in the TTCs with stripe-like patterns. In contrast, intralayer diffusion is dominated by the growth of some islands and holes, resulting in distinct patches in the outer TTC region. This interpretation is supported by the findings connected to Fig. 10.11. In the overall interpretation of this simulation, stripe-like features are attributed to intralayer diffusion, while distinct patches are associated with interlayer diffusion.

10.2.3 Interpretation for Experimental Data

Based on the findings from [155], a correlation between the growth or shrinkage rate and the time scales of the transformations is expected. In addition, the expression of TTC features is linked to the size distribution of islands and holes in the sample, as shown in [155]. As the temperature increases, the pronunciation of the features decreases, indicating an increase in the size distribution. This agrees well with the AFM results in Fig. 10.2 a).

The simulations are a valuable tool in attributing the untypical, non-diagonal TTC features to diffusion processes between and within the layers. For the annealed PTCDI-C8 film, this means the following: At $T_{\text{an}} = 100^\circ\text{C}$, circular-shaped maxima in the TTC indicate a dominance of intralayer diffusion. Here, the molecules have energy primarily for lateral movement within the layer, which leads to the growth or shrinkage of islands and holes. However, the energy is not sufficient to overcome the Ehrlich-Schwoebel barrier [124, 170], which prevents diffusion across an edge into another layer.

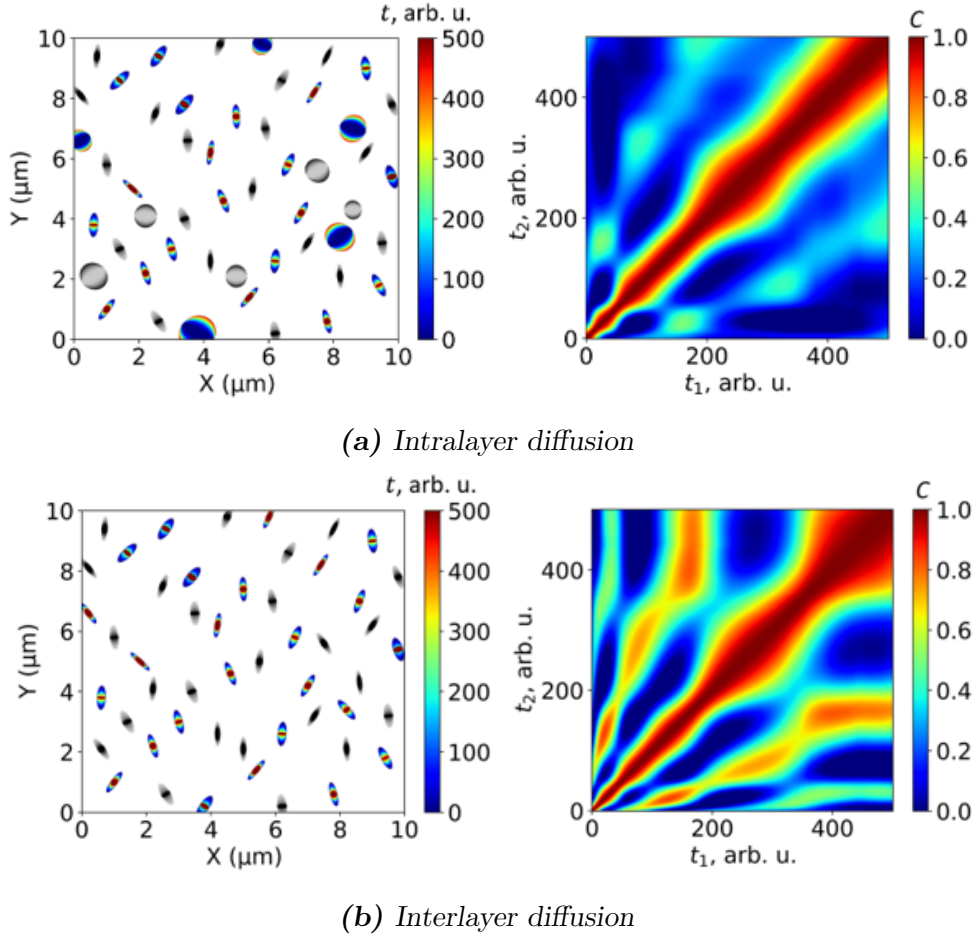


Figure 10.12: Simulated real-space representation (left-hand side), accompanied by the corresponding TTC (right-hand side) [167]. The evolution of island and hole sizes over time is color-coded. To distinguish between islands and holes, the latter are drawn in black and white. a) For the intralayer diffusion, 5 growing and 20 shrinking islands and holes are modeled. The resulting TTC shows circle-shaped maxima in the outer region. b) Interlayer diffusion is modeled by 25 shrinking islands and 25 shrinking holes, resulting in a predominant streak-like pattern in the TTC.

When the annealing temperature increases to $T_{\text{an}} = 150^\circ\text{C}$, a transition from circular-shaped maxima to stripe-like maxima indicates the transition from intralayer to dominant interlayer diffusion. The increased temperature, therefore, provides sufficient energy to overcome the Ehrlich-Schwoebel barrier, facilitating movement across the step edges into another layer. This structural transformation combined with increasing heterogeneity fits well with the AFM observations of changes in the shape of islands and holes (Fig. 10.2 a). Due to the diffusion transition at this temperature, the Ehrlich-Schwoebel barrier for PTCDI-C8 can be estimated to be around 30 – 40 meV.

At $T_{\text{an}} = 190^\circ\text{C}$, the structural evolution of the film slows down and approaches an equilibrium state. As a result, the surface smoothes out without major changes before it finally evaporates.

10.2.4 Scaling of the Simulation

The experimental geometry leads to a considerable footprint of the beam on the sample, which exceeds the feasible scope of the simulation in the context of this work. The simulation of larger surface areas proves to be very time consuming. Nevertheless, it will be tested whether slightly larger simulation surfaces lead to the same interpretations. To validate the results, a $20 \times 20 \mu\text{m}^2$ surface with 150 islands and holes (75 each) is selected. As before, the investigation focuses on the modeling of inter- and intralayer diffusion, with the results shown in Fig. 10.13 a) and b), respectively. The intralayer diffusion is modeled with 15 growing islands and 15 growing holes, which preserves the material at the surface. The resulting TTC again shows distinct spots in the off-diagonal region. Upon interlayer diffusion, all particles shrink, resulting in stripe-like features in the off-diagonal region of the TTC. These results support the previous thesis, suggesting consistent interpretations with higher statistics.

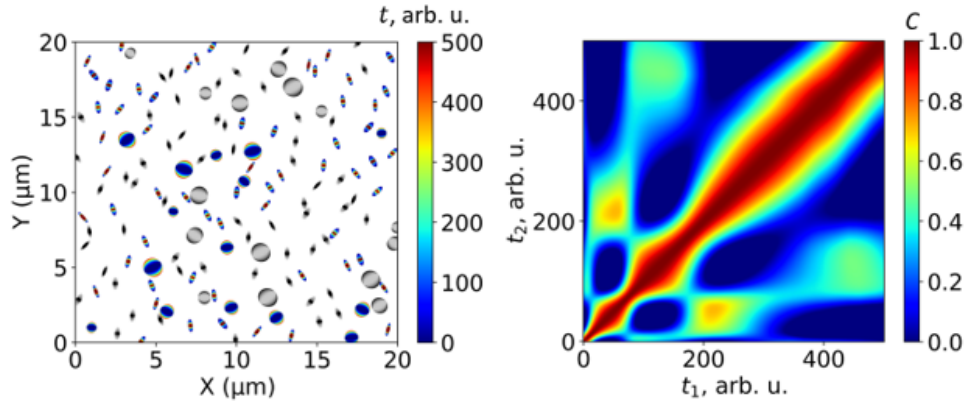
10.3 Conclusions

The annealing process of a PTCDI-C8 layer was investigated, with a focus on studying the surface dynamics at the micrometer level. For this purpose, XPCS was used to investigate the behavior of islands and holes.

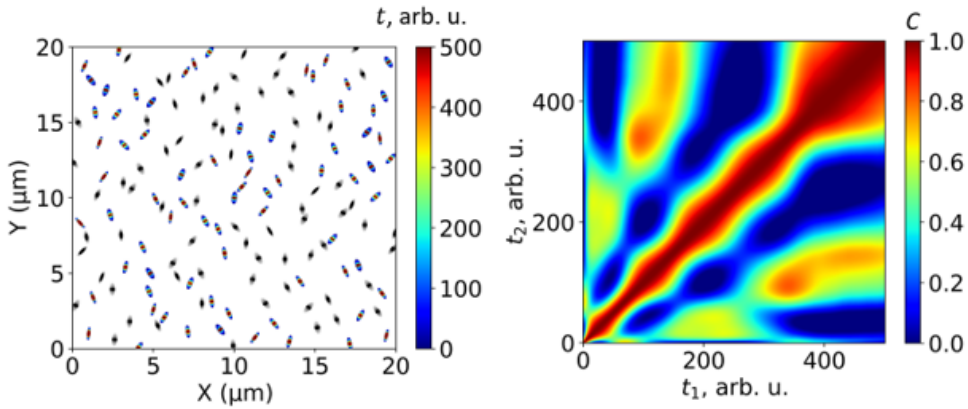
Due to the smooth nature of PTCDI-C8 films, material redistribution during annealing occurred mainly within three open MLs. With increasing temperature, the smoothness of the film increased, accompanied by a clear structural change in the shape of the islands and holes – changing from elliptical to rounder ones.

The XPCS analysis revealed time scales of about 100 seconds, which is associated with the redistribution processes of the surface material. Unusual off-diagonal features appeared in the TTCs, presenting as circle- and streak-like maxima. Simulations suggested an interpretation linking these features to intralayer and interlayer diffusion, respectively. At lower temperatures, the molecular motion remained confined to the original layer and induced the growth or shrinkage of the islands. When a critical temperature was reached ($T_{\text{an}} = 150^\circ\text{C}$), the increased energy facilitated the overcoming of the Ehrlich-Schwoebel barrier, leading to a dominant diffusion between the layers. As a result, the islands and holes mainly shrank, leading to a smoothening of the surface.

These interpretations agreed well with the experimental data from AFM, XRR, and correlation peak studies. However, when translating the TTCs to real space, there is no direct one-to-one translation, which generally makes the interpretation challenging due to various factors leading to similar TTCs.



