Title
X-ray scattering studies of structure and dynamics of surfaces and interfaces of polymeric liquids

Permalink
https://escholarship.org/uc/item/1304106d

Author
Jiang, Zhang

Publication Date
2007

Peer reviewed|Thesis/dissertation
X-ray Scattering Studies of Structure and Dynamics of Surfaces and Interfaces of Polymeric Liquids

A dissertation submitted in partial satisfaction of the requirements for the degree Doctor of Philosophy in Physics by Zhang Jiang

Committee in charge:
Professor Sunil K. Sinha, Chair
Professor John E. Crowell
Professor Terence T. Hwa
Professor Douglas E. Smith
Professor Peter G. Wolynes

2007
The dissertation of Zhang Jiang is approved, and it is acceptable in quality and form for publication on microfilm:

Chair

University of California, San Diego

2007
To my beloved family
<table>
<thead>
<tr>
<th>TABLE OF CONTENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Signature Page ........................................ iii</td>
</tr>
<tr>
<td>Table of Contents ........................................ v</td>
</tr>
<tr>
<td>List of Figures ........................................... vii</td>
</tr>
<tr>
<td>List of Tables ............................................ x</td>
</tr>
<tr>
<td>Acknowledgements ......................................... xi</td>
</tr>
<tr>
<td>Vita and Publications ..................................... xiii</td>
</tr>
<tr>
<td>Abstract of the Dissertation ............................ xv</td>
</tr>
<tr>
<td>1 Introduction ........................................... 1</td>
</tr>
<tr>
<td>2 Principles of Surface Scattering ....................... 4</td>
</tr>
<tr>
<td>2.1 X-ray Interactions with Matter ..................... 4</td>
</tr>
<tr>
<td>2.1.1 Refractive Index .................................. 5</td>
</tr>
<tr>
<td>2.1.2 Differential Cross Section ....................... 7</td>
</tr>
<tr>
<td>2.1.3 Born Approximation ............................... 7</td>
</tr>
<tr>
<td>2.2 Structure of Liquid Surfaces ....................... 10</td>
</tr>
<tr>
<td>2.3 Elastic X-ray Scattering from Surfaces ............. 15</td>
</tr>
<tr>
<td>2.3.1 Reflectivity ...................................... 19</td>
</tr>
<tr>
<td>2.3.2 Diffuse Scattering and Distorted Wave Born Approximation ... 20</td>
</tr>
<tr>
<td>2.3.3 Experimental Considerations .................... 25</td>
</tr>
<tr>
<td>2.4 X-ray Photon Correlation Spectroscopy ............. 27</td>
</tr>
<tr>
<td>2.4.1 Coherent Scattering and Speckles ............... 27</td>
</tr>
<tr>
<td>2.4.2 Photon Correlation Spectroscopy ................ 29</td>
</tr>
<tr>
<td>3 Surface Dynamics on Molten Polystyrene Films ........ 35</td>
</tr>
<tr>
<td>3.1 Capillary Waves on Molten Polymer Surfaces ....... 36</td>
</tr>
<tr>
<td>3.2 Sample Preparation .................................. 41</td>
</tr>
<tr>
<td>3.3 Experiment Details .................................. 42</td>
</tr>
<tr>
<td>3.3.1 Instrumentation and Experiment Setup .......... 42</td>
</tr>
<tr>
<td>3.3.2 XPCS Data Reduction ............................ 47</td>
</tr>
<tr>
<td>3.4 Surface Tension ..................................... 48</td>
</tr>
<tr>
<td>3.5 Surface Dynamics of Spin-cast Films at $T \gg T_g$ .... 49</td>
</tr>
<tr>
<td>3.5.1 Thick Films ($d \gg R_g$) ........................ 51</td>
</tr>
<tr>
<td>3.5.2 Ultra-thin Films ($d \sim R_g$) .................... 57</td>
</tr>
<tr>
<td>3.6 Surface Dynamics of Spin-cast Films at near $T_g$ ..... 63</td>
</tr>
<tr>
<td>3.7 Dry Brushes ......................................... 69</td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>Far field approximation.</td>
<td>9</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Sketch of a rough surface.</td>
<td>11</td>
</tr>
<tr>
<td>Figure 2.3</td>
<td>Sketch of the particle motion in free capillary waves.</td>
<td>14</td>
</tr>
<tr>
<td>Figure 2.4</td>
<td>Sketch of the surface (xy plane) scattering geometry.</td>
<td>15</td>
</tr>
<tr>
<td>Figure 2.5</td>
<td>A system consisting of $N$ interfaces and $N+1$ layers.</td>
<td>17</td>
</tr>
<tr>
<td>Figure 2.6</td>
<td>Schematic of the scattering geometry in the DWBA theory.</td>
<td>23</td>
</tr>
<tr>
<td>Figure 2.7</td>
<td>Frequency-scattering vector space covered by x-ray photon correlation spectroscopy (XPCS) and complementary techniques.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 2.8</td>
<td>Schematic illustrations of detection methods.</td>
<td>30</td>
</tr>
<tr>
<td>Figure 3.1</td>
<td>Geometry and notations of a supported single-layer film.</td>
<td>37</td>
</tr>
<tr>
<td>Figure 3.2</td>
<td>Calculated relaxation time constants of the over-damped surface capillary waves on a viscous PS single-layer film and on a bulk PS liquid.</td>
<td>40</td>
</tr>
<tr>
<td>Figure 3.3</td>
<td>Schematic of (a) a spin-cast PS film, and (b) a PS brush.</td>
<td>42</td>
</tr>
<tr>
<td>Figure 3.4</td>
<td>Grazing incidence x-ray scattering and XPCS apparatus at the Advanced Photon Source. The dashed-line box denotes 8-ID-I end station.</td>
<td>43</td>
</tr>
<tr>
<td>Figure 3.5</td>
<td>Geometry of the scattering and the wave vector transfer.</td>
<td>44</td>
</tr>
<tr>
<td>Figure 3.6</td>
<td>Schematic of Sector 8-ID-E end station.</td>
<td>46</td>
</tr>
<tr>
<td>Figure 3.7</td>
<td>Measured and simulated time-averaged surface diffuse scattering.</td>
<td>49</td>
</tr>
<tr>
<td>Figure 3.8</td>
<td>Structure factors extracted from static diffuse scattering.</td>
<td>50</td>
</tr>
<tr>
<td>Figure 3.9</td>
<td>Surface tensions of PS films.</td>
<td>50</td>
</tr>
<tr>
<td>Figure 3.10</td>
<td>Autocorrelation functions from a PS film of $M_W = 123k$ g/mol and thickness 84 nm at 160 °C.</td>
<td>51</td>
</tr>
<tr>
<td>Figure 3.11</td>
<td>Thickness scaling plot of the over-damped capillary waves.</td>
<td>52</td>
</tr>
<tr>
<td>Figure 3.12</td>
<td>Viscosity vs. temperature obtained from PS films of various molecular weights.</td>
<td>53</td>
</tr>
<tr>
<td>Figure 3.13</td>
<td>(a) Experiment ($\bigcirc$) and calculated relaxation time constants for a PS film of $M_W = 123k$ g/mol and total thickness $d \approx 80$ nm at 150 °C. (b) and (c) are the logarithmic intensity map of $1/</td>
<td>\chi^{(2)}<em>{zz}(q</em>{</td>
</tr>
<tr>
<td>Figure 3.14</td>
<td>Experimental relaxation time constants ($\bigcirc$) for PS film of $M_W = 123k$ g/mol and thickness $d \approx 80$ nm at 150 °C, compared to theoretical calculations for various film models (1)-(4) shown in the inset.</td>
<td>55</td>
</tr>
<tr>
<td>Figure 3.15</td>
<td>Calculated relaxation time constants from various supported PS films at 150 °C.</td>
<td>56</td>
</tr>
<tr>
<td>Figure 3.16</td>
<td>Kelvin function and its approximations at small $x$ values.</td>
<td>58</td>
</tr>
<tr>
<td>Figure 3.17</td>
<td>Transverse diffuse scattering at $q_z = 2$ nm$^{-1}$ for PS (123k) films of thickness $2R_g$ and $4R_g$ at 195 °C.</td>
<td>59</td>
</tr>
<tr>
<td>Figure 3.18</td>
<td>Intensity-intensity autocorrelation functions obtained from PS films of $M_W = 123k$ g/mol and thickness (a) $4R_g$, (b) $2R_g$ and (c) $1R_g$ at 195 °C at four different in-plane wave vectors.</td>
<td>60</td>
</tr>
<tr>
<td>Figure 3.19</td>
<td>Measured time constants for PS films of various molecular weights and relative thicknesses at various temperatures.</td>
<td>61</td>
</tr>
</tbody>
</table>
Figure 3.20: Viscosity (♦) as a function of molecular weight for (a) $2R_g$ films at 185 °C, and (b) $4R_g$ films at 176 °C.

Figure 3.21: The $g_2$ functions obtained at an in-plane wave vector $q_\parallel = 1.8 \times 10^{-2}$ nm$^{-1}$ from a PS film of $M_W=129$ k g/mol and thickness $d=160$ nm at various temperatures.

Figure 3.22: $M_W-T$ diagram constructed from XPCS measurements of the surface dynamics on supported PS films.

Figure 3.23: Over-damped relaxation time constant $\tau$ vs. in-plane wave vector $q_\parallel$ for PS films of an identical thickness ($\sim 160$ nm) but different molecular weights at (a) 151 °C and (b) 111 °C.

Figure 3.24: Fitted viscosity (⃝) vs. molecular weight for PS films of an identical thickness 160 nm, compared with bulk viscosity values (♦).

Figure 3.25: (a) Thickness-scaling plot of $\tau/d$ vs. $q_\parallel$ for films of $M_W=129$ k g/mol and various thicknesses at two temperatures: 111 °C (top-right) and 151 °C (bottom-left). (b) $\tau/d$ vs. $q_\parallel$ for the film of $M_W=290$ k g/mol and $d=160$ nm at 111 °C.

Figure 3.26: $g_2$ vs. time delay at $q_\parallel = 5.3 \times 10^{-3}$ nm$^{-1}$ for a 26 nm thick PS brush and 29 nm thick spin-cast film ($M_n=65$ k g/mol) at 170 °C.

Figure 3.27: $g_2$ functions for a 39 nm thick PS brush at 190 °C at various in-plane wave vectors as labeled. Curves are shifted for clarity.

Figure 3.28: $g_2$ at $q_\parallel = 3.4 \times 10^{-3}$ nm$^{-1}$ for PS brushes of thickness 48, 39 and 26 nm. $g_2$ for the 9 nm thick PS brush was shown at $q_\parallel = 3.1 \times 10^{-3}$ nm$^{-1}$.

Figure 3.29: $g_2$ functions for a 48 nm thick PS brush (top), and for a 30 nm thick PnBA brush (bottom) at various temperatures.

Figure 4.1: Chemical structure of polystyrene and poly(4-bromo styrene).

Figure 4.2: AFM images from bilayers of (a) PS/PBrS, and (b) PBrS/PS.

Figure 4.3: (a) Simulation of the normalized EFI as a function of incident angle $\alpha_i$ and film depth $z$. (b) EFI as a function of incident angle at the surface, interface and substrate.

Figure 4.4: (a) Measured diffuse x-ray intensity from a bilayer of PS(200k, 95 nm)/PBrS(350k, 100 nm) at 175.6 °C. (b) Comparison of the measured and predicted diffuse scattering intensities as a function of incident angle.

Figure 4.5: $g_2$ functions from PS single and PS/PBrS bilayer films measured at $q_\parallel = 4.3 \times 10^{-3}$ nm$^{-1}$.

Figure 4.6: $\tau$ vs. $q_\parallel$ at 195 °C.

Figure 4.7: Temperature and thickness dependence of the relaxation time constants of the bottom interface.

Figure 5.1: Schematic of a vacuum/liquid/substrate system.

Figure 5.2: Calculated $W(K_z, k_{z,2}(\alpha_i), k_{z,2}(\alpha_f))$ as a function of $K_z$ and the incident angle $\alpha_i$ for a 105 nm PS film on a silicon substrate.

Figure 5.3: Comparison of the bulk $S(q)$ (line) and calculated $\tilde{S}(q)$ (▽) at a fixed incident angle $\alpha_i = 0.225°$ for a 20 nm PS film.

Figure 5.4: $\tilde{S}(q)$ values extracted from diffuse scattering intensities for different film thicknesses at various temperatures.
Figure 5.5: Diffuse scattering at a fixed wave vector with $q_\parallel = 2.515$ nm$^{-1}$ and $q_z = 0.616$ nm$^{-1}$ as a function of incident angle for different PS film thicknesses at 160 °C. 99

Figure 5.6: (a) Extrapolated bulk $S(0)$ as a function of temperature for different film thicknesses. (b) Comparison of the obtained compressibility values with the bulk values. 100

Figure 6.1: AFM images showing phase separations in supported DOPC/SM (1:1) bilayers with various CH concentrations. 104

Figure 6.2: Chemical structures of lipid molecules under study. 105

Figure 6.3: Fluid cell used in x-ray scattering experiments. 106

Figure 6.4: (a) X-ray reflectivities from 1:1 DOPC:SM bilayers with various CH concentrations. (b) Corresponding scattering length density profiles. 108

Figure 6.5: (a) X-ray reflectivities from 2:1 DOPC:SM bilayers with various CH concentrations. (b) Corresponding scattering length density profiles. 109

Figure 6.6: (a) X-ray reflectivities from 1:2 DOPC:SM bilayers with various CH concentrations. (b) Corresponding scattering length density profiles. 110

Figure 6.7: (a) X-ray reflectivities from 1:4 DOPC:SM bilayers with various CH concentrations. (b) Corresponding scattering length density profiles. 111

Figure 6.8: (a) Box model of 4 slabs for bilayers composed of pure DOPC. (b) Box model of 5 slabs for bilayers composed of lipid mixtures of DOPC and SM. 112

Figure 6.9: Neutron TOF intensity map (background subtracted) of the diffuse scattering from a bilayer of a mixture of 7:3 DLPC and DSPC lipids. 114

Figure 6.10: Calculated scattering structure factor. 114

Figure A.1: Complex plane. 120

Figure B.1: Scattering geometry of a single surface. 122

Figure B.2: Schematic of multiple scattering processes. 124

Figure C.1: Geometry and notations of a supported bilayer film. 126
LIST OF TABLES

Table 3.1: The radius of gyration $R_g$ of PS of different molecular weights. . . . 58
Table 3.2: Sample characteristics of polymer brushes. . . . . . . . . . . . . . . 70

Table 4.1: Neutron reflectivity results and calculation of a PS/PBrS film. . . . 81
Table 4.2: Surface and interfacial tension of a supported bilayer composed of
PS(200k, 95 nm)/PBrS(350k, 100 nm). . . . . . . . . . . . . . . . . . . . . 84
ACKNOWLEDGEMENTS

First of all, I would like to thank my thesis advisor, Professor Sunil Sinha, for his always helpful and encouraging guidance, and constant support. His serious attitude to science and optimistic (i.e., humorous but thoughtful) wisdom of life have inspired me, and will certainly benefit my future.

This work was done in collaboration with many people. I owe a great and special thank-you to Hyunjung Kim and Larry Lurio for contributing tremendous amount of time and knowledge to this research. I am also grateful to Jyotsana Lal, Miriam Rafailovich, Simon Mochrie, Ali Dhinojwala, Mark Foster, Atul Parikh, Xuesong Hu, Xuesong Jiao, and Mrinmay Mukhopadhyay for many useful discussions and contributions. My colleague Elizabeth Blackburn is also appreciated for previewing the draft of my thesis and providing very useful suggestions. Special thanks go out to my fellow researcher and friend Dr. Tuana Ghaderi who kept debating with me on a vast spectrum of issues and taught me how to use \LaTeX for scientific writing. I would also thank John Crowell, Terence Hwa, Douglas Smith, and Peter Wolynes for their interest and service on my thesis committee. The full list of people to whom I owe thanks is very long, so here I will simply give my sincere thanks to all who have helped me and contributed to this work.