(a) Intralayer diffusion



(b) Interlayer diffusion

Figure 10.13: Simulated real-space representation (left-hand side), accompanied by the corresponding TTC (right-hand side) [167]. The evolution of island and hole sizes over time is color-coded. To distinguish between islands and holes, the latter are drawn in black and white. a) For the intralayer diffusion, 15 growing and 60 shrinking islands and holes are modeled. The resulting TTC shows circle-shaped maxima in the outer region. b) Interlayer diffusion is modeled by 75 shrinking islands and 75 shrinking holes, resulting in a predominant streak-like pattern in the TTC.

Chapter 11

Complementary Data

This chapter provides complementary information to the previous two chapters (Chap. 9 and 10) and offers insights into potential future projects, which require further development and refinement.

The first section focuses on the growth of various materials, in particular, C₆₀, PTCDI-C8, and PEN. A particular challenge arose when measuring C₆₀ and PTCDI-C8 due to the high growth temperatures, which led to instability in the measurements. A proposed improvement is to use a second empty cell that remains open throughout the whole measurement to stabilize the temperature in the chamber and ensure a constant heat flow.

In the second part of this chapter, an additional annealing analysis is presented, based on that from the Chap. 10, with the material PEN. Further annealing data have already been described in Sec. 10.1.4, but this one will be a little more extensive. In addition, the chapter concludes with ex situ annealing data in the last section of the annealing segment.

11.1 Growth

In this section, we investigate surface dynamics during growth using a setup and analysis similar to that described in Sec. 9. The possible extension of the analysis to other materials is discussed, and potential measurement challenges are addressed.

XPCS proves to be a complex method, not only in data interpretation but also in experimental execution. The sensitivity of the method to subtle surface changes requires precision in minimizing external influences that could cause surface movements such as displacements or vibrations. These considerations are explored in the first two sections.

The third section looks at the challenges of interpreting XPCS data and how difficult it is to derive meaningful insights from the results obtained.

11.1.1 C₆₀

The focus is initially on C₆₀ with an experimental setup similar to that presented in Chap. 9. The growth of a C₆₀ film was monitored at $T_{\text{gr}} = 35^\circ\text{C}$ at a rate of 0.4 nm/min, reaching a final thickness of approximately 30 nm. To monitor

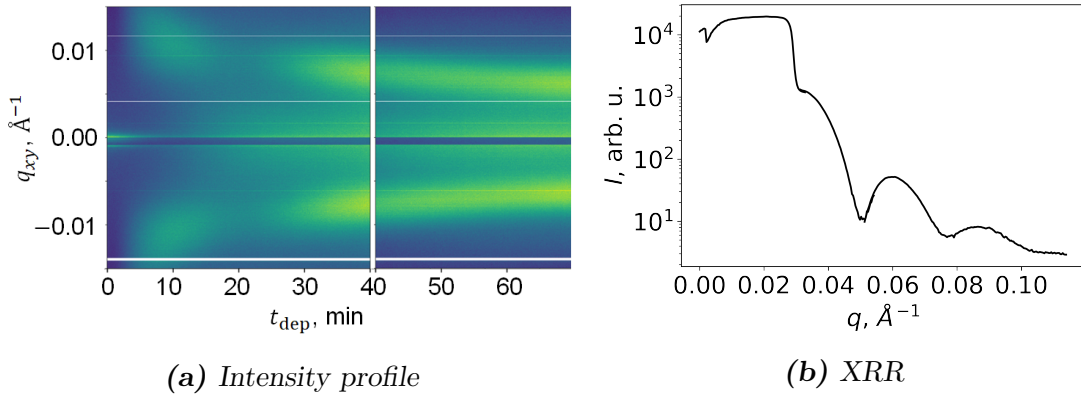


Figure 11.1: Film characterization during and after growth. a) Evolution of the outer intensity profile of a C₆₀ film during the growth at $T_{\text{gr}} = 35^\circ\text{C}$ over deposition time t_{dep} . The intensity was extracted at $q_z \approx 0.075 \text{ \AA}^{-1}$ and averaged over $\Delta q_z \approx 0.01 \text{ \AA}^{-1}$. b) XRR scan after growth.

the film growth, in particular the potential opening and closing of layers, the correlation peaks in the outer intensity profile were tracked at a q position of $q_z \approx 0.075 \text{ \AA}^{-1}$, shown in Fig. 11.1 a).

From the observation of the appearance and absence of diffuse scattering, one could conclude that one layer opens first and the film becomes rough from the second open ML onwards. However, it should be noted that the growth of this ML is unexpectedly slow for a 30 nm film (a ML is about 1 nm in size [171]). A first thought could be, that the measurements may be incorrectly calibrated, suggesting that the growth is much slower than expected, but in Fig. 11.1 b) the XRR directly after growth is shown. From the Kiessig oscillations, a total thickness of about 30 nm can be extracted. Of course, something could have gone wrong during the measurement and the deposition was very slow in the beginning and fast afterwards, but as for all measurements, the deposition rate was tried to be kept constant. Alternatively, there could be some impurities in the material or on the substrate, leading to unexpected growth behavior. During the experiment also a second evaporation cell was installed including DIP, a possible leak could also be an explanation. Nevertheless, without understanding the growth of C₆₀ for those measurements, it is difficult to find clear interpretations for the dynamics. In the following, it will not be referred to as MLs since it is not fully clear if the outer intensity profile shows the opening and closing of pure MLs or layers that consist of several individual molecular layers.

The position of the correlation peaks indicates an average island distance, initially around 50 nm, changing to approximately 100 nm. These values are again expected for the growth of C₆₀. Assuming these sizes can be used as an approximate island size, it implies that islands appear to grow throughout the growth process.

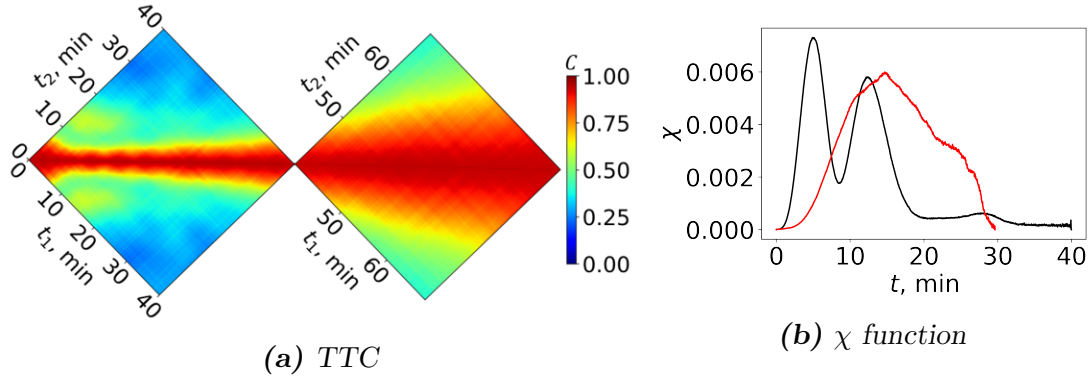


Figure 11.2: XPCS analysis of a C_{60} film grown at $T_{\text{gr}} = 35^\circ\text{C}$ at $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 2.5 \cdot 10^{-3} \text{ \AA}^{-1}$. a) TTC during the growth process. b) Fourth-order correlation function (χ function) extracted from the TTC.

The dynamics are analyzed using XPCS in a selected q region of $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 2.5 \times 10^{-3} \text{ \AA}^{-1}$, corresponding to length scales of $l_z = 20 \text{ nm}$ and $l_{xy} = 250 \text{ nm}$, which resembles the size of molecular clusters such as islands.

In Fig. 11.2 a), the TTC shows parallel streaks in the early stage of growth and slows down with increasing deposition time. The features in the outer region differ from those observed in DIPs. Nevertheless, an attempt is made to adapt similar results and evaluate their physical validity.

The fourth-order correlation function, shown in Fig. 11.2 b), shows several peaks. In the first scan, two distinct peaks could indicate the growth of the first two layers, while a smaller third peak could initiate the roughening period, possibly indicating the overlap of the second and third layer towards the end of the scan. It is important to note that the growth of a layer, as observed in Fig. 11.1, is much slower than the appearance of the second peak in the fourth-order correlation function. This discrepancy raises again the possibility that the lack of diffuse scattering does not accurately reflect the growth of a single ML.

The second scan shows several broad peaks, which indicate possible overlaps and make it difficult to determine a definitive number. This could indicate a rapid roughening of the surface. To test these assumptions, more appropriate simulations could be performed to refine the assignment of length scales and account for additional open layers. Simulations on a molecular level were already performed, as to be found in Ref. [172].

The following subsection discusses stability issues that may have influenced these measurements as well. Consequently, re-measuring and reproducing these results could serve as a valuable validation.

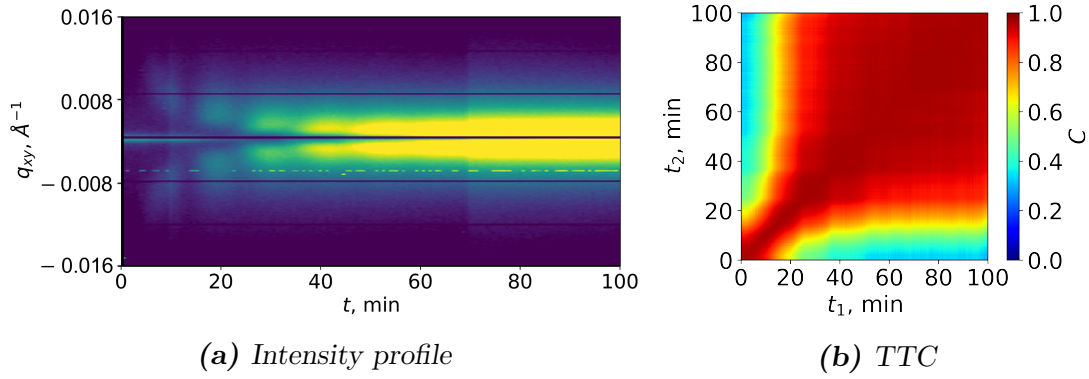


Figure 11.3: Analysis of the growth of a PTCDI-C8 film at $T_{\text{gr}} = 35^\circ\text{C}$. a) Time evolution of the diffuse scattering signal. The intensity was taken at an outer region of $q_z = 0.05 \text{ \AA}^{-1}$ and averaged over $\Delta q_z = 0.005 \text{ \AA}^{-1}$. b) TTCs during the growth process analyzed at $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 4.22 \times 10^{-3} \text{ \AA}^{-1}$.

11.1.2 PTCDI-C8

The same analysis was performed for PTCDI-C8. A thin film was grown at $T_{\text{gr}} = 35^\circ\text{C}$ at a rate of 0.2 nm/min and eventually reached a final thickness of about 20 nm . This material is particularly interesting as it exhibits layer-by-layer growth for several MLs before the film roughens.

In the time evolution of the outer intensity profile shown in Fig. 11.3 a), at a certain q value ($q_z = 0.05 \text{ \AA}^{-1}$), the opening and closing of MLs can be recognized by the appearance or absence of diffuse scattering, up to the fifth ML. This observation is consistent with the layer-by-layer growth characteristics expected for PTCDI-C8. Afterward, the film gets rough. Extracting the average island size from the correlation peaks shows that the islands grow from approximately 60 nm to 300 nm .

XPCS for the PTCDI-C8 film growth was performed within a ROI defined by $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 4.22 \times 10^{-3} \text{ \AA}^{-1}$ and focused on studying diffusion at the length scales of the molecular islands.

The TTC in Fig. 11.3 b) shows a slowdown over the deposition time, a behavior observed for all films so far. Following the results of Ref. [25], the observation of checkerboard-like off-diagonal features was expected. In Ref. [25], this pattern was explained by the development of islands at static positions over the growth of several MLs. However, this behavior may not apply to the present material. Contrary to expectations, the opening and closing of layers in the TTC should be visible as heterogeneous behavior along the diagonal (acceleration followed by deceleration), which is not the case in the data obtained. Further investigation and analysis is required to better understand this.

Difficulties during the measurement

Several difficulties arose during the measurement of the PTCDI-C8 growth, which may explain the unexpected behavior of the dynamic data. The high evaporation temperature of PTCDI-C8 ($T_{\text{ev}} \approx 290^\circ\text{C}$) led to instabilities during the measurements. This instability manifested itself in the form of a decorrelation of intensity when the cell temperature was around 250°C , where minimal if any, deposition was expected. However, surprisingly, the heat flow from the cell to the substrate was clearly visible in the data. As the substrate temperature increased, the effect became less pronounced. This can be explained by the smaller heat difference from the substrate to the cell. The movement of the substrate caused by the heat flux from the cell affects the access to the surface-induced dynamics and, hence, for a proper data analysis.

In addition, the heating and cooling cycles of the substrate caused movements that were evident in the decorrelation of intensity over time during data acquisition without deposition. This phenomenon was not observed in measurements for other materials, raising the possibility of a loose cable or screw in the chamber. Furthermore, this effect mostly arises at lower temperatures, where the heat control causes a strong gradient in the heating current. To control these measurement errors, a stability measurement was performed before the real data was taken.

To summarize, these problems highlight the sensitivity of the XPCS method. They are a reminder that experimental precision is critical to obtaining physically meaningful results. While precision is essential in any measurement, the novelty of the XPCS method makes it difficult to recognize when data are truly useful and interesting and when unexpected features may arise due to measurement errors.

11.1.3 Pentacene

For the growth analysis of PEN, a thin film was deposited at $T_{\text{gr}} = 35^\circ\text{C}$, which grew at a rate of 0.2 nm/min to a final thickness of 15 nm . Fig. 11.4 a) illustrates the changes in the correlation peaks during growth. The peaks shift towards smaller q_{xy} values with increasing deposition time, indicating an increase in island size. The pronunciation of the peaks decreases after about 30 minutes, indicating a possible roughening of the film.

Fig. 11.4 b) shows the TTC for this growth process, analyzed at $q_z = 0.02, \text{\AA}^{-1}$ and $q_{xy} = 0.86 \times 10^{-3}, \text{\AA}^{-1}$, i.e. close to the correlation peaks. The TTC shows unique wing-like features in the outer region that differ from the previously discussed structures. In addition, a relationship with the temporal evolution of the correlation peaks can be observed: When the film starts to get rough after about 30 minutes, the TTC slows down.

The exploration and understanding of these once-new TTC features in the context of PEN growth is a promising topic for future research projects.

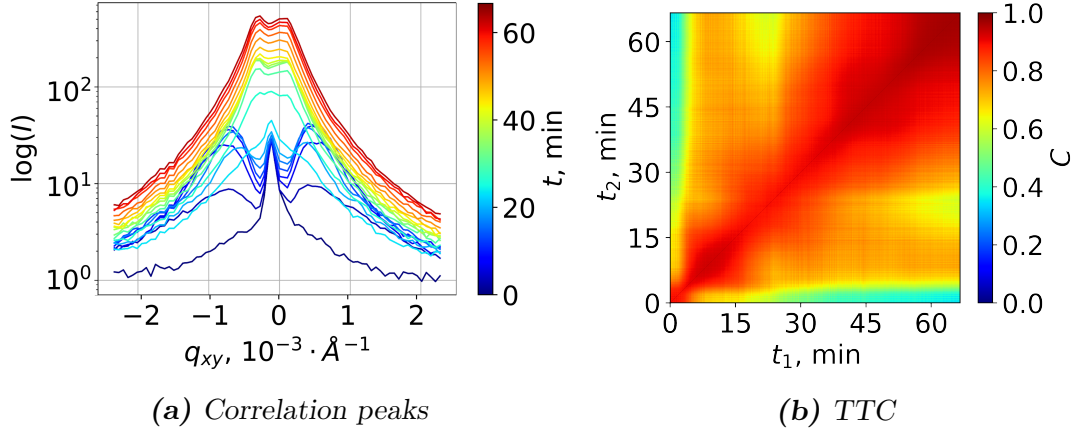


Figure 11.4: Analysis of the growth of a PEN film at $T_{\text{gr}} = 35^\circ\text{C}$. a) Time evolution of the correlation peaks. The intensity was taken at an outer region of $q_z = 0.03 \text{ \AA}^{-1}$ and averaged over $\Delta q_z = 0.008 \text{ \AA}^{-1}$. b) TTC during the growth process analyzed at $q_z = 0.02 \text{ \AA}^{-1}$ and $q_{xy} = 0.86 \times 10^{-3} \text{ \AA}^{-1}$.

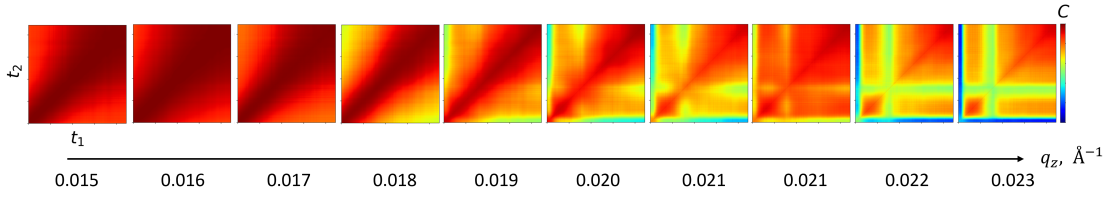


Figure 11.5: q_{xy} -dependence of TTCs during the growth of PEN analyzed at $q_{xy} = 0.86 \times 10^{-3} \text{ \AA}^{-1}$.

In addition, Fig. 11.5 shows a structural change for changing q values in the data. This has not yet been discussed further in this thesis. All possible q values to be analyzed result in the study of micrometer structures, especially islands. Investigating the diffusion of single molecules on the nanometer scale would be interesting as well, but at the moment, data extraction at such high q values is not possible.

Therefore, the q dependence can only be analyzed within the available range. In Chap. 9 it was found that the primary structure of the TTC during growth appears dominantly due to the kinetics of island growth. The q dependence of this phenomenon can be further explored through simulations, as described in App. 15. The observed q dependence in the PEN growth data agrees well with the simulation results and offers potential insights that can help with interpretation but are context for further research.

11.2 Annealing

This section focuses on the surface dynamics during the annealing process. While complementary data for the in-depth analysis of PTCDI-C8 have already been presented in Sec. 10.1.4, a more detailed investigation is carried out again here using the material PEN.

To conclude this section, ex situ annealing data are presented. These data, which primarily serve as a guide for the in situ measurements, provide insight into the time scales of the dynamic processes in this class of materials and analyze their sensitivity to the applied beam.

11.2.1 Pentacene

The annealing analysis was applied to a PEN film grown at low temperatures ($T_{\text{gr}} = -50^\circ\text{C}$) with a final film thickness of about 25 nm. In Fig. 11.6 a), the AFM image serves as a starting point to characterize the original surface before annealing. The initial state shows a rough film ($\sigma_{\text{RMS}} = 1.758\text{ nm}$) with a high density of islands. The island's shape is round with a radius of approximately 80 nm. Several open MLs can be observed in the height distribution function in Fig. 11.6 b).

The development of the film during the annealing process is characterized by XRR. Initially, after growth, no Kiessig oscillations are visible, which indicates a high surface roughness. However, as the annealing process progresses, changes become visible. At $T_{\text{an}} = 20^\circ\text{C}$ the Kiessig oscillations slightly start to appear, but especially at $T_{\text{an}} = 50^\circ\text{C}$ they are clearly visible. This observation indicates that both diffusion processes can appear during the annealing processes, maybe intralayer diffusion dominating at 20°C , and intralayer diffusion dominating at 50°C .

This assumption will be investigated with XPCS using the same q region as for PTCDI-C8 in Chap. 10, namely $q_z = 0.028\text{ \AA}^{-1}$ and $q_{xy} = 1.46 \cdot 10^{-3}\text{ \AA}^{-1}$. The temporal analysis, using TTCs (Fig. 11.7 a) and b)), revealed an extended reorganization period before a deceleration set in, occurring after approximately 30 minutes. This duration is longer compared to the PTCDI-C8 films, indicating that the full reorganization process on the surface takes more time after a temperature change.

At both temperatures, circle- and streak-shaped maxima appear in the off-diagonal region of the TTC. Consequently, the separation and assignment of specific diffusion processes to temperatures are not as straightforward as it was observed for the annealing of PTCDI-C8.

It appears that a considerable amount of diffusion occurs at the surface after the annealing of PEN. Consequently, intralayer diffusion could exert a significant influence throughout the process. Nevertheless, streak-like features appear in the outer region of the TTC, indicating a smoothing of the surface, which agrees well with the XRR results.