This research was funded by NSF Grant No. DMR-0209542. Most of the work was conducted on Sector 8-ID at the Advanced Photon Source (APS), Argonne National Laboratory. I would like to acknowledge the beamline staff Suresh Narayanan, Alec Sandy, and Michael Sprung for their scientific and technical support. Use of the APS was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

Finally, I would like to give my inexpressible thanks to my parents and my wife for their infinite support and encouragement over the past few years.

The text of Chapter 3, in part, is a reprint of the material as it appears in

- Z. Jiang, H. Kim, X. Jiao, H. Lee, Y.-J. Lee, Y. Byun, S. Song, D. Eom, C. Li, M.


The text of Chapter 4, in part, is a reprint of the material as it appears in


The text of Chapter 5, in part, is a reprint of the material as it appears in


The text of Chapter 6, in full, is based on the preliminary work accomplished in collaboration with A. Szmodis and A. Parikh in University of California at Davis. Sector 1-BM-C at the Advanced Photon Source, and SPEAR at the Manual Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory are acknowledged for providing facilities.

xii
VITA

2001 B.S. in Applied Physics, Department of Modern Physics
University of Science and Technology of China, Hefei, China

2001–2002 Teaching Assistant, Department of Physics
University of California at San Diego, La Jolla, California

2002–2007 Research Assistant, Department of Physics
University of California at San Diego, La Jolla, California

2003 M.S. in Physics
University of California at San Diego, La Jolla, California

2003 Summer National School on Neutron and X-ray Scattering
Argonne National Laboratory, Chicago, Illinois

2007 Ph.D. in Physics
University of California at San Diego, La Jolla, California

PUBLICATIONS


ABSTRACT OF THE DISSERTATION

X-ray Scattering Studies of Structure and Dynamics of Surfaces and Interfaces of Polymeric Liquids

by

Zhang Jiang

Doctor of Philosophy in Physics

University of California San Diego, 2007

Professor Sunil K. Sinha, Chair

Thermally excited capillary waves are present and dominate the morphology and dynamics at the surfaces and interfaces of polymer films in a molten state. A statistical description of the capillary waves in terms of the temporal and lateral position dependent height-height correlation functions is directly related to the scattering structure factor. This can be calculated using surface scattering theories and measured by surface sensitive diffuse scattering techniques. A large part of this thesis is devoted to the investigation of the surface and interfacial dynamics of supported single layer polystyrene and bilayer polystyrene/poly(4-bromo styrene) films using x-ray photon correlation spectroscopy (XPCS), a recently developed time-resolved coherent scattering technique on high-brilliance third-generation synchrotron radiation facilities. The static properties, such as thickness, surface tension, and interfacial width, can be obtained by conventional reflectivity and static diffuse scattering experiments. Apart from the surface and interfacial capillary waves, inhomogeneities induced by thermal density fluctuations in the interior of the film also contribute to the total diffuse scattering. Therefore, a bulk scattering theory for thin film geometry is developed and compared with the experimental results from supported molten polystyrene films. We also present the first attempt to probe the structure and dynamics of single lipid bilayers consisting of phase-separated raft-like domains using x-ray and neutron scattering techniques.
Introduction

The term “polymer” is derived historically from the Greek words: “poly” meaning “many”, and “mer” meaning “part”. Despite the fact that natural polymer materials, such as tar, shellac and amber, had been used for centuries, it was not until the 1920s, when Hermann Staudinger proposed the macromolecular hypothesis, that people started to realize that polymers are large molecules composed of long chains of simple repeating chemical units, or “monomers”, held together by covalent bonds. After that the main concepts of polymer science were established, many synthesis methods were developed and refined, and a wide variety of chemical and physical properties were observed in different polymers. One particularly interesting example is the properties of polymer films. Significantly affected by the near-surface region, thin polymer films are of great interest both for basic scientific reasons and on account of their importance in a variety of technological and industrial applications. The latter include coatings, adhesives, biocompatible surfaces for medical implants, computer disk drives, sensor films and electronic packaging materials. The scientific interest in polymer surfaces and polymer films stems from the fact that there are still many aspects of the conformation and dynamics of polymer chains in these systems that are poorly understood from a basic point of view. Examples include the conformation of polymer chains and the monomer density profile at interfaces, the nature of the fluctuations at the surface and within the polymer film, the effects of substrate-polymer interaction and the dynamical behavior of free polymer surfaces and film interiors near the glass transition temperature.

This dissertation mainly considers the structure and dynamics at the surfaces and interfaces of polymer liquids. The first approach to describe the structure of liquid
surfaces was initiated by van der Waals, who considered the liquid/vapor interfacial region as a region whose density changes smoothly from that of the liquid phase to that of the gas phase [169]. An alternative description proposed by Buff, Lovett, and Stillinger [18] assumes a step-like profile at the surface, patterned with temporal and lateral position dependent thermal height fluctuations, the collective effect of which leads to “capillary waves”. It follows that the structural and dynamic information of liquid surfaces can be fully addressed by means of a statistical description of the capillary waves in term of the height-height correlation function [25,164], which can be obtained through hydrodynamic theories. This height-height correlation function is closely related to the scattering structure factor which can be calculated within the Born approximation or distorted wave Born approximation (DWBA) and directly measured by scattering techniques. An enormous number of experiments have been conducted on liquid surfaces in the last two decades and have shown that the capillary wave theory can explain amazingly well both the static structures (surface tension, roughness, and etc.) and dynamic behaviors (fluctuation damping rate, propagating frequency, and etc.), not only for simple liquids [13, 35, 44, 56, 131, 133] but also for polymer liquids [66, 71, 76, 89, 93, 103, 139, 141, 177].

The significantly increased brilliance of x-ray beams since the emergence of the third-generation synchrotron radiation sources enables much more detailed investigations of polymer surface science, on smaller length scales than light scattering can reach. In addition, the use of undulators in synchrotrons [2] produces coherent (or partially coherent) x-rays, so that conventional experiments using coherent laser light, such as holography and photon correlation spectroscopy, can be extended to the x-ray regime, and have yielded prolific results in polymer science.

The organization of the dissertation is as follows: Chapter 2 conducts a brief review of the principles of surface x-ray scattering, where the techniques used here, such as x-ray reflectivity, transverse diffuse scattering, and x-ray photon correlation spectroscopy (XPCS), are discussed in combination with the surface capillary wave theory. Chapter 3, the main body of the dissertation, presents XPCS measurements of the surface dynamics from silicon supported molten polystyrene (PS) films. Chapter 4 focuses on the surface and interfacial structures and dynamics of bilayers composed of polystyrene (PS) on top of poly(4-bromo styrene) (PBrS) measured by x-ray scattering in a standing wave geometry and complementary neutron reflectivity techniques. Apart from the surface
and interface contributions to the total diffuse scattering, thermal density fluctuations within the interior of the film are another large source of scattering. Therefore, in Chapter 5, the bulk scattering theory is developed for thin films and compared with experimental results. Chapter 6 presents our first attempt to probe the raft-like domains in supported single lipid (also a type of polymer) bilayer films using x-ray and neutron diffuse scattering techniques. In Chapter 7, the main findings of this dissertation are summarized, and possible research directions that may be extended from this work are discussed briefly.
Principles of Surface Scattering

In this chapter the principles of x-ray scattering from surfaces will be reviewed. We will begin with the interactions of x-ray photons with matter, where the Born approximation is generally employed to calculate the differential cross section of a scattering process. The concept of the height-height correlation function will then be discussed for liquid surfaces, followed by detailed surface scattering theories. Finally the principles of x-ray photon correlation spectroscopy will be discussed for the study of dynamics.

2.1 X-ray Interactions with Matter

The electromagnetic wave basically interacts with electrons. Although there exists a weak interaction due to the electron spin or its magnetic moment, this phenomenon can be considered negligible when compared to that between the electric field and the electronic charge. When a photon hits an atom, it meets one of the following fates: elastic scattering, inelastic scattering or absorption. In elastic scattering, the energy of the photon is conserved, while in the inelastic scattering regime, there are two possibilities for energy loss: Compton scattering (ejection of an electron) or Raman scattering (the atom is boosted into an excited state). In the absorption process, the photon energy is completely transferred to the atom. Meanwhile fluorescence might occur with a lower-energy photon emitted. The energy transfer involved in an inelastic scattering process, atomic excitation for example, is of the order of 1 eV. It is a big challenge to resolve an energy change of 1 eV in a typical x-ray photon of $10^4$ eV. Hence, in spite of complicated processes associated with the interaction of the electromagnetic field and the matter, the discussions will focus solely on the elastic Thompson scattering process.
2.1.1 Refractive Index

Consider the interaction between a free electron and an electric field. The response of the electron in frequency space is

\[ \mathbf{x}(\omega) = -\frac{e}{m_e\omega^2}\mathbf{E}(\omega). \]  

(2.1)

At this moment, we assume that all the electrons in a compound are free from interactions with the nuclei and with themselves. The polarization (defined as the electric dipole moment per unit volume) of this compound in an external driving electric field is

\[ \mathbf{P}(\omega) = \left[ eN_A \sum_j \frac{\rho_{m,j}}{A_j} f_j^0 \right] \mathbf{x}(\omega), \]

(2.2)

where \( N_A \) is Avogadro’s number, and \( \rho_{m,i} \) is the mass density of element \( i \) with atomic weight \( A_j \) and atomic form factor \( f_j^0 \). The atomic form factor is defined as the Fourier transform of the electron density distribution of the atom, and is approximately equal to the atomic number \( Z_j \) [2]. Since the electric susceptibility \( \chi_e(\omega) \equiv [\mathbf{P}(\omega)/\mathbf{E}(\omega)]/\varepsilon_0 \), one can write the dielectric constant,

\[ \varepsilon(\omega) = \varepsilon_0(1 + \chi_e) = \varepsilon_0 \left[ 1 - \frac{\lambda^2}{\pi r_e N_A \sum_j \frac{\rho_{m,j}}{A_j} f_j^0} \right], \]

(2.3)

where \( \lambda = \frac{2\pi c}{\omega} \) is the x-ray wavelength, and \( r_e = \frac{e^2}{4\pi\varepsilon_0 m_e c^2} = 2.81794 \times 10^{-15} \text{ m} \) is the Thompson scattering length of the electron (also known as the classical electron radius).

In an atom, the electrons in the outer shells are loosely bound with a resonant energy \( E_j \) much less than the typical x-ray energy \( E \), thus these electrons respond to an external driving electric field like free electrons. However, this is not valid for tightly bound electrons in the inner shells. For instance, the binding energy of a K shell electron is comparable to the x-ray photon energy. Therefore, these electrons are expected to interact weakly with the electric field. On the other hand, the screening effect due to the outer shell electrons also weakens the external driving electric field reaching the inner shell electron. Overall, the scattering length of an atom is expected to be reduced by some amount, denoted by \( f'(\omega) \). The response of the bound electrons usually follows the driving field with a phase lag, which can be described by a dissipation term \( if''(\omega) \). Thus the atomic form factor is modified to include the dispersion and
absorption corrections \[2,69\],
\[
f_j(\omega) = f_j^0 + f_j'(\omega) + i f_j''(\omega).
\] (2.4)

The refractive index of a material describes the extent to which the phase velocity of the electromagnetic radiation is slowed relatively to the velocity in vacuum: \(n = \sqrt{\varepsilon \mu / \varepsilon_0 \mu_0}\). For non-magnetic substances, assuming that the frequency of the radiation \(\omega\) is much larger than the atomic resonant frequency \(\omega_j\) in the x-ray scattering regime, the refractive index may be approximated as \[2,127,164\]
\[
n(r, \omega) \approx 1 - \delta(r, \omega) + i \beta(r, \omega),
\] (2.5)

with the dispersion and absorption terms
\[
\delta(r, \omega) = \frac{\lambda^2}{2\pi} r e N_A \sum_j \frac{\rho_{m,j}(r)}{A_j} \left[ f_j^0 + f_j'(\omega) \right],
\] (2.6)

and
\[
\beta(r, \omega) = \frac{\lambda^2}{2\pi} r e N_A \sum_j \frac{\rho_{m,j}(r)}{A_j} f_j''(\omega).
\] (2.7)

If the substance is macroscopically homogeneous, i.e., the electron density \(\rho(r)\) is a constant, and the radiation frequency \(\omega\) is far from the resonant frequency edge \(\omega_j\), the refractive index can be well approximated by
\[
n \approx 1 - \frac{\lambda^2}{2\pi} r e \rho + i \frac{\lambda}{4\pi} \mu,
\] (2.8)
where \(\mu\) is the linear absorption coefficient.

In-house x-ray tubes typically use copper as the stopping target, resulting in emission of x-rays at the so-called \(K\alpha\) line at \(E_{K\alpha} = 8.04\) keV superimposed on a broad background of “bremsstrahlung” radiation. The dispersion \(\delta\) is typically \(\sim 10^{-6}\), and the dissipation \(\beta\) is one to three orders of magnitude smaller. Consider polystyrene \((C_8H_8)_n\) as an example. The mass density is \(\rho_m \approx 1\) g/cm\(^3\) and so at the in-house x-ray energy \(E_{K\alpha} = 8.04\) keV (the corresponding wavelength is \(\lambda = 1.54\) Å), \(\delta = 3.46 \times 10^{-6}\) and \(\beta = 4.75 \times 10^{-9}\).

It is very important to note that, neglecting the absorption term \(\beta\), the refractive index \(n\) in the x-ray regime is smaller than one, whereas in the visible light regime it is larger than one. Although \(\delta\) is very close to zero, at the air/medium interface total external reflection can exist when x-rays are incident onto the medium from the air. Below a critical angle \(\alpha_c \approx \sqrt{2}\delta\), all the incident photons are 100% reflected.
This provides a very powerful technique to characterize surface and interface properties through grazing incidence diffraction measurements and to set up standing waves within thin films to selectively investigate regions at a particular depth.

2.1.2 Differential Cross Section

To tell how strongly a substance scatters x-rays, we need to quantify the scattering strength with the differential cross section \((d\sigma/d\Omega)\) \(^2\). Start with scattering events in which an x-ray beam with flux \(\Phi_0\). The number of scattered photons per second, denoted by \(I_{sc}\), collected by a x-ray detector mounted downstream that subtends a solid angle \(\Delta\Omega\), is written as

\[
I_{sc} = \Phi_0 \Delta\Omega \left( \frac{d\sigma}{d\Omega} \right),
\]

which defines the differential cross section.

2.1.3 Born Approximation

The Born approximation is probably one of the most widely used approximations in scattering theory\(^1\). It is also known as the kinematical approximation, in which the weak-scattering regime is dealt with and therefore, multiple scattering effects may be neglected for simplicity.