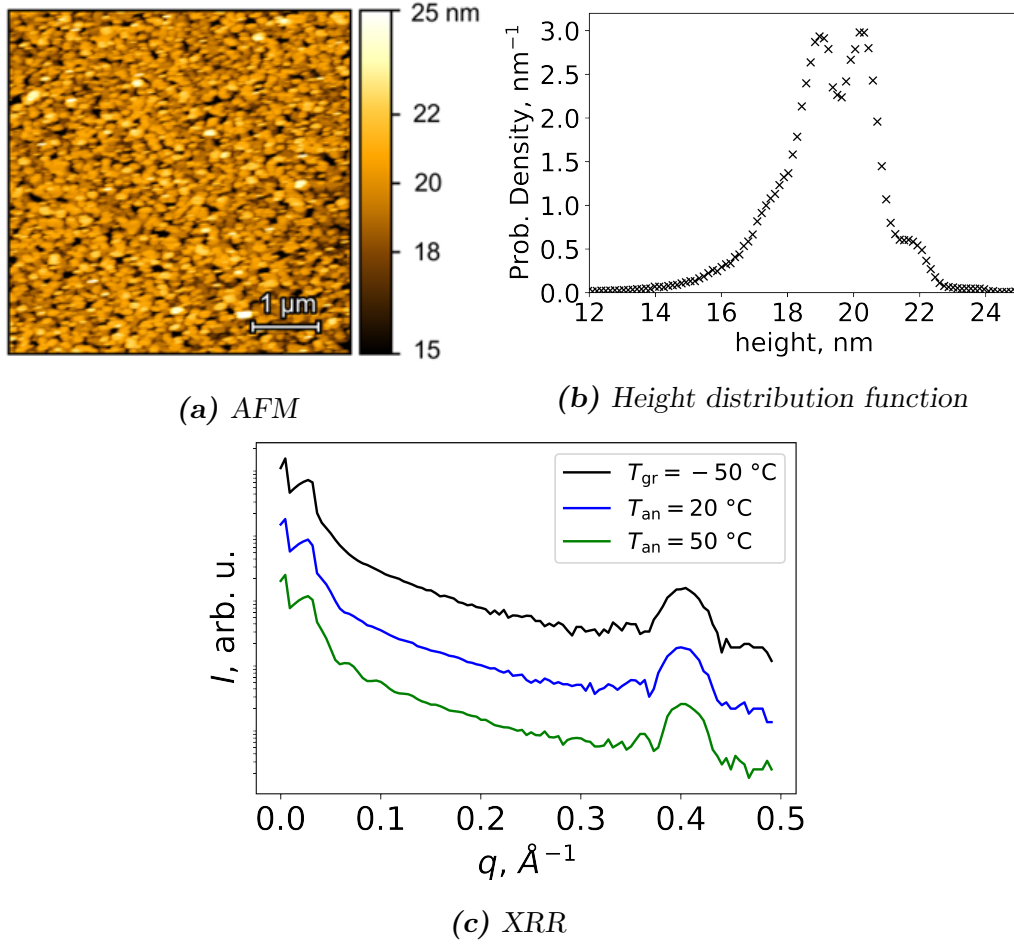


Figure 11.6: Film characterization of a PEN film grown at $T_{\text{gr}} = -50^\circ\text{C}$ and annealed to two different annealing temperatures. a) AFM image after growth. b) Height distribution function extracted from the AFM image. c) XRR data after growth and each annealing step.

However, caution should be advised when transferring the knowledge gained from the simulation to other materials. While the assignment of circle-and streak-shaped maxima in the TTCs to specific surface dynamics seems logical for the length scales associated with the PTCDI-C8 material, it is not trivial to generalize this to the sizes of islands and holes on the average surface of other materials. As a consequence, the simulation should be adapted to appropriate length scales for growing or shrinking PENs islands and holes and more open MLs.

11.2.2 ex situ Annealing of PEN and DIP

The annealing process of PEN and DIP films deposited at different temperatures is investigated. PEN films were grown at temperatures $T_{\text{gr}} = -145^\circ\text{C}$, -50°C , and 45°C with a final layer thickness of 25 nm for each film. Similarly, DIP depo-

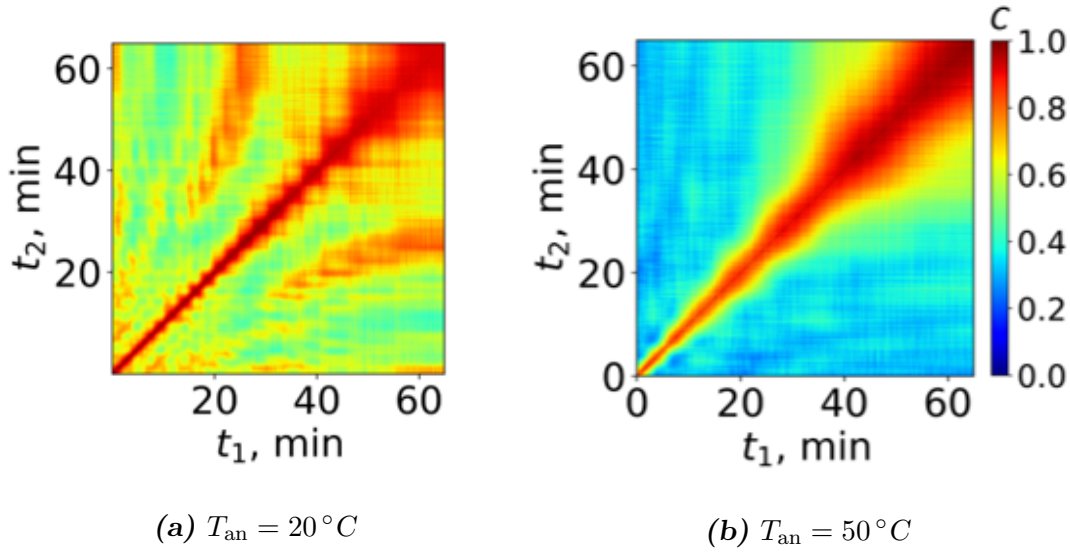


Figure 11.7: XPCS analysis of the annealing process of a PEN film grown at $T_{\text{gr}} = -50^\circ\text{C}$ at $q_z = 0.028 \text{ \AA}^{-1}$ and $q_{xy} = 1.46 \cdot 10^{-3} \text{ \AA}^{-1}$. a) TTC after annealing the film to $T_{\text{an}} = 20^\circ\text{C}$. b) TTC after annealing the film to $T_{\text{an}} = 50^\circ\text{C}$.

sition was carried out at $T_{\text{gr}} = -30^\circ\text{C}$, 30°C , and 100°C , also with a final layer thickness of 25 nm.

Exemplary AFM images for PEN and DIP, grown close to room temperature, are depicted in Fig. 11.8 a) and b), respectively. As the growth temperature increases, the islands exhibit larger sizes, while lower temperatures result in smaller islands post-growth.

The XPCS data were acquired at the synchrotron in GISAXS geometry, with incident angles of 0.1° for PEN and 0.15° for DIP. This comprehensive approach provides valuable insights into the morphological evolution of PEN and DIP films under different deposition and annealing conditions.

In Fig. 11.9 a) and b) the XPCS analysis of an exemplary annealing process of the PEN film grown at $T_{\text{gr}} = 45^\circ\text{C}$ and subsequently annealed to $T_{\text{an}} = 77^\circ\text{C}$, is shown. The XPCS scan was analyzed at $q_z = 0.028 \text{ \AA}^{-1}$ and $q_{xy} = 3.53 \cdot 10^{-3} \text{ \AA}^{-1}$. In Fig. 11.9 a), the TTC shows an intensity correlation decay with time, which is an almost straight diagonal, looking close to an equilibrium process. Consequently, focusing only on the g_2 functions is sufficient to extract physical quantities. The corresponding exemplary g_2 function, which was extracted from the TTC by selecting the time difference $t = |t_2 - t_1|$ and averaging over t_1 , is shown in Fig. 11.9 b).

For different annealing temperatures, predominantly only the initial decay is observed, which emphasizes the usefulness of focusing on the g_2 features. Although occasionally weak features appear in the outer region, they are not further in-

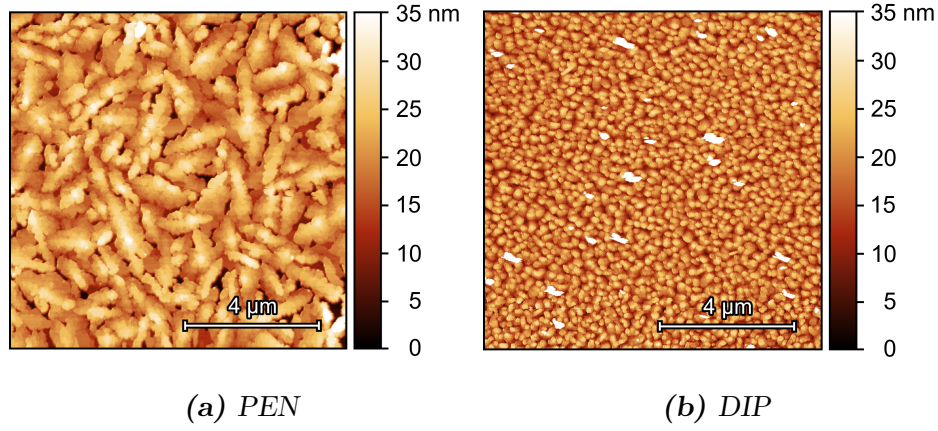


Figure 11.8: AFM images of a) *PEN* grown at $T_{\text{gr}} = 45^\circ\text{C}$ and b) *DIP* grown at $T_{\text{gr}} = 30^\circ\text{C}$.

vestigated in this context. The characteristic time scales extracted from the g_2 function are determined by exponential fits using Eq. (5.3).

All fits show a stable contrast of about 10 %. The fitting results for the relaxation rate τ and the stretching exponent γ are shown in Fig. 11.10 a) and b) for *PEN* and Fig. 11.10 c) and d) for *DIP*. Surprisingly, there is no strong q -dependence for both, q_z and q_{xy} , which is why only the q_{xy} dependence is shown. The stretching exponent remains stable at around 1.6 and decreases to one during evaporation, while the relaxation rate is of the order of a few minutes.

Regarding temperatures, larger structures (i.e., films grown at lower temperatures) exhibit slower dynamics. Further, the dynamics accelerate with temperature (especially for *DIP*). A more visualized interpretation of the data, especially the consistent trend of the stretching exponent moving towards unity for increasing annealing temperature, can be a topic for further investigation.

11.3 Conclusion

This chapter emphasizes the potential of the XPCS analysis in GISAXS geometry. The investigation during film growth focuses, in particular, on the different kinds of TTC patterns that emerge.

The complex nature of growth, which is influenced by numerous adjustable parameters (material, temperature, deposition rate, etc.) to shape the morphology, leads to complex and various different XPCS results. Interpretation of these results requires specific analysis to disentangle the underlying processes and specifically to establish links between TTC features and real-space phenomena.

During the discussion of the growth data, the challenges in measurement were also addressed, highlighting not only the difficulties in data interpretation but also in data collection. Investigating the q dependence in the data can potentially be used to improve the understanding of TTC patterns.

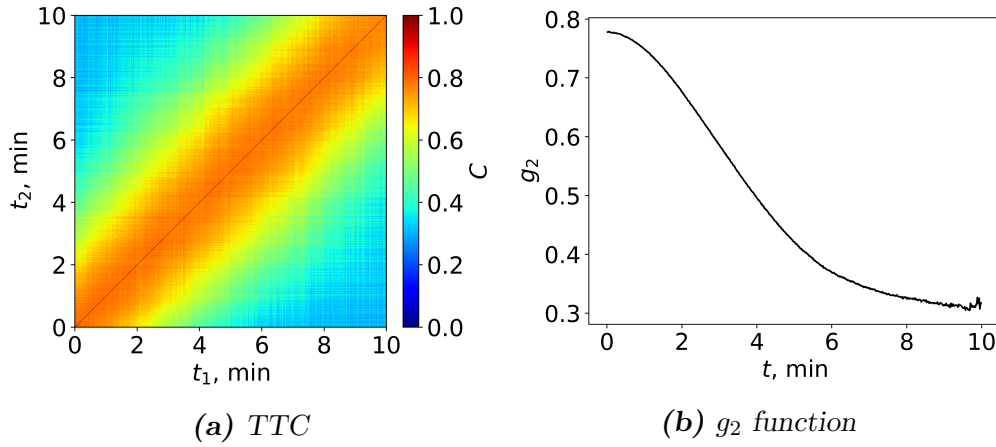


Figure 11.9: Exemplary data of the annealing process of a PEN film grown at $T_{\text{gr}} = 45^\circ\text{C}$ and annealed to $T_{\text{an}} = 77^\circ\text{C}$. a) TTC of the annealing process extracted at $q_z = 0.028 \text{ \AA}^{-1}$ and $q_{xy} = 3.53 \cdot 10^{-3} \text{ \AA}^{-1}$. b) g_2 function of the same process.

Conversely, a simpler scenario arises for the annealing process of already deposited thin films, where consistent similarities in the TTCs allow a more general interpretation of the data.

The analysis of ex situ annealing data is even simpler and focuses on the extraction of characteristic time scales, usually around several minutes. Although these studies do not represent a breakthrough in XPCS surface research, they have laid the foundation for in situ experiments by providing insight into material sensitivity to the synchrotron beam, general stability of the setup, and appropriate measurement times.

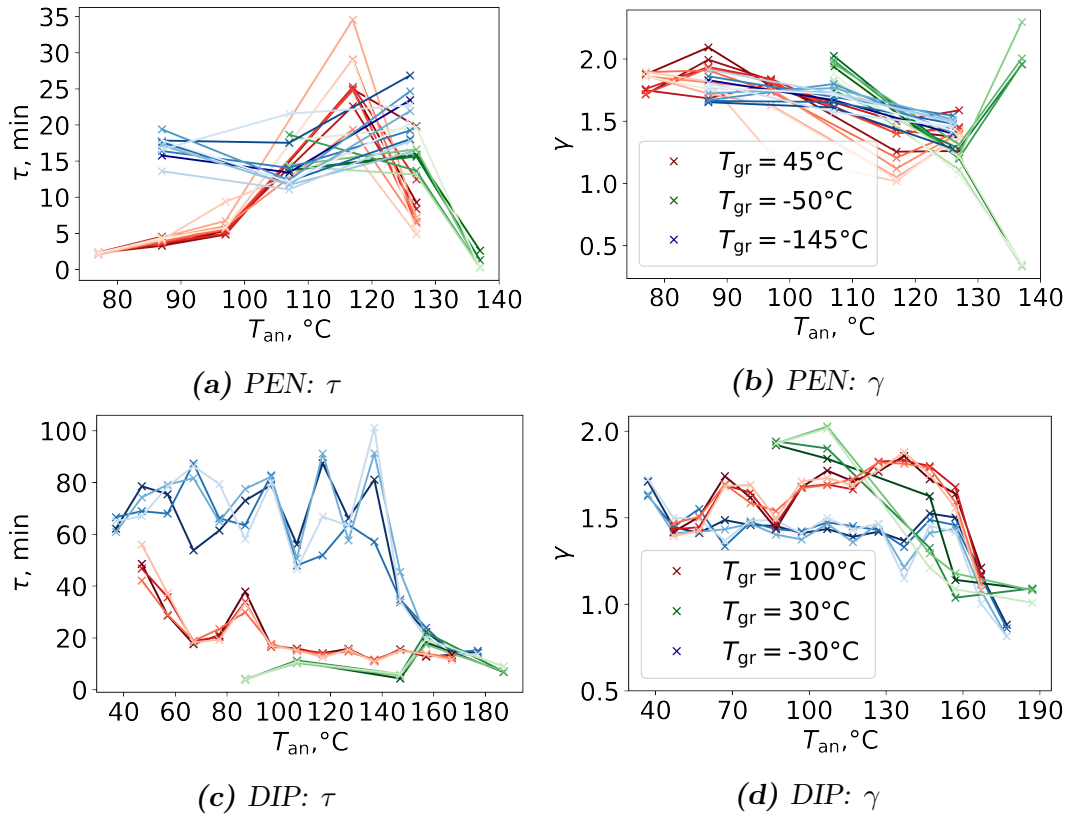


Figure 11.10: Fitting results of the g_2 functions of the annealing processes of three PEN and DIP films, grown at different temperatures. The analysis was performed at $q_z = 0.028 \text{ \AA}^{-1}$ and $q_{xy} = (2 - 15) \cdot 10^{-3} \text{ \AA}^{-1}$ a) Fit parameter τ for three PEN films. b) Parameter γ for the same films. c) Fit parameter τ for three DIP films. d) Parameter γ for the same films.

Part IV

Conclusions

Chapter 12

Conclusion & Outlook

This work dealt with the emerging field of XPCS in GISAXS geometry. In this context, various thin film growth and annealing experiments were performed to reveal the surface dynamics and reorganization processes in the micrometer range and, in particular, to investigate the movement of molecular assemblies such as islands. Throughout the study, the focus was placed on organic materials. The specific choice of material was of secondary importance, as the primary goal was merely to find a representative candidate for the development of an analysis strategy.

The morphological variations in these films, ranging from nearly layer-by-layer growth to rough island growth, depended on growth conditions such as substrate temperature and deposition rate. Thin film growth, a complex process that is determined by numerous parameters, still holds untapped potential in this method. Annealing experiments offer a simplified scenario that can be used to decode the underlying processes, such as cluster formation and surface diffusion, and thus also contribute to the understanding of thin film growth. However, the challenges lie not only in the precise execution of the experiments, but also in the complicated interpretation of the collected data. Simulations have proven to be the most promising tool at this stage, as they provide a way to interpret XPCS data and establish links to processes in real space. Consequently, a clear emphasis on simulations have been placed in this work, resulting in the development of a simulation framework tailored to modeling XPCS data of thin film growth and annealing, with a focus on the growth and shrinkage of structures in the micrometer range.

The first result of these efforts is in the area of thin film growth. For that, the material DIP was used to serve as a semiconductor prototype. The investigation of the diffusion processes showed a transition from layer-by-layer growth to a subsequent almost static development of islands. The fourth-order correlation function was used to further capture the development of the individual layers.

Attention was then turned to the annealing process of a thin film of PTCDI-C8, a film that grows comparatively smoothly in the region of these materials. Using XPCS and simulations, specific TTC features were attributed to either material transport within or between the layers.

The final section of the results included a set of complementary growth and annealing data. These data played a crucial role in the design of the overall experimen-

tal setup by providing insights into the material sensitivity to the synchrotron beam, ensuring the overall stability of the setup, and determining appropriate measurement times. Furthermore, recurring and unusual features in the XPCS data indicate the possible generalizability and open up perspectives for further investigations.

With regard to future studies, there is still potential for further development of simulations. Currently, modeling thin film growth on the required length scales – given that the footprint of the beam on the sample during the experiment is in the range of a few millimeters – poses a significant computational challenge.

In addition, advances in synchrotron technology, characterized by higher coherence and improved beam intensity, could open up opportunities to explore the dynamics of even smaller structures, such as individual molecules. At these smaller length scales, diffusion processes could become more important for understanding the behavior of molecular assemblies.

In summary, it can be said that the limits and understanding of the method are far from being fully explored. The ongoing development of the simulations and the potential improvements in synchrotron capacities indicate that there is still much to be discovered and understood in the investigation of material dynamics on different length scales.

Part V

Appendix

Chapter 13

Scattering Calculations

This chapter will focus on the simulation of the scattering process using the Born Approximation. It is motivated by the observation that the time scales in the experiment seem to match the theory. Since surfaces are considered, where multiple scattering cannot be neglected, the next order calculation, i.e. the DWBA has to be taken into account. Constructing such a simulation will go beyond the scope of this thesis, that is why the already existing software BA was introduced in Sec. 8.2.2.

13.1 XPCS Calculation using Born Approximation

The XPCS technique has already successfully used for several analyses, such as the analysis of solutions containing colloidal particles and hence to study their continuous movement [13]. Adapting this method to surfaces is an area that has been little explored so far. To improve the impression of how that can be done, the Born Approximation will be used as a first simplification.

First, the form factor for a sphere and a cylinder will be calculated. These calculations will be used to determine intensity correlation functions for a growing sphere on a surface. It is important to note that, for surface scattering the DWBA cannot be neglected, as explained in Sec. 8.2.1. However, the calculation provides an insight on which equations the simulations are based on.