We start with the the Helmholtz equation

\[
(\nabla^2 + k^2) \psi(r) = V(r)\psi(r),
\]

where \(k\) is the wave number in a free space and \(V(r)\) is the potential. We will show later on that for electromagnetic radiation, the “potential” is related to the spatial dependence of the refractive index. The solution of Eq. (2.10) is generally given by

\[
\psi(r) = \psi_0(r) + \int dr' G(r - r')V(r')\psi(r'),
\]

where \(\psi_0(r)\) is the solution of the homogeneous equation

\[
(\nabla^2 + k^2) \psi_0(r) = 0,
\]

and \(G(r)\) is three dimensional Green’s function, i.e., the solution of

\[
(\nabla^2 + k^2) G(r) = \delta^3(r).
\]

\(^1\)This approach was first proposed by Rayleigh in 1912 in order to solve the problem of the reflection of electromagnetic waves, and named after Born who later extended it to general scattering processes.
Eq. (2.11) can be easily verified by substituting it into Eq. (2.10). Using Eq. (2.11), we obtain
\[\psi(r') = \psi_0(r') + \int dr'' G(r' - r'')V(r'')\psi(r''),\] (2.14)
and recursively \(\psi(r''), \psi(r''')\) and so on. Thus an exact solution of Eq. (2.10) in a complete form is given by
\[\psi(r) = \psi_0(r) + \int dr' G(r - r')V(r')\psi_0(r') + \int dr'dr'' G(r - r')G(r' - r'')V(r')V(r'')\psi_0(r'') + \ldots.\] (2.15)

This expression involves terms of higher orders, which have a physical meaning — multiple scattering. In the beginning of this section, we mentioned that the Born approximation is made by assuming a weak interaction in which only single scattering events are taken into account. Following this idea and keeping terms up to the first order (thus usually referred as the first-order Born approximation), we may obtain
\[\psi(r) \approx \psi_0(r) + \int dr' G(r - r')V(r')\psi_0(r').\] (2.16)

Assume that a scattering process occurs upon the incidence of a monochromatic plane wave, \(\psi_0(r) = e^{ik \cdot r}\). The final wave function \(\psi(r)\) consists of two parts, the incident plane wave and the scattered outgoing wave. As shown in Appendix A, there are two solutions of the Green’s function, among which the outgoing branch
\[G^+(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r}\] (2.17)
is of interest in order to calculate the final wave function. Therefore, under the Born approximation in Eq. (2.16),
\[\psi(r) \approx e^{ik \cdot r} - \frac{1}{4\pi} \int dr' \frac{e^{ik|r-r'|}}{|r-r'|} V(r')e^{ik \cdot r'}.\] (2.18)

In a typical scattering experiment, the detector is usually mounted at a distance much larger than the sample size (Fig. 2.1). Applying the far field approximation \(|r'/r| \ll 1\), we have the approximation
\[|r - r'| = \sqrt{r^2 - 2r \cdot r' + r'^2} \approx r - \hat{r} \cdot r',\] (2.19)
where \(\hat{r} = k'/k\) is the unit vector along the direction of the outgoing scattered wave. The final wave function is then written as
\[\psi(r) \approx e^{ik \cdot r} + \frac{e^{ikr}}{r} f(\theta, \varphi).\] (2.20)
where

\[ f(\theta, \varphi) = -\frac{1}{4\pi} \int dr' e^{-i\mathbf{q} \cdot \mathbf{r}'} V(r'). \]  

(2.21)

Here we introduced a very important concept, wave vector transfer, which is defined as the vector difference between the wave vectors of the outgoing and incident waves,

\[ \mathbf{q} \equiv \mathbf{k}' - \mathbf{k}. \]  

(2.22)

In the expression of the final wave function, there are several important points to be noticed. First, the negative sign in the expression of \( f(\theta, \varphi) \) indicates a phase shift of \( \pi \) between the incident wave and the scattered wave. Secondly, from the pre-factor \( e^{i\mathbf{k} r}/r \), it can be seen that the outgoing wave is a spherical wave whose amplitude is inversely proportional to the distance it is observed away from the sample. Lastly, the differential cross section \( (d\sigma/d\Omega) \) can be derived from Eq. (2.20). Suppose the incident plane wave has an intensity \( I_0 \) and cross section area \( A_0 \). If a detector is mounted at distance \( r \) with a solid angle \( \Delta\Omega \), then the observed scattered intensity \( I_{sc} \) over the detector’s facial area \( r^2 \Delta\Omega \) can be written as

\[ I_{sc} = I_0 \left| \frac{\psi_f}{\psi_0} \right|^2 \frac{r^2 \Delta\Omega}{A_0}, \]

(2.23)

where \( \psi_f \) denotes outgoing wave function (the second term on the right side of Eq. 2.20). According to the definition of the differential cross section in Eq. (2.9), we can find

\[ \frac{d\sigma}{d\Omega} = \frac{I_{sc}}{(I_0/A_0)\Delta\Omega} = |f(\theta, \varphi)|^2 = \left| -\frac{1}{4\pi} \int dr' e^{-i\mathbf{q} \cdot \mathbf{r}'} V(r') \right|^2. \]

(2.24)

The integral should be done over the volume of the scatterers. Since \( V(r) \) stands for the potential introduced by the scatterers, it is an intrinsic property of the medium itself.
see how to evaluate $V(r)$, let’s visit the general form of the propagation wave equation for electromagnetic waves in a medium with refractive index $n(r)$,

$$\nabla^2 \psi(r, t) - \frac{n^2}{c^2} \frac{\partial^2 \psi(r, t)}{\partial t^2} = 0,$$  \hspace{1cm} (2.25)

where $c$ is the speed of light in vacuum. Substituting $\psi(r, t) = e^{i(k \cdot r - i\omega t)}$ into Eq. (2.25) and applying the dispersion relation in vacuum $k = \omega/c$, we have

$$\nabla^2 \psi(r) + (nk)^2 \psi(r) = 0.$$  \hspace{1cm} (2.26)

A comparison with Eq. (2.10) yields

$$V(r) = k^2 \left[ 1 - n^2(r) \right],$$  \hspace{1cm} (2.27)

thus identifying the “potential” which appears in Eq. (2.24). Using the relations for the refractive index and electron density given in Eqs. (2.5-2.8) and meanwhile neglecting the dissipation part, we finally show that $V(r) = 4\pi r e \rho(r)$. Therefore, the differential cross section is simply the square modulus of the Fourier transform of the electron density,

$$\frac{d\sigma}{d\Omega} = r^2 \left| \int d\mathbf{r} \rho(r) e^{-i\mathbf{q} \cdot \mathbf{r}} \right|^2.$$  \hspace{1cm} (2.28)

This relation is derived under the first order Born approximation which deals with weak interactions, and will be inappropriate in explaining multiple scattering processes, for example, surface and interfacial scattering in the vicinity of the critical angle. However, Eq. (2.28) provides a simple and clear insight into the physics involved, and will be used as one of the most basic concepts throughout the following discussions.

### 2.2 Structure of Liquid Surfaces

To begin, let’s consider a single surface. In the real world, there never exist absolutely smooth surfaces, and the surface height always fluctuates in space for solids and in time, as well, for liquids. Therefore, any given surface may be described by a height contour function

$$z(r_\parallel) = \bar{z} + \delta z(r_\parallel),$$  \hspace{1cm} (2.29)

where $\delta z(r_\parallel)$ denotes the height variation at a lateral in-plane position $r_\parallel = (x, y)$ with respect to the mean value of the height fluctuations $\bar{z} = \langle z(r_\parallel) \rangle_{r_\parallel}$, as shown in Fig. 2.2.
However, except for some strictly periodic surfaces, the knowledge of $\delta z(r_{||})$ of a real surface is nearly impossible to obtain in practice. If the local surface structure is not of interest, such as how the atoms are aligned or vibrating at a particular spot on the surface, a statistical treatment with only a few parameters may apply to describe the surface morphology sufficiently. The height fluctuations of most surfaces in nature are randomly distributed and their probability distribution functions are invariant under any arbitrary in-plane spatial translation, and are therefore called homogeneous surfaces. Given a height probability distribution, there exist uncountable configurational realizations, the collection of which is called the ensemble. As a consequence of homogeneity, the ensemble average of any functional described by $\{z(r_{||,1}), z(r_{||,2}), \ldots, z(r_{||,N})\}$ does not depend upon the absolute in-plane positions. Instead, it is only a function of the collection of vector distances between an arbitrarily chosen reference point $r_{||,j}$ and all other points [25,164],

$$\{R_{j1}, R_{j2}, \ldots, R_{jj}, \ldots, R_{jk}, \ldots, R_{jN}\},$$

where $R_{jk} \equiv r_{||,j} - r'_{||,k}$. Although each statistical realization may have its own characteristic local structure, its spatial average over $r_{||}$ can be equivalent to the ensemble average over all the realizations, i.e., the surface holds the property of ergodicity [25]. Therefore, for a homogeneous and ergodic surface, we may introduce the mean quadratic height difference function $g(R)$ as defined by

$$g(R) \equiv \langle (\delta z(r_{||}) - \delta z(r_{||} + R))^2 \rangle = \langle (\delta z(0) - \delta z(R))^2 \rangle = 2\sigma^2 - 2C(R), \quad (2.30)$$

where $\sigma = \sqrt{\langle \delta^2 z \rangle}$ is the roughness, and $C(R)$ is the height-height correlation function defined by

$$C(R) \equiv \langle \delta z(0)\delta z(R) \rangle. \quad (2.31)$$
If any rotational operation does not statistically change the surface morphology either, we call this property isotropy. Hence, $g(R) = g(R)$ and $C(R) = C(R)$. In the following discussions, we will only consider homogeneous, isotropic and ergodic surfaces.

Although $g(R)$ and $C(R)$ are equivalent in describing surface morphologies, $C(R)$ is more frequently used. Different surface categories can be modeled with different height-height correlation functions [164], among which only the type for liquid surfaces will be investigated in the present study.

Liquid surfaces have been of great interest to both the theoretical and experimental communities since the pioneering work of van der Waals [169] more than a century ago. In his simple version of the density functional theory, the extensive descriptions of which can be found in Refs. [20,125], a liquid-vapor interface is viewed as a finite region where the density profile smoothly changes from liquid density $\rho_{m,l}$ to vapor density $\rho_{m,v}$, and the equilibrium state of this non-uniform system is obtained by minimizing the free energy, which depends on both the local density and its spatial derivatives.

An alternative approach for describing a liquid surface was proposed by Buff, Lovett, and Stillinger [18], who treated the surface as a sharp step-like profile decorated with height variations attributed to the thermal excitations of capillary waves. The emergence of high-brilliance third-generation synchrotron radiation sources in recent years enables a direct investigation of the liquid surface properties. It turns out that the capillary wave model gives a very accurate description of the in-plane structures and also predicts the interfacial roughness much better than van der Waals’s theory [24,112]. Therefore, we will limit the following discussions to within the framework of capillary wave model, as it is usually adopted.

At this moment, consider a surface on an ideal (zero viscosity so that the energy dissipation is neglected) liquid with infinite depth in a gravitational field. For convenience, suppose that the the mean position $\bar{z}$ of the liquid-vapor surface profile $z(r_\parallel)$ is placed at the plane $z = 0$. In many cases of the flow of liquids, their density may be invariable throughout the volume, i.e., they can be considered as incompressible liquids. Hence, Laplace’s equation is written as,

$$\nabla \cdot \nabla \phi = 0,$$  \hspace{1cm} (2.32)

where $\phi$ is the velocity potential of a steady irrotational flow [80]. Consider a wave propagating along the $x$ direction and uniform in the $y$ direction. We then seek a simple periodic solution to Eq. (2.32) in the form of $\phi(x,z,t) = f(z) \cos(qx - \omega t)$ where $q$ is the
wave number, $\omega$ the circular frequency and $f(z)$ an unknown pre-factor. Supplemented by the boundary condition at the surface, where capillary pressure due to surface tension $\gamma$ is necessarily taken into account, Laplace’s equation leads to

$$\phi(x, z, t) = ae^{qz} \cos (qx - \omega t), \quad (2.33)$$

where $a$ is a constant determined by the initial conditions. The dispersion relation can be obtained simultaneously [79,80,83],

$$\omega = \sqrt{gq + \frac{\gamma q^3}{\Delta \rho_m}}, \quad (2.34)$$

where $\Delta \rho_m = \rho_{m,l} - \rho_{m,v}$ is the mass density contrast across the boundary. For long wavelengths such that $q \ll q_{l,c}$, where $q_{l,c} \equiv \sqrt{g \Delta \rho_m / \gamma}$, the dispersion relation becomes $\omega = \sqrt{gq}$ and the capillarity effect can be neglected. Hence we have a pure gravity wave. On the other hand, for relatively short wavelengths such that $q \gg q_{l,c}$, $\omega = \sqrt{\gamma q^3 / \Delta \rho_m}$ and the waves are called capillary waves. Therefore, $q_{l,c}$ is often referred to as the lower wave vector cutoff, and is typically of the order of $10^{-8} \sim 10^{-7} \text{Å}^{-1}$. $\xi = 1/q_{l,c}$ is called the capillary length or surface correlation length. Via $\mathbf{v} = \nabla \phi$, the velocities and positions of the molecules engaged in the motions that result in an overall propagating wave can be obtained, which is shown schematically in Fig. 2.3.

If the height variation $z(r_{||})$ is everywhere small, i.e., the surface fluctuation deviates only slightly from $z = 0$, the interfacial area element is given by

$$dS = dr_{||} \sqrt{1 + \left| \nabla_{r_{\perp}} z(r_{||}) \right|^2} \approx dr_{||} \left[ 1 + \frac{1}{2} \left| \nabla_{r_{||}} z(r_{||}) \right|^2 \right]. \quad (2.35)$$

Neglecting energy dissipation, i.e., viscosity $\eta \ll 1$, equilibrium is obtained by the minimization of the total free energy as expressed by

$$F = \int dV \Delta \rho_m g z(r_{||}) + \int dS \gamma$$

$$\approx \frac{1}{2} \int dr_{||} \Delta \rho_m g z^2(r_{||}) + \int dr_{||} \gamma \left[ 1 + \frac{1}{2} \left| \nabla_{r_{||}} z(r_{||}) \right|^2 \right]$$

$$= F_0 + \frac{1}{2} \int dr_{||} \left[ \Delta \rho_m g z^2(r_{||}) + \gamma \left| \nabla_{r_{||}} z(r_{||}) \right|^2 \right], \quad (2.36)$$

where $F_0 = \int dr_{||} \gamma$ is the total free energy of an unperturbed surface. Application of Parseval’s theorem [99] leads to a representation in reciprocal space,

$$F = F_0 + \frac{1}{(2\pi)^2} \int dq_{||} \gamma \left( q_{l,c}^2 + q_{||}^2 \right) \left| z(q_{||}) \right|^2, \quad (2.37)$$
where \( z(q) = \int d\mathbf{r} z(\mathbf{r}) e^{-i\mathbf{q} \cdot \mathbf{r}} \). Applying the equipartition theorem in thermodynamics, which states that each mode corresponds an energy of \( k_B T/2 \), to the effective Hamiltonian (the integrand on the right side), we have

\[
\langle |z(q)|^2 \rangle = \frac{k_B T}{\gamma} \frac{1}{q_c^2 + q^2}.
\] (2.38)

The height-height correlation function is then given by

\[
C(R) = \langle z(\mathbf{r}) z(\mathbf{r}') \rangle = \frac{1}{(2\pi)^2} \int dq \langle |z(q)|^2 \rangle e^{i\mathbf{q} \cdot \mathbf{R}}.
\] (2.39)

Therefore, Eq. (2.38) is actually \( \widetilde{C}(q) \), the height-height correlation function in reciprocal space. The capillary roughness \( \sigma_c \) is obtained by letting \( R = 0 \) in Eq. (2.39), so that

\[
\sigma_c^2 = \frac{B}{4 \ln \frac{q_{\text{max}}^2 + q_c^2}{q_{\text{max}}^2}},
\] (2.40)

where \( B = k_B T/(\pi\gamma) \), and an upper wave vector cutoff \( q_{\text{max}} \) is introduced to prevent the divergence of the integral when \( q \to \infty \). Typically \( q_{\text{max}} = 2\pi/r_0 \) with \( r_0 \) being the distance between nearest liquid molecules for simple liquids, or the monomer size for polymer liquids. The full expression for the height-height correlation function is found...
Figure 2.4: Sketch of the surface (xy plane) scattering geometry. The wave vectors of the incident and outgoing waves are $k_i$ and $k_f$, with $\alpha_i$ and $\alpha_f$ the corresponding incident and outgoing angles. The azimuthal angle $\chi$ is the out-of-plane scattering angle. The projections of the wave vector transfer $q = k_f - k_i$ onto the xy plane and z axis are denoted by $q_\parallel = (q_x, q_y)$ and $q_z$, respectively.

\[ C(R) = \frac{B}{2} K_0 \left( q_{l,c} R \right), \]  \hspace{1cm} (2.41)

where $K_0(x)$ is the modified Bessel function of the second kind [50], and can be approximated as $K_0(x) \approx -\ln(x/2) - \gamma_e$ when $x \ll 1$ with $\gamma_e \approx 0.5772$ being Euler’s constant. To prevent divergence at the atomic length scale when $R \to 0$, $C(R)$ is, in practice, written as

\[ C(R) = \frac{B}{2} K_0 \left( q_{l,c} \sqrt{R^2 + r_0^2} \right). \]  \hspace{1cm} (2.42)

These discussions can be easily extended to special cases, such as viscous liquids, supported thin liquid films with finite depth, surfaces with curvature corrections or bending rigidity included, and molten polymer brushes [164].