13.1.1 Sphere

The simplest case is to consider spherical particles. The form factor for a sphere with radius R can be calculated using Eq. (3.14) to

$$f_{\text{sphere}}(q, R) = \rho \int_0^{2\pi} d\phi \int_0^\pi \sin \theta d\theta \int_0^R r dr \exp(iqr \cos \theta) \quad (13.1)$$

$$= 3 \rho \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}. \quad (13.2)$$

Since a sphere is considered, spherical coordinates are best suited for the integration. The radius will later change with time, i.e. $R \rightarrow r(t)$. Furthermore, particles

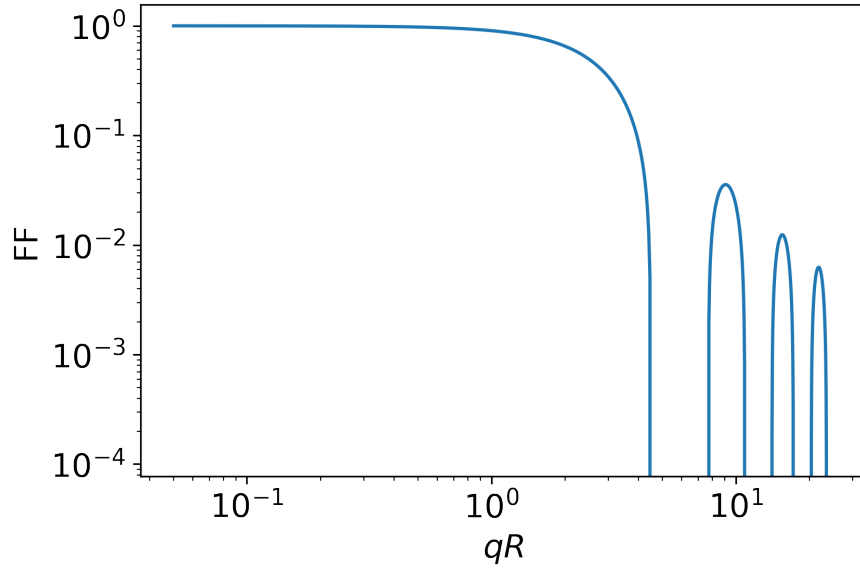


Figure 13.1: Form factor of a sphere, calculated with Eq. (13.2).

constant density inside their core are considered. Therefore a the density in case of spherical particle can be described by

$$\rho(\mathbf{x}) = \begin{cases} 1 & , |\mathbf{x}| < R \\ 0 & , \text{else} \end{cases}, \quad (13.3)$$

with the space-coordinate $\mathbf{x}$. The form factor of a sphere is shown in Fig. 13.1 for $0 < qR < 25$.

13.1.2 Cylinder

Since cylindrical particles are used in the simulations the form factor of this slightly more complex particle should be used. Based on Eq. (3.14) a cylinder with radius R and length l is calculated to

$$f_{\text{cyl}}(q, R) = \rho \int_0^{2\pi} d\phi \int_{-h/2}^{h/2} dh \int_0^R r dr \exp(i(q_y \cdot \sin \phi + q_z \cdot h)) \quad (13.4)$$

$$= \frac{4\pi}{q_y q_z} \sin\left(q_z \frac{h}{2}\right) \cdot R \cdot J_1(q_y R). \quad (13.5)$$

For the calculation cylinder coordinates were used, as well as the symmetry in the xy-plane. Again, if the radius is time dependent, R is replaced by $r(t)$. Further, particles with a constant density inside their cores are considered.

The following calculations will continue with a sphere for simplicity, but in prin-

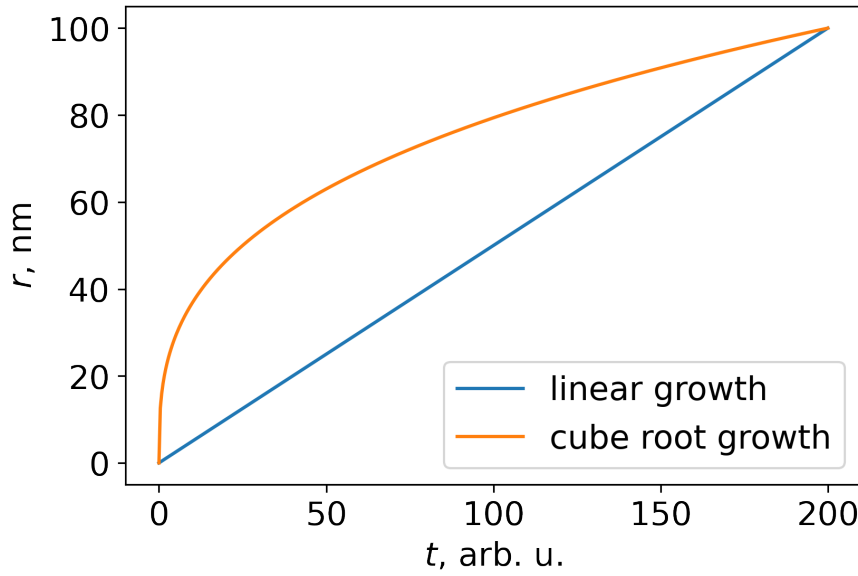


Figure 13.2: Linear change in radius and volume (cube root growth) according to Eq. (13.6) and (13.7), respectively.

ciple they can be adapted to the more complex case of a cylinder using the results from this section.

13.1.3 Radius Change

The most simple growth would be linear in time, i.e.

$$r_{\text{lin}}(t) = r_{0,\text{lin}} \cdot t, \quad (13.6)$$

with a constant factor given by the final radius R divided by the number of time steps t_{max} , i.e. $r_{0,\text{lin}} = R/t_{\text{max}}$. However, as a constant material flux is used in the experiments, the particle volume changes linearly and hence,

$$r(t) = r_0 \cdot t^{1/3}, \quad (13.7)$$

where again $r_0 = R/t_{\text{max}}^{1/3}$ is a constant factor. Both possible changes in the radius with time are depicted in Fig. 13.2 for 200 time steps and a final radius of $R = 100$ nm serving as an example.

13.1.4 Intensity Correlation

The scattered intensity can be obtained by inserting the results from Eq. (13.2) into Eq. (3.34) and Eq. (3.35) and a subsequent integration of the varying radius size, which is a function of the time variable.

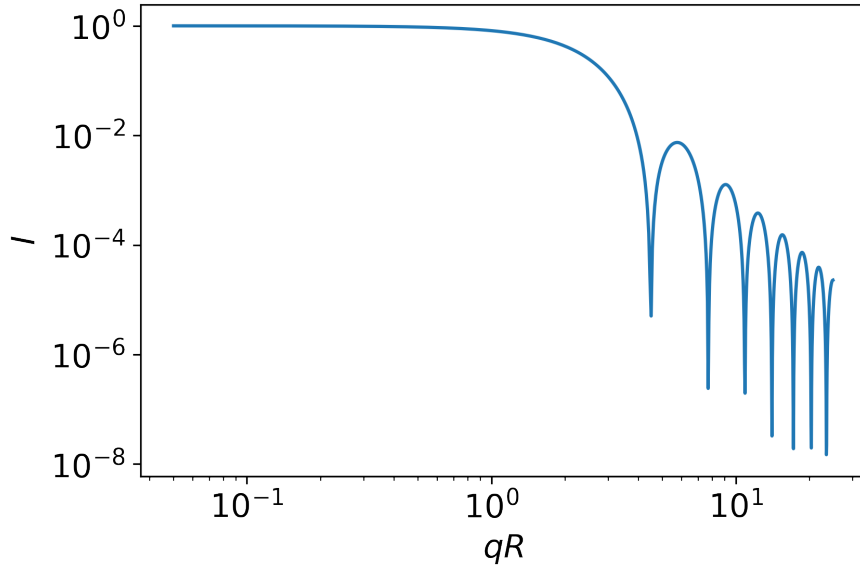


Figure 13.3: Scattered intensity of a single spherical particle, calculated with Eq. (13.10).

By understanding the change in intensity over time, it is possible to calculate intensity-intensity correlation functions. In equilibrium systems this results in Eq. (5.1).

A non-equilibrium growth is considered, which is determined by a TTC using Eq. (5.5). With this function, the time evolution of the system can be investigated. To understand the influence of pure growth on the TTC features, a system with a single growing particle will be considered.

13.2 Growth of One Particle

For one particle, i.e. in the case for one growing sphere, the latter equations simplify a lot. Starting from Eq. (3.33) the intensity can be calculated to

$$I(q) = N(\Delta\rho)^2 P(a, \xi) \quad (13.8)$$

$$= |f(q, t)|^2. \quad (13.9)$$

For only one particle and not an ensemble of for example different orientations, the averaging over different orientations and sizes is omitted. Consequently, Eq. (13.9) will become

$$I_{\text{sphere}}(q, t) = \left| 3 \frac{\sin(qr(t)) - qr(t) \cos(qr(t))}{(qr(t))^3} \right|^2. \quad (13.10)$$

The intensity for $0 < qR < 25$ is depicted in Fig. 13.3.

To calculate a TTC from that, Eq. (13.10) can be inserted into Eq. (5.5). This

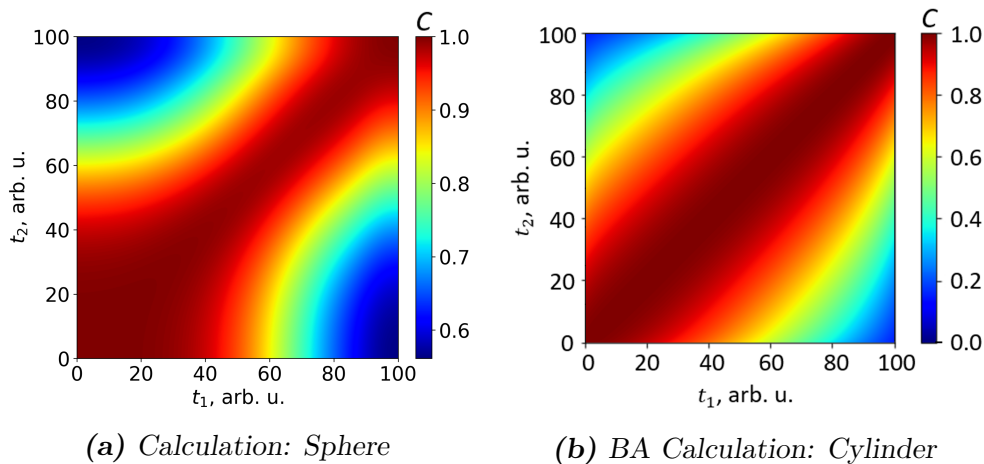


Figure 13.4: TTC for the growth of one particle which changes its radius from 0 – 100 nm, according to Eq. (13.7). a) Calculation of a spherical particle using Eq. (13.11). b) Calculation of a cylindrical particle using the software BA.

leads to a rather complicated integration which is performed numerically to decrease computation time. The full equation is given as

$$C(t_1, t_2) = \frac{\int dq I_{\text{sphere}}(q, r(t_1)) \cdot I_{\text{sphere}}(q, r(t_2))}{\int dq I_{\text{sphere}}(q, r(t_1)) \cdot \int dq I_{\text{sphere}}(q, r(t_2))} \cdot \Delta q. \quad (13.11)$$

For the calculation the transmitted intensity is investigated. The intensity pattern will be a spherically symmetric image. A ring of q -values will be selected for the analysis, fixing the integration variables in Eq. (13.11). Comparable values to the experimental data are used, i.e. $q_{\text{start}} = 0.03 \text{ nm}^{-1}$ and $q_{\text{end}} = 0.09 \text{ nm}^{-1}$.