### 2.3 Elastic X-ray Scattering from Surfaces

Now let us investigate the details of the x-ray scattering from surfaces. A typical scattering geometry is displayed in Fig. 2.4. We are interested in the elastic scattering
regime, so that $|\mathbf{k}_f| = |\mathbf{k}_i| = k$. Therefore the three components of the wave vector transfer $\mathbf{q}$ are, in terms of angles, given by

\begin{align*}
q_x &= k (\cos \alpha_f \cos \chi - \cos \alpha_i), \quad (2.43) \\
q_y &= k \cos \alpha_f \sin \chi, \quad (2.44) \\
\text{and} \quad q_z &= k (\sin \alpha_f + \sin \alpha_i). \quad (2.45)
\end{align*}

A reflectivity (or specular) measurement takes place when $\alpha_i = \alpha_f$ and $\chi = 0$, so that $\mathbf{q} = (0, 0, 2 \sin \alpha_i)$. Only $q_z$ survives, thus this type of measurement allows the characterization of the structure normal to the surface. Any other measurements with non-zero $q_x$ or $q_y$ fall into the catalog of diffuse (or off-specular) measurements, among which the most commonly employed are grazing incidence diffraction (GID), transverse diffuse scans and longitudinal diffuse scans. These diffuse scans are used to characterize the surfaces and interfaces. In GID, the incident angle $\alpha_i$ is below $\alpha_c$, the critical angle, and the detector moves in the out-of-plane direction. In transverse diffuse scans, $\alpha_i + \alpha_f$ is fixed, which is equivalent to the condition where we rock the sample in the scattering plane while holding the beam source and the detector fixed (hence it is often called rocking scan). The advantage of this type of scan is that when both $\alpha_i$ and $\alpha_f$ are small, $q_z$ is almost kept constant when rocking the sample. Thus the contribution due to the modulation in the direction normal to the surface becomes trivial and it becomes much easier to deal with the experimental data. A longitudinal diffuse scattering experiment is performed by varying $q_z$ in the scattering plane ($q_y = 0$) while keeping a constant small offset in $q_x$. The experiment data from this type of scan are usually treated as the diffuse background and are subtracted from the reflectivity scans.

For the purpose of universality, assume the system under study has $N$ interfaces, each of which extends to infinity in the $xy$ plane with two homogeneous media on each side, as shown in Fig. 2.5. At each interface, $\delta z_j(x, y)$ is used to denote the height fluctuation with respect to the average fluctuation height $\bar{z}_j$. The incident beam hits the top surface from medium 1, and the illuminated area $S_j = A$ for every interface. Since the refractive index is very close to 1, for convenience at this moment, we can assume the magnitude of the wave vector $k$ is the same in all $N + 1$ layers. We will come back to this assumption later. Hence, according to Eq. (2.28), the differential cross section is
Figure 2.5: A system consisting of \( N \) interfaces and \( N + 1 \) layers, with \( S_j \) the area of each interface and \( \rho_j \) the electron density of each layer. The topmost and bottommost layers extend to \( z \to +\infty \) and \( z \to -\infty \), respectively. The position of the mean height fluctuation of each interface is labeled as \( \bar{z}_j \).

Gauss's theorem is then applied to transform each of the above volume integrals into an integral over the surface encircling that volume. Each layer has two surfaces, except layer 1 and layer \( N + 1 \) for which the integrals over the surfaces \( S_0 \) and \( S_{N+1} \) at \( \pm \infty \) are assumed to vanish, because in practice the scattering waves will eventually disappear due to absorption effect after propagating an enough long distance. Hence,

\[
\frac{d\sigma}{d\Omega}(q) = \rho^2 \int_{V_j} \left| \sum_{j=1}^{N+1} \int_{V_j} dr \rho_i(r) e^{-iq \cdot r} \right|^2.
\]
where $\Delta \rho_j = \rho_{j+1} - \rho_j$ is the electron density contrast across the $j$th interface. It may include an imaginary part to account for absorption.

From a statistical point of view, we may be able to take the ensemble average of the integrals in Eq. (2.47). Another assumption will be made that the height fluctuations $\delta z_j$ are Gaussian, which is actually quite close to most real systems. Therefore, according to the Baker-Hausdorff theorem\(^2\)

\[
\langle e^{-iq_z(\delta z_j(\vec{r}) - \delta z_k(\vec{r}'))} \rangle = e^{-\frac{1}{2}q^2 g_{jk}(R)},
\]

(2.48)

where $g_{jk}(R)$ is the pair mean quadratic height difference function for the $j$th and $k$th interfaces defined by

\[
g_{jk}(R) \equiv \langle [\delta z_j(0) - \delta z_k(R)]^2 \rangle = (\sigma_j^2 + \sigma_k^2) - 2C_{jk}(R).
\]

(2.49)

Here $C_{jk}(R)$ is the pair height-height correlation function defined by

\[
C_{jk}(R) \equiv \langle \delta z_j(0)\delta z_k(R) \rangle.
\]

(2.50)

If $j = k$, Eqs. (2.49) and (2.50) reduce to Eqs. (2.30) and (2.31), respectively. After exchanging $\int_A\int_A d\vec{r}\,d\vec{r}'$ in Eq. (2.47) with $A\int_A d\vec{R}$, we have

\[
\frac{d\sigma}{d\Omega}(q) = \frac{Ate^{2}}{q^2} \sum_{j,k=1}^{N} (\Delta \rho_j \Delta \rho_k^*) e^{-i\frac{q^2}{2}(\sigma_j^2 + \sigma_k^2)} e^{-iq_z(\bar{z}_j - \bar{z}_k)} \int_A d\vec{R} e^{iq_z \cdot \vec{R}}. \quad (2.51)
\]

In general, the height-height correlation of two points vanishes when the distance is large enough, so that $C_{jk}(R \to +\infty) \to 0$. The integral on the right side then gives rise to a two dimensional delta function of $\delta^2(q)$. Therefore, the differential cross section can be explicitly written in terms of the sum of a specular part and a diffuse part,

\[
\frac{d\sigma}{d\Omega} = \left( \frac{d\sigma}{d\Omega} \right)_{\text{spec}} + \left( \frac{d\sigma}{d\Omega} \right)_{\text{diff}}, \quad (2.52)
\]

\(^2\)The classical Baker-Hausdorff theorem states that if the statistical variation $x$ is Gaussian, then $\langle e^{-iq_x} \rangle = e^{-\frac{1}{2}q^2 \langle x^2 \rangle}$ [2]. A simple proof: the Fourier transform of a Gaussian is still Gaussian, so that $\langle e^{-iq_x} \rangle = \frac{1}{\sqrt{2\pi\sigma^2}} \int_{-\infty}^{+\infty} dx e^{-\frac{x^2}{2\sigma^2}} e^{-iqx} = e^{-\frac{1}{2}q^2\sigma^2} = e^{-\frac{1}{2}q^2 \langle x^2 \rangle}$. 

where,

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{spec}} = \frac{4\pi^2 A r_z^2}{q_z^2} \sum_{j,k=1}^{N} (\Delta \rho_j \Delta \rho_k^*) e^{-\frac{1}{2} q_z^2 (\sigma_j^2 + \sigma_k^2)} e^{-i q_z (\bar{z}_j - \bar{z}_k)} \delta(q_y) \delta(q_y),
\]

(2.53)

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{diff}} = \frac{A r_z^2}{q_z^2} \sum_{j,k=1}^{N} (\Delta \rho_j \Delta \rho_k^*) e^{-\frac{1}{2} q_z^2 (\sigma_j^2 + \sigma_k^2)} e^{-i q_z (\bar{z}_j - \bar{z}_k)} \int dR \left[ e^{q_z^2 C_{j,k}(R)} - 1 \right] e^{-i q_y \cdot R}.
\]

(2.54)

### 2.3.1 Reflectivity

As was mentioned at the beginning of this section, a reflectivity scan is performed in the scattering plane with \( \alpha_i = \alpha_f \) varied simultaneously. Reflectivity is defined as the ratio of the specularly reflected intensity to the incoming beam intensity falling onto the sample surface, i.e.,

\[
R \equiv \frac{I_{sc}}{I_0}.
\]

Here \( I_0 = \Phi_0 A_0 \) with \( \Phi_0 \) the incident flux and \( A_0 = A \sin \alpha_i \) the beam cross section area. According to the definition of the differential cross section in Eq. (2.9), we have

\[
R = \frac{1}{A \sin \alpha_i} \int d\Omega \left( \frac{d\sigma}{d\Omega} \right)_{\text{spec}},
\]

(2.56)

where \( d\Omega = \delta \alpha_f \delta \chi \). From Eqs. (2.43) and (2.44), \( \delta \alpha_f \approx \delta q_x / (k \sin \alpha_f) \) and \( \delta \chi \approx \delta q_y / k \). Thus the reflectivity for a multi-interface sample is

\[
R(q_z) = \frac{16\pi^2 r_z^2}{q_z^2} \sum_{j,k=1}^{N} (\Delta \rho_j \Delta \rho_k^*) e^{-\frac{1}{2} q_z^2 (\sigma_j^2 + \sigma_k^2)} \cos [q_z (\bar{z}_j - \bar{z}_k)].
\]

(2.57)

The cosine term gives oscillations with a period \( 2\pi / (\bar{z}_j - \bar{z}_k) \), which are famously known as the Kiessig fringes. Interfacial roughness does not alter the oscillations. Instead it provides an exponentially damping envelope, which is very similar to the Debye-Waller factor employed in solid state physics to describe the atomic displacement from a lattice site in a crystal due to thermal vibrations. To extend the discussions to include graded interfaces, where the electron density gradually changes across interfaces, we reformulate the reflectivity into a more popular integral form,

\[
R(q_z) = R_F(q_z) \left| \frac{1}{\rho_\infty} \int_{-\infty}^{+\infty} dz \left[ \frac{d\rho(z)}{dz} e^{-i q_y z} \right]^2 \right|.
\]

(2.58)
where $\rho_\infty$ is the asymptotic electron density deep inside the medium, and $R_F$ is the Fresnel reflectivity (Appendix B) in the Born approximation given by

$$R_F(q_z) = \frac{16\pi^2 r_0^2 \rho_\infty^2}{q_z^2}. \quad (2.59)$$

In a layered system, if the height distribution is Gaussian so that the electron density gradient across each interface is

$$\frac{1}{\rho_\infty} \frac{d\rho(z)}{dz} = \frac{1}{\sqrt{2\pi}\sigma^2} e^{-\frac{z^2}{2\sigma^2}}, \quad (2.60)$$

the expression in Eq. (2.58) naturally reduces to its equivalent form in Eq. (2.57). Here, with a Gaussian distribution, the electron density profile is an error function. It is predicted that the profile at a liquid/vapor interface or at an interface dividing two immiscible polymer melts has a hyperbolic tangent form. Nevertheless, the difference between these two profiles is very tiny and always less than 5% [164]. Essentially, either of them may be used in the reflectivity data analysis.

So far, we have discussed the reflectivity within the kinematical approximation. Such treatment fails in the presence of strong multiple scattering events, for example, at grazing incidence angles close to the critical angle. A dynamical calculation is then developed to take into account these multiple scattering effects. The most cited paper on this work was published in 1954 by Parratt [108]. This method, usually referred to as Parratt’s exact recursive method, is briefly described in Appendix B.

### 2.3.2 Diffuse Scattering and Distorted Wave Born Approximation

The differential cross section derived so far is in the first order Born approximation which deals with weak interactions, but which fails in explaining processes with multiple scattering events, e.g., in the vicinity of the critical angle. Therefore better approximation techniques have been developed such as Wentzel-Kramers-Brillouin (WKB) approximation [82, 185] and the distorted wave Born approximation (DWBA) [26, 63, 64, 118, 120, 132, 134, 152, 156, 173], the latter being most widely employed in the surface scattering field.

In the DWBA theory, two undisturbed states, an incident plane wave state $|\psi_i \rangle$ and a final plane wave state $|\psi_f \rangle$, are considered and correspond to the wave fields in an ideal system, i.e., the interfaces have sharp step-like profiles. The roughness at each interface plays a role as a weak perturbation to the scattering process. It has been demonstrated
that the Born approximation is sufficient for describing large angle scattering, and that DWBA should fail in this regime \[152\]. This is mainly ascribed to the fact that at large incident and scattered angles, the roughness morphology becomes so important that it cannot be treated simply as a perturbation, and thus perturbation theory loses its validity. However, at grazing incidence angles, especially below the critical angle, DWBA works very well, while the Born approximation diverges because it does not take into account the total external reflection. Furthermore, the DWBA method successfully explains the nature of the Yoneda peak \[152,182\], which manifests itself as an enhanced intensity when either the incident angle or the scattered angle approaches the critical angle.

In order to keep universality, let us consider the application of DWBA to a multi-layer. Again, start with the Helmholtz equation

\[ \nabla^2 + k_0^2 |\psi\rangle = V(r) |\psi\rangle, \]  

(2.61)

where \( k_0 = 2\pi/\lambda \) is the wave vector in vacuum, and \( V(r) \) is the scattering potential. We may split the potential into two parts,

\[ V(r) = \overline{V}(r) + \delta V(r). \]  

(2.62)

The first term corresponds to the potential of the undisturbed system, and is given by

\[ \overline{V}(r) = 4\pi r e \sum_{j=1}^{N+1} \rho_j W_j(r), \]  

(2.63)

where

\[ W_j(r) = \begin{cases} 1, & \overline{z}_j < z < \overline{z}_{j-1} \\ 0, & \text{elsewhere} \end{cases} \]  

(2.64)

The second term represents the perturbation caused by the interfacial roughness in terms of the height fluctuations \( \delta z_j(x, y) \), and is written as

\[ \delta V(r) = 4\pi r e \sum_{j=1}^{N} \Delta \rho_j P_j(r), \]  

(2.65)

where

\[ P_j(r) = \begin{cases} 1, & \overline{z}_j < z < \overline{z}_j + \delta z_j(x, y) \text{ for } \delta z_j(x, y) > 0 \\ -1, & \overline{z}_j + \delta z_j(x, y) < z < \overline{z}_j \text{ for } \delta z_j(x, y) < 0 \\ 0, & \text{elsewhere} \end{cases} \]  

(2.66)
Assume a normalized incoming plane wave $\phi_i = e^{i k \cdot r}$ is incident on the 1st interface from the topmost medium. Based on the Fresnel theory given in Appendix B, the eigenstates of the ideal system with $\delta V(r) = 0$ are given by

$$
|\psi_i(r)\rangle = T_i(z) e^{i k_i(z) \cdot r} + R_i(z) e^{i k'_i(z) \cdot r},
$$

(2.67)

and

$$
|\tilde{\psi}_f(r)\rangle = T^*_f(z) e^{i k'_f(z) \cdot r} + R^*_f(z) e^{i k_f(z) \cdot r},
$$

(2.68)

with the latter one being time-reversed. Here $k$ and $k'$ denote the incoming and outgoing wave vectors within the medium, respectively. $T(z)$ and $R(z)$ are position-dependent complex total amplitude transmittivity and reflectivity coefficients obtained from Parratt’s exact recursive method.

Within the frame of perturbation theory, the transition matrix for scattering between states $|k_i\rangle$ and $|k_f\rangle$ can be rewritten as

$$
\langle f | T | i \rangle \approx \left\langle \tilde{\psi}_f \mid \tilde{V} \mid \phi_i \right\rangle + \left\langle \tilde{\psi}_f \mid \delta V \mid \psi_i \right\rangle.
$$

(2.69)

The differential cross section may then be calculated from Fermi’s golden rule,

$$
\frac{d\sigma}{d\Omega} = \frac{\langle |f | T | i \rangle^2 \rangle_e}{16\pi^2} = \frac{\langle |\tilde{V}_{i-f} + \delta V_{i-f}|^2 \rangle_e}{16\pi^2},
$$

(2.70)

where $\langle \ldots \rangle_e$ denotes the ensemble average over all the possible roughness configurations. This differential cross section can then be separated into the sum of specular and diffuse parts given by

$$
\left( \frac{d\sigma}{d\Omega} \right)_{\text{spec}} = \left| \frac{\tilde{V}_{i-f} + \langle \delta V_{i-f} \rangle_e}{16\pi^2} \right|^2,
$$

(2.71)

and

$$
\left( \frac{d\sigma}{d\Omega} \right)_{\text{diff}} = \left| \frac{\langle \delta V_{i-f} \rangle_e^2 - |\langle \delta V_{i-f} \rangle_e|^2}{16\pi^2} \right|.
$$

(2.72)

A detailed calculation of the specular part can be found in Refs. [64,152]. A typical specular reflectivity scan runs to an angle much higher than the critical angle, where the DWBA specular part does not work well. However, DWBA is very successfully applied to surface diffuse scattering which is often performed in the vicinity of the critical angle. So only the diffuse part will be discussed here.

The scattering geometry at the $j$th interface in the DWBA theory is shown in Fig. 2.6. An explicit form for $\delta V_{i-f}$ is then calculated to be

$$
\delta V_{i-f} \approx 4\pi r_e \sum_{j=1}^{N} \sum_{m=0}^{3} G_{j+1}^{m} F_{j}(q_{j+1}^{m}),
$$

(2.73)
where

$$F_j(q^m_{j+1}) = \int_{A_j} dx dy \int_{z_j} z_j + \delta z_j(x,y) dz e^{-i q^m_{j+1} \cdot r}, \quad (2.74)$$

where $A_j$ is the illuminated area at the $j$th interface. For convenience, $A_j$ is assumed to be identical at each interface, and denoted as $A$. $G^m_j$ is defined as

$$G^0_j = T^f_j T^i_j, \quad G^1_j = R^f_j T^i_j, \quad G^2_j = T^f_j R^i_j, \quad G^3_j = R^f_j R^i_j, \quad (2.75)$$

and $q^m_j$ is defined as

$$q^0_j = k^f_j - k^i_j = (q_{||}, q^0_{z,j}) = (q_{||}, k^i_{z,j} + k^f_{z,j}),$$

$$q^1_j = k^f_j - k^i_j = (q_{||}, q^1_{z,j}) = (q_{||}, k^i_{z,j} - k^f_{z,j}),$$

$$q^2_j = k^f_j - k^i_j = (q_{||}, q^2_{z,j}) = (q_{||}, -q^1_{z,j}),$$

$$q^3_j = k^f_j - k^i_j = (q_{||}, q^3_{z,j}) = (q_{||}, -q^0_{z,j}). \quad (2.76)$$

The ensemble average of $F_j(q^m_{j+1})$ can be easily obtained and approximated as

$$\langle F_j(q^m_{j+1}) \rangle_e \approx \frac{i}{q^m_{z,j+1}} A \delta(q_{||}) e^{-i q^m_{z,j+1} \gamma_j} \left[ e^{-\frac{1}{2} (q^m_{z,j+1} \sigma_j)^2} - 1 \right]. \quad (2.77)$$
Similar to the calculation of the ensemble average of Eq. (2.47), we have
\[
\langle F_j(q_{j+1}^m) F_k^*(q_{k+1}^n) \rangle_e = \langle F_j(q_{j+1}^m) \rangle_e \langle F_k^*(q_{k+1}^n) \rangle_e = \mathcal{A} e^{-i \rho_{z+1}^m, z_j} e^{i \rho_{z+1}^n, z_k} \\
\times S_{jk}^{mn}(q_{z,j+1}, q_{z,k+1}),
\]
where
\[
S_{jk}^{mn}(q_{z,j+1}, q_{z,k+1}) = \frac{1}{q_{z,j+1}^m q_{z,k+1}^n} e^{-\frac{1}{2}[(q_{z,j+1}^m \sigma_j)^2 + (q_{z,k+1}^n \sigma_k)^2]} \\
\times \int dR \left[ e^{q_{z,j+1}^m q_{z,k+1}^n C_{jk}(R)} - 1 \right] e^{-i q_{z} \cdot R},
\]
can be viewed as a structure factor with \( C_{jk}(R) \) the pair height-height correlation function between the \( j \)th and \( k \)th interfaces as defined in Eq. (2.50). For small \( q_z \) values, by keeping to the second order of the Taylor expansion on the right side of Eq. (2.79), we may notice that \( S_{jk}^{mn}(q_{z,j+1}, q_{z,k+1}) \) is essentially proportional to the Fourier transform of the height-height correlation function. The diffuse part of the differential cross section is then written as
\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{diff}} = Ar^2 \sum_{j,k=1}^{N} (\Delta \rho_j \Delta \rho_k^*) \sum_{m,n=-0}^{3} \left( \tilde{G}_{j+1}^{m} \tilde{G}_{k+1}^{n*} \right) S_{jk}^{mn}(q_{z,j+1}, q_{z,k+1}),
\]
where \( \tilde{G}_{j+1}^{m} \equiv G_{j+1}^{m} e^{-i \rho_{z,j+1}^m, z_j} \).

Although DWBA treatment of the diffuse scattering is supposed to be valid only for small \( q_z \) values, simple calculations show that, for large incident or exit angles, Eq. (2.80) surprisingly reduces to the result of the Born approximation for a multi-layer in Eq. (2.54). This point can be seen by noticing that \( T_j \rightarrow 1 \) and \( R_j \rightarrow 0 \) at large angles so that only \( G^0_j = 1 \) survives, and that \( q^0_{z,j} \) at different layers can be approximated to be \( q^0_{z,1} = k_l (\sin \alpha_i + \sin \alpha_f) \). This wide applicability enables DWBA to be a very powerful tool for the analysis of the diffuse scattering data obtained under many different experimental conditions.

In particular, if the scattering occurs at a single interface, Eq. (2.80) reduces to the same result as derived in Ref. [152],
\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{diff}} = Ar^2 |T_i|^2 |T_j|^2 e^{-\frac{1}{2}[(q_{z,t})^2 + (q_{z,t}^*)^2]} \sum_{m,n=-0}^{3} \int_A dR \left[ e^{q_{z,t}^2 C(R)} - 1 \right] e^{-i q_{z} \cdot R},
\]
where \( q_{z,t} \) is the transmitted wave vector transfer in the underneath subphase and is usually approximated by \( q_z \) in the vacuum.
2.3.3 Experimental Considerations

The measured intensity in the detector is determined by the integration of the differential cross section over the subtended solid angle in the detector. However, in an x-ray scattering setup, depending on the particular experimental geometry, many corrections have to be taken into account due to the effects of pre-sample optics and instrumental geometrical factors, such as wavelength dispersion, beam angular divergence, detector acceptance, and illuminated sample area [17, 25, 29, 49, 138, 164, 166]. In other words, the incident and exit wave vectors, \( k_i \) and \( k_f \) are dispersed, instead of well defined single values. The optical elements before the sample, x-ray source and monochromator for example, cause the dispersion of \( k_i \), while the dispersion of \( k_f \) is basically due to the geometry of the sample and detector acceptance.

In general, the uncertainties of \( k_i \) and \( k_f \) can be expressed in terms of the wave vector transfer uncertainties. After taking the partial derivatives of Eqs. (2.43)-(2.45), we obtain

\[
\delta q_x = \frac{\delta \lambda}{\lambda} q_x + k \left( -\delta \alpha_f \sin \alpha_f \cos \chi - \delta \chi \cos \alpha_f \sin \alpha_i \right), \quad (2.82)
\]
\[
\delta q_y = \frac{\delta \lambda}{\lambda} q_y + k \left( -\delta \alpha_f \sin \alpha_f \sin \chi + \delta \chi \cos \alpha_f \cos \chi \right), \quad (2.83)
\]
and
\[
\delta q_z = \frac{\delta \lambda}{\lambda} q_z + k \left( \delta \alpha_f \cos \alpha_f + \delta \alpha_i \cos \alpha_i \right). \quad (2.84)
\]

For most surface x-ray scattering experiments, the wavelength dispersion \( \Delta \lambda/\lambda \) is usually less than \( 10^{-4} \), and the radiation monochromaticity does not affect the resolution function significantly.

Frequently, a simple resolution-function-folding procedure is carried out to calculate the observed intensity, i.e., the theoretical differential cross section calculated in an ideal condition has to be convoluted with an instrumental resolution function \( \tilde{R}(\delta q) \). This is generally defined, for convenience, as the Gaussian joint-distribution function of independent random deviations \( \delta q_x, \delta q_y, \) and \( \delta q_z \) [170],

\[
\tilde{R}(\delta q) = e^{-\frac{1}{2} \delta q^T \mathcal{A}^{-1} \delta q}, \quad (2.85)
\]

where \( \mathcal{A} \equiv [\delta q_j \delta q_k] \) is the covariance matrix of the random deviation \( \delta q \). The eigenvalues of \( \mathcal{A} \) are then assigned to be \( \Delta q_x^2, \Delta q_y^2, \) and \( \Delta q_z^2 \). The observed intensity in a detector at a point \( q \) in reciprocal space is written via a convolution

\[
I(q) = \frac{d\sigma}{d\Omega}(q) \otimes \tilde{R}(\delta q) = \int dq' \frac{d\sigma}{d\Omega}(q') \tilde{R}(q - q'). \quad (2.86)
\]
In the ideal case where $\Delta q \to 0$, $\tilde{R} \to \delta(\delta q)$, and the resolution is infinitely good. Otherwise, the resolution function plays a role as the smearing factor to the ideal differential cross section in reciprocal space, and is equivalent to an average of many regions of the sample in real space, because by applying the convolution theorem to Eq. (2.28), we can rewrite Eq. (2.86) in another form

$$I(q) = \frac{r_c^2}{q_i^2} \int drdr' \rho(r) \rho(r') R(r - r') e^{-iq \cdot (r - r')},$$  \hspace{1cm} (2.87)

where $R(r)$ is the Fourier transform of $\tilde{R}(\delta q)$. $R(r)$ effectively acts as a “cutoff function” in real space, and is usually viewed as the definition of “coherence volume” [153,164,165].

For practical reasons the parameters in the resolution function are often treated as fitting parameters until the best fit to the observed intensity is obtained. In a reflectivity fitting process, $\tilde{R}(\delta q_z) = e^{-\delta q_z^2/(2\Delta q_z^2)}$ is commonly used to convolute with the reflectivity calculated using Parratt’s exact recursive method, where $\Delta q_z$ is to be fitted for. In a typical single interface scattering experiment, after introducing a factor to conserve the resolution volume during the transformation from the angular ($\alpha_i$ and $\alpha_f$) to wave vector ($q_z$ and $q_\parallel$) representations for the resolution function [25], we can write the measured total intensity without splitting into specular and diffuse parts,

$$I(q) = I_0 \frac{4r_c^2(\Delta \rho)^2}{q_i^2} \left( \frac{1}{2k_0 \sin \alpha_i} \right) |T_i|^2 |T_f|^2 e^{-q_i^2\sigma^2} \int dR e^{q_i^2C(R)} e^{-i\delta q_i \cdot R} \otimes \tilde{R}(\delta q_\parallel),$$  \hspace{1cm} (2.88)

where $\tilde{R}(\delta q_\parallel) = e^{-\delta q_\parallel^2/(2\Delta q_\parallel^2)}$ is the resolution function, and a normalization has been performed with respect to the incident beam intensity $I_0$ instead of the incident flux, giving rise to a factor $1/\sin \alpha_i$. Usually in the transverse diffuse scattering, the defining slit in front of the detector is intentionally set widely open in the direction perpendicular to the scattering plane ($xz$ plane in Fig. 2.4), leading to an infinite $\Delta q_y$ in the resolution function. Therefore, an integration over the entire wave vector spectrum along $q_y$ has to be performed for Eq. (2.88), yielding [177]

$$\frac{I(q_x, q_z)}{I_0} = R_F(q_z) \left( \frac{q_z}{2k_0 \sin \alpha_i} \right) |T_i|^2 |T_f|^2 \sqrt{\frac{\pi}{2}} e^{-q_i^2\sigma^2} \Delta q_x$$

$$\times \int_0^\infty dX e^{q_i^2C(X,0)} \cos (q_x X) e^{-\frac{1}{2} \Delta q_\parallel^2 X^2},$$  \hspace{1cm} (2.89)

where $R_F(q_z)$ is the Fresnel reflectivity. In particular, for a liquid surface decorated with thermally excited capillary waves, whose height-height correlation function can be
described by Eq. (2.41), the observed intensity is given by \[6,131\]
\[
\frac{I(q_x,q_z)}{I_0} = R_F(q_z) \left( \frac{q_z}{2k_0 \sin \alpha_i} \right) |T_i|^2 |T_f|^2 \frac{1}{\sqrt{\pi}} e^{-q_z^2 \sigma_{\text{eff}}^2} \\
\times \Gamma \left( \frac{1 - \eta}{2} \right) _1 F_1 \left( \frac{1 - \eta}{2} ; \frac{1}{2} ; -\frac{q_z^2}{2\Delta q_x^2} \right),
\]
(2.90)
where \( \eta = \frac{1}{2} Bq_z^2 \) with \( B \) defined as \( k_B T / (\pi \gamma) \), \( \Gamma(x) \) is the gamma function, \( _1 F_1(x; y; z) \) is the confluent hypergeometric function of the first kind or Kummer’s function, and \( \sigma_{\text{eff}} = \left[ \sigma^2 + \frac{1}{2} B\gamma e - \frac{1}{2} B \ln \left( \sqrt{2\Delta q_x} / q_{l,c} \right) \right]^{\frac{1}{2}} \) is considered as the effective surface mean square roughness.

### 2.4 X-ray Photon Correlation Spectroscopy

Synchrotron radiation was discovered half a century ago. However, it was not until the invention of the third-generation synchrotron in the last two decades that the tremendous advantages of the coherent properties of x-rays were realized. Here we will focus on the study of dynamic phenomena utilizing a recently developed time-dependent coherent x-ray scattering technique: x-ray photon correlation spectroscopy (XPCS).

#### 2.4.1 Coherent Scattering and Speckles

In a scattering experiment, with a finite sampling time in the detector, the differential cross section in the kinematical approximation, as shown in Eq. (2.28), may be expressed as
\[
\frac{d\sigma}{d\Omega} = r_e^2 \int \int d\mathbf{r} d\mathbf{r}' \langle \rho(\mathbf{r}) \rho(\mathbf{r}') \rangle_T e^{-i\mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')},
\]
(2.91)
where \( \langle \ldots \rangle_T \) denotes the time average within one sampling period. If the sample is non-ergodic and carries some static random disorder, the scattered electric field at a given point in the sample has some phase relation with that at another distant point, and the electric field amplitudes are superimposed coherently, exhibiting sharp and random fluctuations in reciprocal space, thus giving rise to a so-called “speckle” pattern. However, if the system is ergodic with fluctuations occurring on a time scale much shorter than the integrated sampling time, the system undergoes many structural configurations during one sampling period, so that the time average is equivalent to the spatial ensemble average resulting in a smeared-out speckle pattern, which is also similar to the result of a scattering process with incoherent photons. Therefore, in order to reconstruct the
absolute position-dependent structure via phase retrieval procedure for speckle patterns, a coherent (or at least partially coherent) source is required.