The resulting TTC for a spherical particle is presented in Fig. 13.4 a) for a growing radius of $r = 0 - 100 \text{ nm}$, according to Eq. (13.7). For comparison, a similar scenario of a single growing cylinder is presented in Fig. 13.4 b). The main part of the calculation was performed with the software BA, as introduced in Sec. 9.2. The difference between the calculation presented here and the one using the software BA is the choice of particles (spherical versus cylindrical particle), as well as the usage of the DWBA and finally also the calculation at slightly different q -values. Consequently, both TTCs do not look the same. Nevertheless, the time scales are similar, which is a reasonable result.

The g_2 function for $q_{\text{start}} = 0.02 \text{ nm}^{-1}$ can be calculated using Eq. (5.1). For that, the radius is used as a variable instead of the time. To extract dynamical parameters, an exponential fit is performed according to

$$g(r) = \exp \left(-2 \left(\frac{r}{R_0} \right)^\gamma \right), \quad (13.12)$$

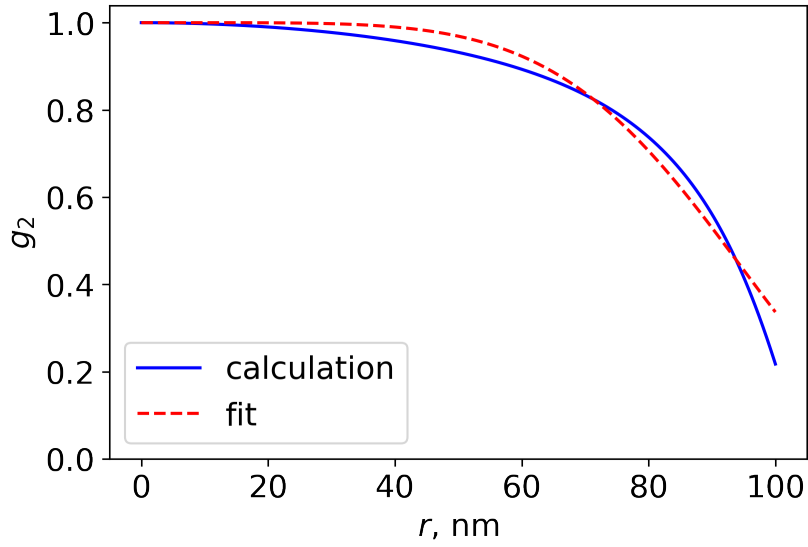


Figure 13.5: Calculated g_2 function for a sphere with growing radius from 0 – 100 nm. The function is fitted with Eq. (13.12).

with the free fit parameters R_0 and γ . The result is shown in Fig. 13.5, and the fit parameters are given as

$$R_0 = 98.4 \text{ nm}, \quad \gamma = 2.5. \quad (13.13)$$

The fit parameter R_0 is close to the final radius of the sphere. This seems to be a reasonable result, since only the growth of a single particle is considered, which can subsequently be extracted from the g_2 function.

Chapter 14

Stability Measurements

This chapter explains how the in situ measurements at the synchrotrons were constructed. To determine suitable measurement times and temperature changes some pre-measurements were performed on already deposited films. The first section focuses on the material stability under the influence of synchrotron X-rays. Those high energetic radiation can cause damage to the materials [173, 174]. Additionally, XPCS is a very sensitive technique. Consequently, tiny movements in the chamber can already have an influence on the results. This will be further addressed in the second section of this chapter.

14.1 Material Stability under X-Ray Influence

To check the stability of the thin films made of the organic molecules introduced in this thesis, some ex situ pre-measurements of previously deposited thin films were performed at the synchrotron. Therefore, the films were radiated with coherent X-rays under stable conditions, i.e. stable room temperature. Since the films were grown at least several days before the measurements the speckle pattern should remain stable, resulting in fully correlated intensity functions for the XPCS analysis. If the material is damaged and burned by radiation, a decrease is expected in the intensity correlation functions.

For the pure organic films, the speckle pattern and subsequently the TTCs remained constant for several minutes. An exemplary result for a PEN and DIP film, which was radiated for 30 minutes, is shown in Fig. 14.1 a) and b), respectively. Neither TTC shows a drop in the intensity correlation, indicating no surface movement. Therefore, no radiation damage is to be expected in this time interval. For the measurements in the result chapters of this work (Chap. 9-11), this was checked again at the beginning of the series of measurements, but the results here already indicate a stability of these molecules over several tenths of a minute under the influence of X-rays.

To gain a better understanding in which cases beam damage is more likely pure and doped phenacene was investigated. Again, the pure material is stable for several minutes, as shown in Fig. 14.2 a). For comparison, also phenacene doped with gold was irradiated for the same amount of time. The TTC corresponding to this measurement is presented in Fig. 14.2 b). After approximately five minutes,

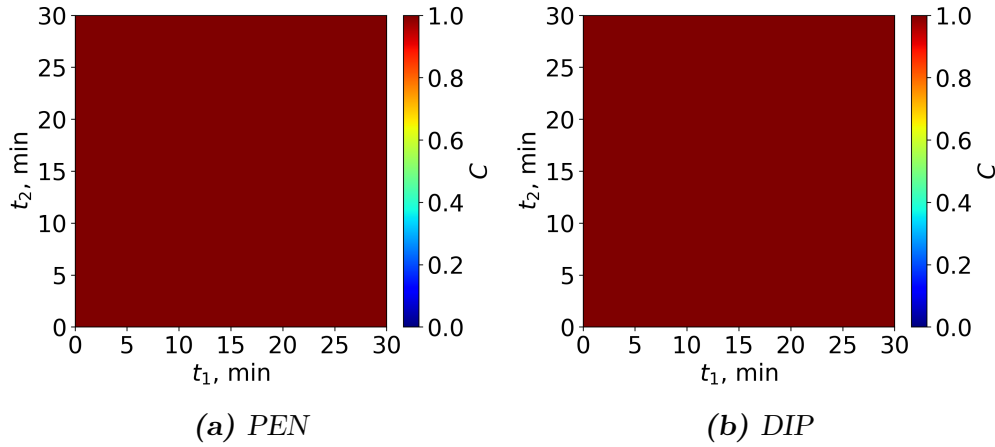


Figure 14.1: Stability check under X-ray influence of a) PEN and b) DIP under stable room temperature condition. The TTC was calculated at the 1. Bragg point at approximately $q_z = 0.04 \text{ \AA}^{-1}$. Due to the signal-to-noise ratio, an ROI of 100×100 pixels was selected for the analysis.

the intensity correlation decreases, indicating that the sample has been damaged by the beam. Similar behaviour can also be observed for phenacene doped with potassium.

In summary, it can be stated that pure organic films appear to be more stable under X-rays than those with additional material. This can be explained by the higher number of electrons in non-pure organic films, which lead to a stronger interaction with the X-ray beam. As a result, they are damaged more quickly.

14.2 Temperature Stability

During the initial measurements on ex situ thin films, instabilities were observed during the heating of the samples. Due to the sensitivity of the XPCS techniques, those were only visible in the analysis, specifically in the TTCs.

One example was the annealing of a 25 nm PEN film, which was heated from $70 - 80^\circ\text{C}$ with a ramp of $1^\circ\text{C}/\text{min}$. The measurement was carried out during 10 minutes of heating and 10 minutes after reaching a stable temperature. The resulting TTC is shown in Fig. 14.3. There, an immediate transition between the changing and the stable temperature is visible, regardless of the q -value. The data of this observation indicates a thermal expansion of the copper cladding on which the thin film is located. Nevertheless, the signal of this expansion seems to stabilize quickly. As a result, further measurements were taken promptly after the stabilization of the temperature to avoid a mixing of the signal of the surface dynamics with that of the setup, but still captures as many surface dynamics as possible that arise from the heating process.

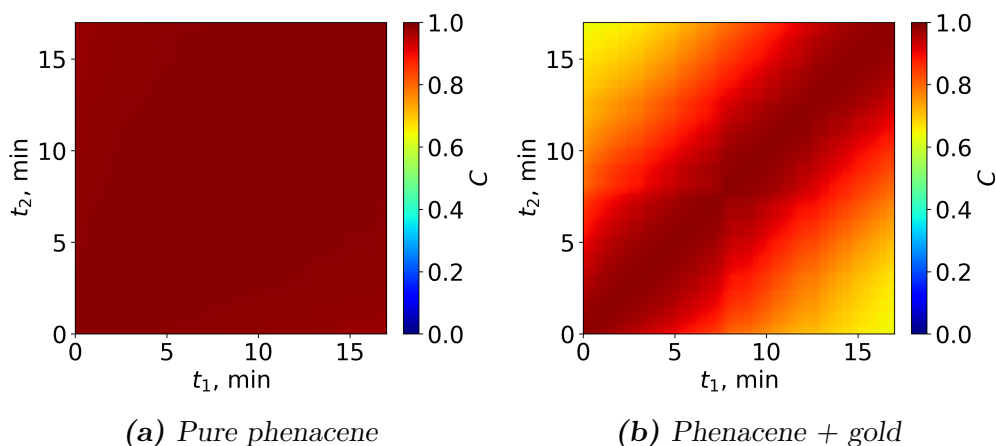


Figure 14.2: Stability check under X-ray influence of a) pure phenacene and b) phenacene with gold. The TTCs were calculated at $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 1.5 \cdot 10^{-3} \text{ \AA}^{-1}$.