Speckle patterns from light scattering have been known for hundreds of years, especially since the invention of lasers. A famous example is Young’s double slit diffraction experiment. However, to observe a speckle pattern with coherent x-rays is a big challenge. Most x-rays are generated from incoherent sources, where the coherent volume is very small and the coherent intensity is usually ten orders of magnitude less than that from a typical optical laser [91]. The emergence of high-brilliance third-generation synchrotron radiation sources brought a giant leap in source brilliance (the number of photons emitted per second per solid angle per source area per relative wavelength dispersion), making coherent x-ray scattering possible by sacrificing a large amount of photons using a tiny aperture opening in order to obtain a partially coherent beam. Even with synchrotron radiation, to obtain a speckle pattern is not an easy task. The coherent volume has to be sufficiently large to cover the typical length scale of the spatial fluctuations in the sample, and the instrumental resolution has to be good enough in order not to smear the speckles in the convolution procedure [164]. In addition, the x-ray wavelength is typically of the order of angstroms and it is much more difficult to fulfill the conditions for Fraunhofer diffraction with x-rays than with light. Because of these effects, a complete theoretical handling of the coherent scattering becomes extremely complicated [48, 153, 159, 165].

The first reported x-ray speckle pattern was obtained from the coherent x-ray diffraction of Cu₃Au [160] in 1991. Since then speckle patterns have been observed from many other systems, such as diblock copolymer films [21] and aerogel [167], leading to the development of a new technique, coherent x-ray holography, which aims at an indirect imaging of buried nanoscale structures [36, 96]. With the new generations of x-ray sources, x-ray free-electron laser (XFEL) and energy recovery linac (ERL), around the corner, more applications of coherent x-ray scattering will be explored.

---

3Coherent volume is defined as the volume within which the incoming photons are in phase and the scattered photons are summed in amplitude instead of intensity. It is usually characterized by two quantities: longitudinal coherent length \( \xi_l = (1/2)\lambda^2/\Delta\lambda \) and transverse coherent length \( \xi_t = (\lambda/2)R/D \), where \( \Delta\lambda \) denotes the beam monochromaticity in terms of wavelength \( \lambda \), \( R \) and \( D \) are the distance of the observation to the source and the source size, respectively [2].
2.4.2 Photon Correlation Spectroscopy

When a coherent beam is incident on a sample whose spatial arrangement of disorder varies with time, the speckle pattern also changes and the time-dependent intensity variation at a particular point \( q \) in reciprocal space provides information on the dynamic properties at corresponding length scales \( 2\pi/q \) within the system. This is the principle of photon correlation spectroscopy (PCS). Correlation spectroscopy with visible light, known as dynamic light scattering (DLS), has been well established and is a widely used technique [7,22,34,81].

As an extension of DLS, XPCS has an ability to study the dynamics on a much smaller length scale than can be achieved by traditional DLS and on a slower time scale than the neutron spin echo technique can usually reach. It also allows a study of samples that are opaque to visible light, and the broadening problem of the wave vector due to multiple scattering in DLS can be resolved. Fig. 2.7 shows the frequency and wave vector ranges accessible to XPCS compared with other frequently used techniques for the study of dynamics.

We will first recapitulate the detection methods commonly used in scattering experiments: filter, homodyne and heterodyne methods, as illustrated in Fig. 2.8 for light scattering. The filter method is usually used to study relatively rapid molecular dynamic processes occurring on time scales faster than \( 10^{-6} \) sec [7]. The last two methods are optical mixing techniques used for slower processes and will be of interest in the current study.

In the homodyne (also referred to as “self-beat”) method, only the scattered beam is detected and then correlated with itself, whereas in the heterodyne method a reference beam, which is quite often a small part of the incident beam separated before impinging on the sample, is mixed with the scattered beam. In the heterodyne detection mode, the measured intensity as a function of time and wave vector transfer is written as

\[
I(q, t) = |E_s(q, t) + E_r(q, t)|^2 = I_s(q, t) + I_r(q, t) + 2\text{Re} \left[ E_s(q, t)E^*_r(q, t) \right],
\]

where \( E_s \) and \( E_r \) denote electric fields of the scattered and reference beams, respectively, with \( I_s \) and \( I_r \) the corresponding intensities. The intensity-intensity autocorrelation is
Figure 2.7: Frequency-scattering vector space covered by x-ray photon correlation spectroscopy (XPCS) and complementary techniques: photon correlation spectroscopy with visible coherent light (PCS), Raman and Brillouin scattering, inelastic neutron (INS) and x-ray scattering (IXS), neutron spin-echo and nuclear forward scattering (NFS) [52].

Figure 2.8: Schematic illustrations of detection methods in scattering experiments [7]. (a) filter, (b) homodyne, and (c) heterodyne.
then computed to be

\[
G(q,t) \equiv \langle I(q,t')I(q,t' + t) \rangle \\
= \left[ \langle I_s(q,t') \rangle + \langle I_r(q,t') \rangle \right]^2 + 2 \langle I_s(q,t') \rangle \langle I_r(q,t') \rangle g_s^{(1)}(q,t) \\
+ \langle I_s(q,t') \rangle^2 \left[ g_s^{(2)}(q,t) - 1 \right],
\]

(2.93)

where \( \langle \ldots \rangle \) denotes the average over time \( t' \), and \( g_s^{(1)}(q,t) \) and \( g_s^{(2)}(q,t) \) are the normalized first and second order correlation functions respectively for the scattered electric field and defined as

\[
g_s^{(1)}(q,t) = \frac{\langle E_s(q,t')E_s^*(q,t' + t) \rangle}{\langle I_s(q,t') \rangle},
\]

(2.94)

and

\[
g_s^{(2)}(q,t) = \frac{\langle I_s(q,t')I_s(q,t' + t) \rangle}{\langle I_s(q,t') \rangle^2}.
\]

(2.95)

In deriving Eq. (2.93), we have applied \( g_r^{(1)}(q,t) = g_r^{(2)}(q,t) = 1 \) for the reference beam.

In DLS, heterodyne mixing is quite often employed. In x-ray scattering, although the Bragg reflection or the totally reflected beam present within the interference regime due to the failure of fulfilling the Fraunhofer diffraction condition may occasionally serve as an effective reference beam at small wave vector transfers [56,93], most XPCS experiments are carried out without a reference beam, leading to the homodyne method with \( \langle I_s \rangle \gg \langle I_r \rangle \) in Eq. (2.93).

For an electric field that obeys Gaussian statistics, the first and second order correlation functions are connected by the Siegert relation [22]

\[
g_s^{(2)}(q,t) = 1 + \left| g_s^{(1)}(q,t) \right|^2.
\]

(2.96)

The first order correlation function of the scattered field is essentially proportional to the electron density-density correlation for x-ray scattering represented in reciprocal space, i.e., \( g_s^{(1)}(q,t) \propto \langle \rho(q,t')\rho^*(q,t' + t) \rangle \), where \( \rho(q,t) = \text{FT} [\rho(r,t)] \). Therefore, \( g_s^{(1)}(q,t) \), and thus \( g_s^{(2)}(q,t) \) as well, are related to the time-dependent differential cross section of the sample. This point can be seen as follows.

Suppose that an electric field \( E_i(r,t) = E_i(r,t)e^{i(k_r - \omega t)}\hat{e}_i \), with \( \hat{e}_i \) the direction of polarization and \( E_i(r,t) \) the complex electric field amplitude varying very slowly compared with \( \omega^{-1} \), is incident at time \( t \) on a sample whose local electron density \( \rho(r,t) \) also fluctuates on a time scale much slower than \( \omega^{-1} \). As shown in Section 2.1.3, with the far field approximation, the observed scattered electric field at a distant point \( r \) at
time \( t' = t + r/c \) can be written as

\[
\mathbf{E}_s(\mathbf{r}, t') = -\hat{e}_s P r e^{-i\omega t} \int_V dr' e^{-iq \cdot \mathbf{r}'(\mathbf{r}', t') E_i(\mathbf{r}', t + \mathbf{q} \cdot \mathbf{r}'/\omega)} ,
\]

(2.97)

where the integral should be performed over the illuminated sample volume \( V \), \( \hat{e}_s \) is the direction of polarization of the scattered electric field, and \( P = \hat{e}_s \cdot \hat{e}_s \) is introduced as the polarization factor for scattering processes with vector waves. If the scattering plane is perpendicular to the electric field plane, \( P = 1 \). We will discard this factor in order to keep clear conceptual discussions. It then follows that the mean scattered intensity

\[
\langle |E_s|^2 \rangle = \frac{r^2_e}{r^2} \int d\mathbf{r}_1' d\mathbf{r}_2' e^{-i\mathbf{q} \cdot \mathbf{r}_1'} \langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_2', 0) \rangle
\]

\[
\times \langle E_i(\mathbf{r}_1', \mathbf{q} \cdot \mathbf{r}_1'/\omega) E_i^*(\mathbf{r}_2', \mathbf{q} \cdot \mathbf{r}_2'/\omega) \rangle
\]

\[
\approx \frac{r^2_e}{r^2} \langle |E_s|^2 \rangle \int d\mathbf{r}_1' d\mathbf{r}_2' e^{-i\mathbf{q} \cdot \mathbf{r}_1'} \langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_2', 0) \rangle ,
\]

(2.98)

where \( \langle |E_s|^2 \rangle \) is used to approximate \( \langle E_i(\mathbf{r}_1', \mathbf{q} \cdot \mathbf{r}_1'/\omega) E_i^*(\mathbf{r}_2', \mathbf{q} \cdot \mathbf{r}_2'/\omega) \rangle \) in the integrand, because the coherent length of the incident field is typically much larger than the length scale of the correlation of the electron density fluctuations in the sample. According to the definition in Eq. (2.95), we may have

\[
g_s^{(2)}(\mathbf{q}, t) = \frac{\langle |E_s(0)|^2 |E_s(t)|^2 \rangle}{\langle |E_s|^2 \rangle^2} = \frac{r^4_e}{r^4} \langle |E_s|^2 \rangle^2 \int d\mathbf{r}_1' d\mathbf{r}_2' d\mathbf{r}_3' d\mathbf{r}_4' e^{-i\mathbf{q} \cdot \mathbf{r}_1'} e^{-i\mathbf{q} \cdot \mathbf{r}_3'} \langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_2', 0) \rho(\mathbf{r}_3', t) \rho^*(\mathbf{r}_4', t) \rangle
\]

\[
\times \langle E_i(\mathbf{r}_1', \mathbf{q} \cdot \mathbf{r}_1'/\omega) E_i^*(\mathbf{r}_2', \mathbf{q} \cdot \mathbf{r}_2'/\omega) \rangle \langle E_i(\mathbf{r}_3', \mathbf{q} \cdot \mathbf{r}_3'/\omega) E_i^*(\mathbf{r}_4', \mathbf{q} \cdot \mathbf{r}_4'/\omega) \rangle .
\]

(2.99)

For a set of real stochastic variables \( \{x_1, x_2, x_3, x_4\} \) that obey Gaussian distribution, the average of the product of these variables can be decoupled into the sum of the averages over pair products [8], i.e.,

\[
\langle x_1 x_2 x_3 x_4 \rangle = \langle x_1 x_2 \rangle \langle x_3 x_4 \rangle + \langle x_1 x_3 \rangle \langle x_2 x_4 \rangle + \langle x_1 x_4 \rangle \langle x_2 x_3 \rangle .
\]

(2.100)

Therefore, we are able to write

\[
\langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_2', 0) \rho(\mathbf{r}_3', t) \rho^*(\mathbf{r}_4', t) \rangle = \langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_2', 0) \rangle \langle \rho(\mathbf{r}_3', t) \rho^*(\mathbf{r}_4', t) \rangle
\]

\[
+ \langle \rho(\mathbf{r}_1', 0) \rho(\mathbf{r}_3', t) \rangle \langle \rho^*(\mathbf{r}_2', 0) \rho^*(\mathbf{r}_4', t) \rangle
\]

\[
+ \langle \rho(\mathbf{r}_1', 0) \rho^*(\mathbf{r}_4', t) \rangle \langle \rho^*(\mathbf{r}_2', 0) \rho(\mathbf{r}_3', t) \rangle .
\]

(2.101)
Since the integral in Eq. (2.99) becomes non-trivial only when \( r'_1 \approx r'_2 \) and \( r'_3 \approx r'_4 \), or \( r'_1 \approx r'_4 \) and \( r'_2 \approx r'_3 \), the contribution from the second term in Eq. (2.101) is negligible. Considering that the coherence time of the source is typically much shorter than the characteristic correlation time of the density fluctuations, we may write

\[
g_s^{(2)}(q, t) \approx 1 + \frac{r'_e \langle |E_i|^2 \rangle}{r^4} \int \int \int \int d r'_1 d r'_2 d r'_3 d r'_4 e^{-i q \cdot (r'_1 - r'_2)} e^{-i q \cdot (r'_2 - r'_3)} \langle \rho(r'_1, 0) \rho^*(r'_4, t) \rangle \langle \rho^*(r'_2, 0) \rho(r'_3, t) \rangle
\]

\[
= 1 + \left| \int \int d r'_1 d r'_2 e^{-i q \cdot (r'_1 - r'_2)} \langle \rho(r'_1, 0) \rho^*(r'_2, t) \rangle \int \int d r'_1 d r'_2 e^{-i q \cdot (r'_1 - r'_2)} \langle \rho(r'_1, 0) \rho^*(r'_2, 0) \rangle \right|^2 .
\]

(2.102)

This relation is derived assuming perfect coherence. However, in reality, a detector has a non-zero active area and therefore sees different scattered fields at different points on the sample, so that the resolution has to be taken into account. In addition, the illuminated sample volume occasionally exceeds or is comparable to the coherent volume of the incident beam. Therefore, \( g_s^{(2)} \) is usually rewritten as

\[
g_s^{(2)}(q, t) = 1 + \beta |f(q, t)|^2 .
\]

(2.103)

Here \( \beta \) is a factor which represents the degree of spatial coherence of the scattered field and is usually written as the ratio of the coherent volume to the illuminated sample volume or even more accurate but more sophisticated expressions to account for the effects of source properties and finite detector acceptance [88, 117]. In the ideal case, \( \beta = 1 \), whereas in real XPCS experiments with a non-zero detector and a partially coherent x-ray beam, \( \beta \) is much less than 1. Since \( \beta \) is a sample-independent parameter and is usually not of interest, it is then regarded as an unimportant fitting parameter during data analysis. In Eq. (2.103), \( f(q, t) \) is the normalized intermediate scattering function (ISF) and is defined as

\[
f(q, t) \equiv \frac{S(q, t)}{S(q)} ,
\]

(2.104)

with \( S(q, t) \) the ISF and \( S(q) \) the static structure factor respectively given by

\[
S(q, t) = \int \int d r'_1 d r'_2 e^{-i q \cdot (r'_1 - r'_2)} \langle \rho(r'_1, 0) \rho^*(r'_2, t) \rangle ,
\]

(2.105)

and

\[
S(q) = \int \int d r'_1 d r'_2 e^{-i q \cdot (r'_1 - r'_2)} \langle \rho(r'_1, 0) \rho^*(r'_2, 0) \rangle .
\]

(2.106)
For those XPCS experiments probing bulk dynamics, $S(q, t)$ is related to the bulk density-density correlation function. Typical bulk systems whose dynamics have been investigated by XPCS are metal colloids in glycerol [31,163], the binary alloy Fe$_{3}$Al [15], antiferromagnetic domains [146], phase-separated block copolymers [37,98], concentrated polystyrene latex spheres in glycerol [90], charged aging clay suspensions [4], and polymer blends [38,87]. On the other hand, for surface sensitive XPCS experiments, it is noted that the scattering contrast arises from the electron density variations which depend on the surface profile, so that the ISF is simply connected to the time-dependent surface height-height correlation function [48], i.e., $S(q_{\parallel}, t) = \tilde{C}(q_{\parallel}, t) = \langle \delta z(q_{\parallel}, 0) \delta z(q_{\parallel}, t) \rangle$.

Example systems studied by surface geometry XPCS are liquid crystal membranes [39,92,115,148], water surfaces [55,56], miscible binary fluids [93], molten polymer single layer films [71,76] and bilayer films [65], and metal/polymer nanocomposite thin films [102,157].
Surface Dynamics on Molten Polystyrene Films

Liquid surface structure and dynamics have been of great interest for more than a century. The most commonly used description of liquid surfaces is the capillary wave model, in which a step-like local profile is assumed for the surface whose large-scale width results from the fluctuations of the surface due to the propagation of thermally excited capillary waves [18]. All the structural and dynamic information about the surface is then contained in its profile. A typical feature of capillary waves is that their amplitude is much smaller than their wavelength. Light scattering has been successfully applied to measure the spectrum of liquid surfaces which was found to be consistent with the capillary wave theory [81]. However, the length scales achievable by visible light are of the order of 1 micrometer, and light scattering is not quite surface sensitive because of the mixing of bulk scattering signals due to large penetration depth. On the contrary, the x-ray wavelength two orders of magnitude smaller than light allows investigators to probe sub-nanometer length scales, and due to the less-than-one refraction index, x-ray scattering can be easily made sensitive only to surfaces, with a typical penetration depth of the evanescent wave field of less than $\sim 5$ nm. The presence of capillary waves on liquid surfaces at a broader range of length scale has been indirectly verified by measuring the fingerprints of the capillary waves, such as the capillary roughness (Eq. 2.40) via x-ray reflectivity experiments [13, 103, 133, 141], or the power-law behavior originating from the in-plane height-height correlation functions imposed by the capillary wave theory (Eq. 2.90) via static x-ray diffuse scattering [131]. Nevertheless, these measurements aim
at capturing the static time-averaged structure rather than the dynamics of the surface fluctuations. To investigate the dynamic properties of liquid surfaces, it is necessary to carry out time-dependent x-ray scattering measurements. The wave excitations on liquid surfaces usually occur on an extremely fast time scale so that a very short sampling time is required, which leads to a measured intensity far below the statistical requirements if conventional x-ray sources are used, for example, rotating anode x-ray tubes. Another restriction is that, as we have discussed in Section 2.4, to obtain the instant structure of a liquid surface and its dynamic behavior, a coherent source is demanded. Mainly due to these technical limitations, the goal of investigating liquid surface dynamics was not accomplished only until the birth of the extremely brilliant third-generation synchrotron sources. In this chapter, we will discuss recent progresses on the studies of surface dynamics from single-layer liquid polymer films using time-resolved coherent synchrotron radiation.

### 3.1 Capillary Waves on Molten Polymer Surfaces

In order to obtain a complete understanding of liquid surfaces in both static and dynamic points of view, the spectra and dynamics of capillary waves on homogeneous bulk liquids and supported liquid single-layer films have been studied theoretically [60, 68]. The basic approach is that, using the classical fluctuation dissipation theorem, the spectrum of small amplitude thermal capillary waves can be derived from the dynamic susceptibility $\chi_{zz}(k, \omega)$ which specifies the linear response of the surface vertical displacement $u_z$ to a periodic external force field $P_z$ acting vertically on the liquid surface (Fig. 3.1). Starting with the linearized Navier-Stokes equation with a non-slip boundary condition at the substrate, and assuming a solution with monochromatic plane wave form $e^{i(kx-\omega t)}$, Jäckle [68] obtained the dynamic susceptibility for surfaces of incompressible single-layer films,

$$\chi_{zz}(k, \omega) = \chi_{zz}(k, 0) \left[ 1 + \left( \frac{(\nu k^2)^2}{\omega_s(k)^2} \frac{N_0}{D_0} \right)^2 \right]^{-1},$$

where $\chi_{zz}(k, 0)$ is the static susceptibility given by

$$\chi_{zz}(k, 0) = \frac{1}{\gamma k^2 + g \rho},$$

$k$ is the wave number of the surface waves, corresponding to the in-plane wave vector transfer $q_\parallel$ when connected to scattering theories and experiments. Both notations will be used depending on convenience.
Figure 3.1: Geometry and notations of a supported single-layer film of thickness $d$, surface tension $\gamma$, dynamic viscosity $\eta$ and mass density $\rho$ (hence $\nu = \eta/\rho$ is the kinematic viscosity). The vertical surface displacement and the amplitude of the external force field are denoted by $u_z$ and $P_{z,0}$, respectively.

$\omega_s(k)$ is the dispersion relation for free surface waves on an ideal bulk liquid with an infinite depth,

$$\omega_s(k) = \left(\frac{\gamma k^3 + g k}{\rho}\right)^{1/2}, \quad (3.3)$$

and $N_0$, $D_0$, $\zeta$ are defined as

$$N_0 = -4\zeta(1 + \zeta^2) + \zeta \left[4 + (1 + \zeta^2)^2\right] \cosh(kd) \cosh(\zeta kd) - \left[4\zeta^2 + (1 + \zeta^2)^2\right] \sinh(kd) \sinh(\zeta kd), \quad (3.4)$$

$$D_0 = \zeta \sinh(kd) \cosh(\zeta kd) - \sinh(\zeta kd) \cosh(kd), \quad (3.5)$$

and

$$\zeta = \left(1 - \frac{i \omega}{\nu k^2}\right)^{1/2}. \quad (3.6)$$

For an ultra-thin film, Eqs. (3.2) and (3.3) can be readily modified to include the van der Waals interactions with the substrate [164], so that

$$\chi_{zz}(k, 0) = \frac{1}{\gamma k^2 + g \rho + A_{\text{eff}}/(2\pi d^4)}, \quad (3.7)$$

and

$$\omega_s(k) = \left[\frac{\gamma k^3}{\rho} + \left(g + \frac{A_{\text{eff}}}{2\pi d^4 \rho}\right) k\right]^{1/2}, \quad (3.8)$$

where $A_{\text{eff}}$ is the effective Hamaker constant. In the case of relatively high viscosity, e.g., polymer melts, the gravitational effect is negligible. The competition of the effects due to the surface tension and the van der Waals interaction on surface dynamics yields a lower wave vector cutoff $k_{\text{vdW}} = (A_{\text{eff}}/2\pi \gamma)^{1/2} d^{-2}$, above which the surface tension dominates. Since this cutoff diminishes as $d^{-2}$, the van der Waals effect is very often negligible for thick films.
We have also extended the above hydrodynamic approach to the surface and interfacial dynamics of bilayer films [72], the theory of which is given in Appendix C. It is obvious that our calculations for bilayer dynamics reduce to the single layer case when an infinite viscosity for the bottom layer (Fig. C.1) is assumed, i.e., this layer is treated effectively as a solid substrate. With a non-slip boundary condition, Eq. (3.1) is regained, while the susceptibility with a perfect slip boundary condition can be easily derived to be

\[ \chi_{zz}(k, \omega) = \chi_{zz}(k, 0) \left[ 1 + \frac{(\nu k^2)^2}{\omega_s(k)^2} L_0 \right]^{-1}, \]  

(3.9)

where

\[ L_0 = (1 + \zeta^2) \frac{\cosh(kd)}{\sinh(kd)} - 4\zeta \frac{\cosh(\zeta kd)}{\sinh(\zeta kd)}. \]  

(3.10)

According to the generalized fluctuation dissipation theorem for classical fluids, the imaginary part of the dynamic susceptibility determines the thermal fluctuation power spectrum

\[ S(k, \omega) = 2k_B T \frac{\text{Im} \left[ \chi_{zz}(k, \omega) \right]}{\omega}. \]  

(3.11)

The Fourier transform of this surface spectrum in temporal representation is primarily the ISF given in Eq. (2.105). For low-viscosity liquids, for example water, it can be easily found from the surface spectrum that the frequency of the thermally excited capillary waves takes a complex form \( \omega = \omega_0 + i\Gamma \) [68, 83], where \( \omega_0 \) denotes the propagation frequency and \( \Gamma \) gives the characteristic damping rate. However, on highly viscous liquid surfaces, the propagating modes are usually suppressed, and only over-damped modes exist. Therefore, the characteristic over-damped relation time (defined as \( 1/\Gamma \)) for a single-layer film with a non-slip boundary condition is found from Eq. (3.1) to be

\[ \tau_{\text{nonslip}}(k) \simeq \frac{2\eta}{\gamma k} \frac{H}{F}, \]  

(3.12)

where \( F \) and \( H \) are dimensionless functions of \( kd \):

\[ F = \sinh(kd) \cosh(kd) - kd, \]  

(3.13)

\[ H = \cosh(kd)^2 + (kd)^2. \]  

(3.14)

On the other hand, with a perfect slip boundary condition, it is found from Eq. (3.9) that

\[ \tau_{\text{slip}}(k) \simeq \frac{2\eta}{\gamma k} \frac{\cosh(kd) \sinh(kd) + kd}{\sinh(kd)^2}. \]  

(3.15)
We note that both equations (3.12) and (3.15) can be re-expressed in thickness-independent forms, because \( \tau_{\text{nonslip}}(k)/d \) and \( \tau_{\text{slip}}(k)/d \) are functions of \( kd \) only and directly proportional to \( \eta/\gamma \). This means that at a certain temperature, the behavior of the capillary waves on films with different thicknesses can be scaled and should collapse onto a single master curve. If \( kd \gg 1 \), both Eq. (3.12) and Eq. (3.15) naturally reduce to the capillary wave relaxation time for highly viscous bulk liquids with an infinite depth [19,83,140]

\[
\tau_{\text{bulk}}(k) \simeq \frac{2\eta}{\gamma k}.
\] (3.16)

This result can also be obtained qualitatively by dimensional analysis. As an analog, consider a horizontal spring hooked to a mass submerged in a viscous liquid. Suppose that \( K_s \) is the spring force constant and \( b \) the velocity-dependent frictional constant. If the liquid is sufficiently viscous, the oscillation mode does not exist and only the over-damped mode is considered. The time required for the spring to pull the mass back to zero tension position is then simply given by \( \tau \sim b/K_s \). Analogously, \( K_s \) and \( b \) may be written as \( K_s \rightarrow \gamma \) and \( b \rightarrow \eta/k \) in order to keep correct dimensions. Therefore, the relaxation time constant for over-damped waves on highly viscous deep liquid is expected to be \( \tau \sim b/K_s = \eta/(\gamma k) \).

A comparison of the over-damped capillary wave relaxations from polystyrene (PS) films with non-slip and slip boundary conditions, as well as those from a bulk PS liquid, is shown in Fig. 3.2. Here, film thickness \( d \) is 80 nm; viscosity \( \eta = 4.4 \times 10^5 \) Nsec/m² and surface tension \( \gamma = 31.4 \) mN/m are interpolated from bulk values [113,178] of PS with molecular weight \( M_W = 123,000 \) g/mol at 150 °C. When the capillary wavelength is much smaller than the film depth \( d \) (or the wave vector is larger than \( 2\pi/d \) as marked by the vertical dashed line), i.e., the elliptical motions of the liquid elements engaged in surface capillary waves are much less affected by the substrate, liquid films with either non-slip (Eq. 3.12) or slip (Eq. 3.15) boundary conditions behave as bulk liquids (Eq. 3.16).

If polymer chains are grafted onto the substrate, the elasticity due to the pinning of chains has to be taken into account. Following Refs. [60,100], a constitutive frequency dependent shear modulus \( G(\omega) = \mu - i\omega\eta \) is assumed, hence a frequency dependent viscosity \( \eta(\omega) = \eta + i\mu/\omega \) is introduced into the Navier-Stokes equation, where \( \mu \) is the real and frequency independent shear modulus. We then obtain the characteristic
over-damped relaxation time for viscoelastic polymer films

\[ \tau_{ve}(k) = \frac{\tau_{\text{nonslip}}(k)}{1 + \tau_{\text{nonslip}}(k)(\mu/\eta)}, \]  \hfill (3.17)

and the static fluctuation spectrum \( S(k) \)

\[ S(k) = \frac{k\mu T}{\gamma k^2 + 2\mu k H/F}. \]  \hfill (3.18)

There are two asymptotes of the viscoelastic model [Eq. (3.17)]: \( \tau_{\text{nonslip}}(k) \ll \eta/\mu \) reduces \( \tau_{ve}(k) \) to \( \tau_{\text{nonslip}}(k) \), which is the purely viscous model used to describe a free liquid surface without elastic effects; in the limit that \( \tau_{\text{nonslip}}(k) \gg \eta/\mu \), \( \tau_{\text{nonslip}}(k) \approx \eta/\mu \), which is a manifestation of viscoelasticity. Considering the asymptotic behaviors of \( H/F \), i.e.,

\[ \frac{H}{F} = \begin{cases} 3/(2k^3d^3), & kd \ll 1, \\ 1, & kd \gg 1, \end{cases} \]  \hfill (3.19)

the spectrum in Eq. (3.20) can be approximately rewritten as

\[ S(k) \approx \frac{k\mu T}{\gamma k^2 + 2\mu k + 3\mu/(k^2d^3)}. \]  \hfill (3.20)
This static spectrum for polymer brushes can also be derived alternatively based on an argument of the free energy for a distorted incompressible isotropic viscoelastic polymer brush [45]. As depicted in Fig. 3.1, the surface height is displaced about the equilibrium uniform height $z = d$ according to

$$u_z(x) = u_{z,0} \cos(qx),$$  \hspace{1cm} (3.21)

where the amplitude $u_{z,0}$ is assumed to satisfy $u_{z,0} \ll d$. It can then be shown that the elastic part of the free energy excess is expressed as

$$\Delta f_e = \begin{cases} 3\mu u_{z,0}^2/(4k^2d^3), & kd \ll 1, \\ \mu u_{z,0}^2k/2, & kd \gg 1. \end{cases}$$  \hspace{1cm} (3.22)

Therefore, the total free energy excess per area, including both elastic and surface tension contributions for a brush subject to an arbitrary two-dimensional, low-amplitude distortion, can be written approximately as

$$\Delta f \approx \frac{1}{(2\pi)^2} \int dk \frac{1}{2} \left( \gamma k^2 + 2\mu k + \frac{3\mu}{k^2d^3} \right) |z(k)|^2.$$  \hspace{1cm} (3.23)

By invoking the equipartition theorem, the surface spectrum is then recovered, identical to Eq. (3.20).

### 3.2 Sample Preparation

**Spin-cast PS films**

Spin-cast homogeneous PS films were prepared by dissolving PS powders (purchased from Polymer Source Inc. and Pressure Chemical Company) of different molecular weights ($M_W$) and typical polydispersity $M_W/M_n \leq 1.08$ in toluene and then spin-casting onto optically flat 0.5 mm silicon wafers. The silicon substrates had been pre-treated with piranha etch and dilute hydrofluoric acid solution in order to remove organic impurities and native silicon oxides. According to the standard spin-casting procedure for PS films [106], desired film thicknesses were obtained by adjusting the concentration of PS in toluene and the spin-casting angular velocity. After spin-casting, samples were then annealed in high vacuum ($< 10^{-6}$ Torr) for approximately 24 hours at 170 °C to ensure complete solvent removal, and then quenched to room temperature.
PS brushes

PS brushes were synthesized by Dr. Foster’s group in the University of Akron using atom transfer radical polymerization (ATRP), described elsewhere [12]. Briefly, a self assembled monolayer (SAM) of 11-((2-bromo-2-methyl)-propionyloxy) undecyltrichlorosilane initiator was deposited on a silicon substrate that was cleaned using piranha etch. Polymerization of the PS monomer using ATRP was initiated from the immobilized SAM to form the homopolymer brush of high grafting density (typically \( \sim 0.6 \) chains/nm\(^2\)) and chain length polydispersity less than 1.2. Different thicknesses were obtained by varying the reaction time. The brushes were exhaustively extracted to remove all chains not tethered to the surface. The brushes were then annealed in high vacuum for 18 hours at 150 °C to remove residual solvent to form dry brushes and then cooled at \( \sim 40 \) °C/min to room temperature. A schematic of the brush structure is shown in Fig. 3.3 in comparison with a spin-cast PS film.