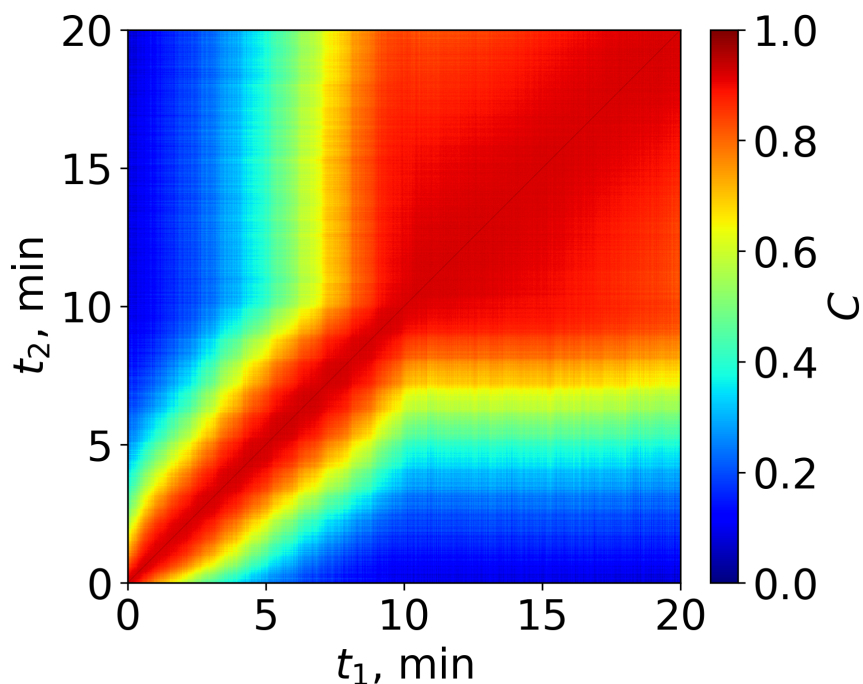


Figure 14.3: TTC of a PEN film during alternating temperatures. The film was heated from 70°C to 80°C for the first 10 minutes and then kept at a stable temperature for further 10 minutes. The calculation was performed at $q_z = 0.03 \text{ \AA}^{-1}$ and $q_{xy} = 1.5 \cdot 10^{-3} \text{ \AA}^{-1}$.

Chapter 15

q-Dependence of Simulated TTCs

In the following, the q -dependence of the simulation data will be investigated by using the cylinder representation. As an example scenario, the growth of 50 cylinders of the same size is used, growing in the range of $r = (175 - 205)$ nm and $h = (66 - 80)$ nm (see last section). For this case, the TTC is calculated at different q -positions, both vertically (q_z) and horizontally (q_{xy}), as shown in Fig. 15.1.

Structural changes in the TTC can be observed both in vertical and horizontal directions. In the vertical direction (Fig. 15.1 a), the structure repeats after 6×25 pixels. After this distance, the location of the ROI on the 2D detector is again similar placed between the intensity minima and maxima as before (see Fig. 9.14 b).

The experimental data shows the same phenomena (see Fig. 11.5). Unlike to the simulation, the repetition appears after a longer time period, since the size of the cylinders can deviate between the simulation and the experiment.

The horizontal direction shows a stronger structural change (Fig. 15.1 b). In this case, the ROI moves through the vertical intensity minima on the 2D detector with increasing q_{xy} , while it always remains in a horizontal intensity minimum. The interplay between two minima always results in the same number of heterogeneity peaks for all q_{xy} , hence the conclusions made in Sec. 9.2.2 stay unchanged. Although the simulations still show a significant structural change in the TTCs, only minor structural changes are observed in the experimental data along the horizontal direction. This deviation is potentially influenced by the noise in addition to the deviating island sizes.

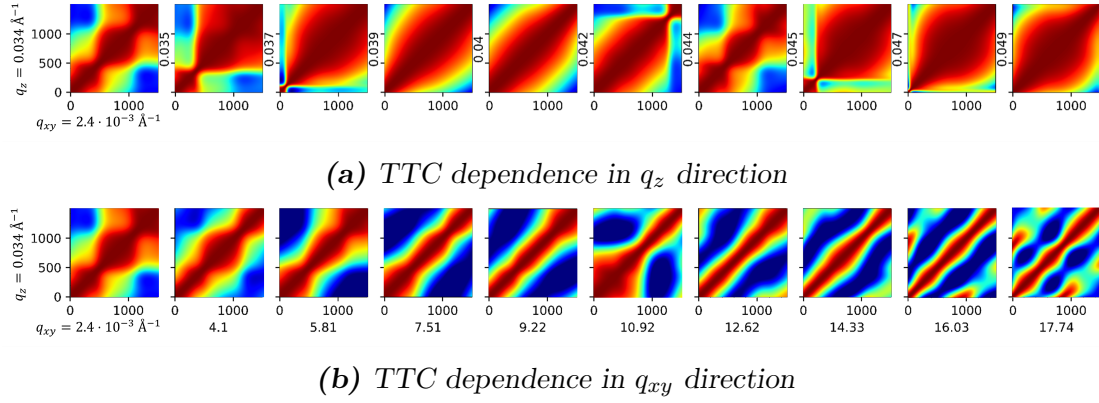


Figure 15.1: q -dependence of the TTC, calculated from the growth of 50 identical cylinders with increasing radius ($r = (175 - 205) \text{ nm}$) and height ($h = (66 - 80) \text{ nm}$). a) Dependence in vertical (q_z) direction. b) Dependence in horizontal (q_{xy}) direction.

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List of own Publications

- 1.) **I. Dax**, I. Zaluzhnyy, V. Starostin, Y. Chushkin, L. Pithan and F. Schreiber, Capturing the Dynamics of Structural Changes in Real Time during Thin-Film Annealing (submitted to *Phys. Rev. Lett.*)
- 2.) A. Pylypenko, E. Chulanova, F. Unger, J. Keck, I. Zaluzhnyy, **I. Dax**, M. Schwartzkopf, A. Gerlach, A. Hinderhofer, A. Meixner and F. Schreiber, Thin films of conjugated chalcogenadiazole: growth, structure and optical properties of substituted selenadiazoloquinoxaline (submitted to *J. Phys. Chem. C*)
- 3.) **I. Dax**, I. Zaluzhnyy, A. Pylypenko, N. Rußegger, V. Starostin, R. Rysov, F. Westermeier, M. Sprung, A. Hinderhofer, L. Pithan and F. Schreiber, Insight into heterogeneous dynamics of growing islands using coherent x-ray scattering, *New J. Phys.* 25 (2023), 103033.
- 4.) A. Greco, V. Starostin, E. Edel, V. Munteanu, N. Rußegger, **I. Dax**, C. Shen, F. Bertram, A. Hinderhofer, A. Gerlach and F. Schreiber, Neural network analysis of neutron and X-ray reflectivity data: automated analysis using mlreflect, experimental errors and feature engineering, *J. Appl. Cryst.* 55 (2022), 362.

List of Contributions

Chapters 9 and 10 of this Ph.D. thesis contain collaborative work based on two published or submitted manuscripts. All figures and tables taken from previous publications are referenced in the respective captions.

Analyzing Island Dynamics during DIP Thin Film Growth (Chapter 9)

Publication

I. Dax, I. Zaluzhnyy, A. Pylypenko, N. Russegger, V. Starostin, R. Rysov, F. Westermeier, M. Sprung, A. Hinderhofer, L. Pithan and F. Schreiber, Insight into heterogeneous dynamics of growing islands using coherent x-ray scattering, New J. Phys. 25 (2023), 103033.

Supervision & Scientific Input

The project was initiated and supervised by F. Schreiber, A. Hinderhofer and I. Zaluzhnyy. Further, L. Pithan significantly contributed to the project through scientific discussions.

Sample & Measurement Preparation

The AFM and XRR measurements of the DIP thin films, as well as the preparation of the beamtime, were done by I. Dax.

Beamtime at the Synchrotron (DESY)

The beamtime data was collected by I. Zaluzhnyy, A. Pylypenko, N. Rußegger, R. Rysov, and I. Dax, supported by the beamline scientists F. Westermeier and M. Sprung.

Data Analysis

The data analysis was carried out by I. Dax.

Simulation

Part of the simulation code for the real space was originally developed by L. Pithan and E. Empting and adapted to the project by I. Dax. The idea and first simple use of the BornAgain software came from V. Starostin.

Paper Writing

The main part of the paper was written by I. Dax. In addition, I. Zaluzhnyy and F. Schreiber contributed to the writing of the paper. All co-authors contributed to the proofreading.

Structural Surface Changes during the Annealing of PTCDI-C8 (Chapter 10)

Publication

I. Dax, I. Zaluzhnyy, V. Starostin, Y. Chushkin, L. Pithan and F. Schreiber, Capturing the Dynamics of Structural Changes in Real Time during Thin-Film Annealing (submitted to Phys. Rev. Lett.).

Supervision & Scientific Input

The project was supervised by F. Schreiber and I. Zaluzhnyy.

Sample & Measurement Preparation

The AFM and XRR measurements of the PTCDI-C8 thin films, as well as the preparation of the beamtime, were done by I. Dax.

Beamtime at the Synchrotron (ESRF)

The beamtime data was collected by I. Zaluzhnyy, V. Starostin, L. Pithan, and I. Dax, supported by the beamline scientist Y. Chushkin.

Data Analysis

The data analysis was carried out by I. Dax.

Simulation

The simulation was performed by I. Dax.

Paper Writing

The main part of the paper was written by I. Dax. In addition, I. Zaluzhnyy and F. Schreiber contributed to the writing of the paper. All co-authors contributed to the proofreading.

Complementary Data (Chapter 11)

Sample & Measurement Preparation

All AFM and XRR measurements of the thin films were performed by I. Dax, with support of H. Mauser and L. Fischer. An overall introduction to the laboratory methods and preparation of the samples was given by G. Duva. Support during sample measurements was given by I. Zaluzhnyy.

Beamtime at the Synchrotron (DESY & ESRF)

The data was collected by I. Zaluzhnyy, E. Chulanova, A. Pylypenko, Niels Scheffczyk, J. Hagara, N. Rußegger, R. Rysov, A. Hinderhofer, M. Zwadlo, J. Hagenlocher and I. Dax, supported by the beamline scientists F. Westermeier, M. Sprung and F. Zontone.

Data Analysis

The data analysis was carried out by I. Dax.

List of Acronyms

OSCs	organic solar cells
OFETs	organic field-effect transistors
OLEDs	organic light-emitting diodes
DIP	diindenoperylene
PTCDI-C8	N,N'-dioctyl-3,4,9,10-perylenedicarboximide
PEN	pentacene
C₆₀	buckminsterfullerene
GISAXS	grazing-incidence small-angle X-ray scattering
TTC	two-time correlation
XPCS	X-ray photon correlation spectroscopy
OMBD	organic molecular beam deposition
AFM	atomic force microscopy
XRR	X-ray reflectivity
QCM	quartz crystal microbalance
2D	two dimensional
3D	three dimensional
COM	center of mass
DWBA	distorted wave Born approximation
BA	BornAgain
ROI	region of interest
ML	monolayer
DESY	Deutsches Elektronen-Synchrotron
ESRF	European Synchrotron Radiation Facility

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