3.3 Experiment Details

3.3.1 Instrumentation and Experiment Setup

XPCS

All the XPCS experiments were carried out on Sector 8-ID-I at the Advanced Photon Source (APS), Argonne National Laboratory. Fig. 3.4 portrays the scattering geometry. The incident beam was generated by the first harmonic of an APS undulator with a certain gap yielding a first harmonic energy centered at 7.35 keV. Higher harmonics of the undulator were removed by reflection from a flat Si mirror. A Germanium channel-cut double-bounce monochromator selected a narrow energy range from the undulator.
Figure 3.4: Grazing incidence x-ray scattering and XPCS apparatus at the Advanced Photon Source. The dashed-line box denotes 8-ID-I end station.
harmonic. The beam was then collimated to $20 \times 20 \, \mu m^2$ using the defining slits, the parasitic scattering from which was then removed by the guard slits. Samples were vertically mounted on top of a thermal-conducting copper stage assembled with heating elements and temperature controller sensors in a vacuum chamber. Because of high viscosity, the polymer melt on films would not drift. To make the scattering surface sensitive, the incident angle during the XPCS data collection was usually fixed at $\alpha_i = 0.14^\circ$, below the PS critical angle ($\alpha_c \approx 0.16^\circ$ at x-ray energy $E = 7.35 \, keV$), so that the penetration of the evanescent wave field intensity was limited to $\sim 9 \, nm$ near the surface. Fig. 3.5 illustrates the scattering geometry and definitions of the wave vector transfers. When arriving at the sample, the x-ray transverse coherent lengths were 7 and $90 \, \mu m$ in the horizontal and vertical directions. Because of the projection of the beam cross section in the grazing incidence geometry, the horizontal coherent length was boosted by a factor of about 400, giving rise to sufficient coherence for XPCS experiments. The time-dependent surface diffuse scattering was collected using a Princeton Instruments x-ray charged-couple device (CCD) mounted downstream. This CCD camera consists of a $1340 \times 1300$ pixel array with the effective size of each pixel $22.5 \times 22.5 \, \mu m^2$. The specularly reflected beam was intercepted by a beamstop (made of a PIN diode current integrating detector) just in front of the CCD, in order to measure the direct beam intensity and protect the camera from direction illumination.

X-ray radiation damage is always a concern for soft matter materials, including polymers. Hence, samples were translated to a fresh area after about every 10 minutes’ exposure. This does not mean that the achievable maximum time span is only 10 minutes. In full-frame CCD mode, it usually takes $\sim 1.8$ sec to read out the data from the CCD memory, during which the beam was blocked with a front shutter synchronized with the CCD in order to save the sample. In addition, in case of very slow surface dynamics,
an arbitrary sleep time may be deliberately inserted between consecutive frames. In principle, there should be no upper limit. However, due to environmental vibrations, the empirical maximum time span that can be reached on Sector 8-ID-I to ensure scattering stability is $\sim 10^3$ sec for reflection geometry, and $> 5 \times 10^3$ sec for transmission geometry. In order to check the film thickness and radiation damage, reflectivity scans were taken before and after each measurement.

Although the readout time of the CCD camera is 1.8 s, it is still possible to achieve a time scale as fast as 30 ms, by means of the kinetics mode feature of the camera. Detailed discussions of this mode can be found in Ref. [88]. Briefly, the kinetics mode allows us to rapidly take multiple successive exposures, using a fraction (hereafter called “slice”) of the CCD area for illumination, and thus for data acquisition. The previously illuminated CCD image is subsequently shifted electronically into the unilluminated region as fast as 50 $\mu$s. After the whole CCD is full, multiple slices are read out once as a full frame image. In doing so, a sequence of large images with poor time resolution can be effectively traded for a sequence of smaller slices but with improved time resolution. However, using only a small portion of the CCD in the kinetics mode narrows the probed in-plane wave vector range (and hence the length scales), compromising the major advantage of the CCD-based area detectors over the conventional single-channel avalanche photodiode detector. Another unavoidable consequence is that, given a certain incident coherent flux, a very short pulse-like exposure may not guarantee enough scattered photons to provide sufficient signal-noise ratio for the calculation of the intensity-intensity autocorrelation functions.

**Transverse diffuse scattering**

Transverse diffuse scattering was carried out on the GISAXS beamline in Sector 8-ID-E end station. The scattering geometry (Fig. 3.6) is similar to the XPCS setup on Sector 8-ID-I, except that the sample was mounted on a 4-cycle Huber diffractometer and a fast NaI scintillation detector (Cyberstar) mounted on the Huber $2\theta$-arm was used to collect the data. During the measurement, the detector position was fixed at a desired in-plane scattering angle, i.e., $\chi = 0$ and $\alpha_i + \alpha_f$ was fixed, so that the vertical wave vector transfer $q_z$ was a constant, and the sample was then rocked in order to vary the in-plane wave vector transfer $q_x$. 
Figure 3.6: Schematic of Sector 8-ID-E end station.
3.3.2 XPCS Data Reduction

As we have discussed in Section 2.4, the crucial step in XPCS is to calculate the normalized intensity-intensity autocorrelation function $g_2$ as a function of time delay. This procedure is quite established in DSL. However, to meet the challenge of low photon count rates in XPCS experiments, a series of technical operations have to be executed to convert a sequence of raw CCD images into the final $g_2$ functions [11, 88]. This task requires a lot of computing capabilities and was basically performed with the help of two customized analysis software packages.

Prior to any analysis, a few corrective adjustments have to be carried out for the raw image on a pixel-by-pixel basis in order to extract real photon counts in each pixel. These corrections include removal of saturated pixels, background subtraction (due to dark current and electronic noise), flatfield normalization to bring the per-photon response of each pixel to uniform levels, lower-level discrimination to improve the signal-to-noise ratio in the presence of low intensities, and conversion of voltages in analog-to-digital unit (ADU) to discrete number of photons.

To calculate the intensity-intensity correlation $\langle I(q, t')I(q, t + t') \rangle$ for each pixel, a multi-$\tau$ correlation protocol is applied, where the intensities of each pixel in several consecutive frames are averaged before long-delay correlations are evaluated. This protocol improves the signal-to-noise ratio and logarithmically reduces the number of delays involved. Since the area detector measures intensities at multiple $q$’s simultaneously, after each pixel is mapped to a certain wave vector transfer value through simple geometrical configurations, the correlation functions can be normalized via a multi-speckle normalization procedure which uses the average across pixels of the same wave vector transfer, as well as the average over time, to further improve the signal-to-noise ratio and obtain more reliable correlation functions.

\footnote{For simplicity, a shorter notation $g_2$ will replace $g_2^{(2)}$ from now on.}

\footnote{The first package named “coherent” was developed in the Yorick interpreted language mainly by Matthew A. Borthwick and Peter Falus in MIT. Later another package with graphical-user-interface (GUI) was developed in Matlab with improved graphical and data-processing features by Michael Sprung (Sector 8-ID-I, Advanced Photon Source) and the author. Both packages are available for download at http://8id.xor.aps.anl.gov/8id.html}
3.4 Surface Tension

Surface tension is the dominant force that relaxes thermally excited capillary waves on a liquid surface, and has to be measured before the dynamic behavior can be studied. To this end, many techniques have been employed, such as tensiometry and pendant drop shape analysis. However, these techniques are based on mechanical deformations imposed on the surface, and cannot be used to measure surface tensions on thin liquid films. One well-established method is surface diffuse x-ray scattering [89]. As shown in Chapter 2, the intensity of surface diffuse x-ray scattering is related to the Fourier transform of the liquid surface height-height correlation function $C(R)$, which is in turn determined by the surface tension.

Based on the principles of the liquid surface scattering with DWBA approximation, the differential cross section can be rewritten as

$$\frac{d\sigma}{d\Omega} = A n^2 \rho^2 |E_i|^2 |E_f|^2 S(q),$$

(3.24)

where $S(q)$ is known as the structure factor and is given by

$$S(q) \approx \frac{4\pi}{q^2 r_0^2} e^{-q^2 r_0^2} \left( \frac{r_0 q_\parallel}{2\pi \rho \gamma e} \right)^\eta \left\{ \frac{\Gamma \left( 1 - \frac{1}{2}\eta \right)}{\Gamma \left( \frac{1}{2}\eta \right)} + \left( \frac{r_0 q_\parallel}{2} \right)^2 \frac{\Gamma \left( 1 - \frac{1}{2}\eta \right)}{\Gamma \left( 1 + \frac{1}{2}\eta \right)} - \left( \frac{r_0 q_\parallel}{2} \right)^{\eta - 1} \frac{1}{1 - \frac{1}{2}\eta} \right\}.$$  

(3.25)

Here $r_0 \approx 0.27 \text{ nm}$ is introduced as the monomer size to prevent the divergence at large wave vectors. In the limit of small $q_z$, $S(q)$ can be simplified to a $q_z$-independent expression,

$$S(q_\parallel) \approx \frac{k_B T}{\gamma q_\parallel^2}.$$  

(3.26)

Hence, the scattering intensity drops quickly as a power law with respect to $q_\parallel^{-2}$. However, the full expression in Eq. (3.25) was used in the analysis for surface tension $\gamma$.

A CCD camera was used to collect the diffuse scattering signals. The resolution is set by the size of the CCD pixels, $U = 22.5 \mu m$. It turns out that in the small angle limit, e.g., $\alpha_f < 1^\circ$, the resolutions in $q_x$ and $q_y$ are approximately $\Delta q_x \approx 2\pi U \sin \alpha_f / (\lambda r) = 4 \times 10^{-6} \text{ nm}^{-1}$ and $\Delta q_y \approx 2\pi U / (\lambda r) = 2.4 \times 10^{-4} \text{ nm}^{-1}$, where $r = 3500 \text{ mm}$ is the sample-to-CCD distance and $\lambda = 0.169 \text{ nm}$ is the x-ray wavelength. Both are much smaller than the typical minimum accessed in-plane wave vector $\sim 10^{-3} \text{ nm}^{-1}$. Therefore, resolution broadening will not affect the analysis.
Figure 3.7: (a) CCD image of the static time-averaged surface diffuse scattering from a PS film of $M_W = 123$ k g/mol and thickness 84 nm at 160 °C. (b) Calculated static scattering with DWBA approximation on the basis of the capillary wave theory.

In Fig. 3.7, the static diffuse scattering image from a PS film of 84 nm at 160 °C is compared with theoretical calculations using Eq. (3.25) [76]. The wave-like oscillations arise from the formation of standing waves in film geometry and will be discussed in detail in Chapter 4. There is very good agreement between the data and the simulation, indicating that the surface morphology of molten polymers is governed by capillary waves. Fig. 3.8 shows an example of the surface tension analysis for a 142 nm PS film. For each $q_z$ value, the structure factor is a function of $q_\parallel$, and the surface tension is obtained by fitting all these curves simultaneously to Eq. (3.25). In Fig. 3.9a, fitted surface tension is plotted as a function of temperature for PS films of $M_W = 123$ k g/mol and various thicknesses. Surface tension values are only slightly higher than bulk values, and show a similar temperature dependence as bulk PS with no systematic variation as a function of film thickness. In addition, surface tension does not show significant dependent on molecular weight either, as shown in Fig. 3.9b. Therefore, in the current study, surface tensions of bulk PS melts are usually used for dynamic analysis.

3.5 Surface Dynamics of Spin-cast Films at $T \gg T_g$

Although surface dynamics of simple liquids, e.g., water and glycerol, have been studied extensively by DLS, and recently by XPCS as well, there had been no experimental report, before the year of 2003, on how well the capillary wave theory applies to surface dynamics of polymer films. In particular, it remained ambiguous as to whether or not capillary wave theory is still valid when the film thickness approaches the typical
Figure 3.8: Structure factors extracted from static diffuse scattering at different $q_z$ values for a PS film of $M_W = 123k$ g/mol and thickness 142 nm at 160 °C. Data are shifted vertically for clarity. Solids lines denote the best fits to Eq. (3.25), with fitted surface tension $\gamma = 0.0291$ N/m.

Figure 3.9: (a) Surface tension vs. temperature for PS films of $M_W = 123k$ g/mol and different thicknesses [89]. (b) Surface tension vs. molecular weight for PS films of an identical thickness 160 nm at $T = 122$ °C. Solid lines represent the bulk PS surface tensions [178].
length scale of the polymer chains, i.e., the radius of gyration radius $R_g$. Therefore, a systematic investigation was performed using XPCS to measure the surface dynamics of Si-supported PS films of various molecular weights (30k $\sim$ 900k g/mol) and thicknesses (from $1R_g$ to hundreds of nm). We first started with temperatures well above the glass transition temperature $T_g$ of bulk PS, which is around 95 $\sim$ 100 °C for $M_W > 30k$ g/mol. The reason for doing this is that due to the limit of the maximum time window of the instruments, $T \gg T_g$ promises observable dynamics for highly viscous PS melts.

### 3.5.1 Thick Films ($d \gg R_g$)

The work to measure surface dynamics on thick PS film were accomplished by Kim et al. in 2003 [76,77]. In Ref. [76], PS films of various thicknesses ($d = 84, 170, 177, 312.5$ nm) but identical molecular weight ($M_W =123k$ g/mol, hence $R_g = 9.4$ nm) were studied. The normalized $g_2$ correlation functions defined in Eq. (2.95) were obtained through the

---

4For PS in $\theta$ conditions, $R_g = 0.67(N/6)^{1/2}$ nm, where $N$ is polymerization index.
Figure 3.11: Thickness scaling plot: $\tau/d$ vs. $q_d$ for films of $M_W=123k$ g/mol and thicknesses 84 nm (squares), 170, 177 nm (triangles), and 312.5, 318, 333 nm (diamonds) at three temperatures. Solid lines are fits to Eq. (3.12).

data reduction procedure discussed in Section. 3.3.2. Representative experimental correlation functions acquired from a 84 nm film at 160 °C are shown as symbols in Fig. 3.10 for four different in-plane wave vectors. The lines denote the fits to

$$g_2(q, t) = 1 + \beta e^{[-2(t/\tau)^\alpha]},$$

(3.27)

where $\beta$ is the coherent contrast, $\tau = \tau(q)$ is the relaxation time for equilibrium surface height, and $\alpha$ is the stretching exponent. It is found that $\alpha = 1$ provides a good description of the data.

$\tau(q)$ values obtained from the fitting of the $g_2$ correlation functions are scaled with film thicknesses and plotted as a function of $q_d$ in Fig. 3.11. Solid lines denote the fits to the thickness-scaling relation adapted from Eq. (3.12)

$$\frac{\tau(q)}{d} \approx \frac{2\eta}{\gamma(q) d} \left[ \frac{\cosh(q_d)^2 + (q_d)^2}{\sinh(q_d) \cosh(q_d) - q_d} \right].$$

(3.28)

There is excellent agreement between the experiment and theory, with a single fitting parameter, the ratio of $\eta/\gamma$. Therefore, the film viscosity can be obtained by knowing the surface tension via static surface diffuse scattering analysis. It proves that dynamical capillary wave theory is satisfactory, and that its premise of a wave vector and thickness independent viscosity is appropriate for the films studied here. Viscosity values for various molecular weights are shown in Fig. 3.12, as compared to literary bulk values [113].
Polymers show quite different behaviors from those in the bulk state as the length scale of the system gets smaller and smaller. For example, since Keddie et al. first systematically investigated $T_g$ in polymer films [75], various techniques, such as ellipsometry, x-ray reflectivity, local thermal analysis and so on, have been employed to measure $T_g$ in thin films, and it was found that $T_g$ shows a pronounced reduction for silicon supported PS films [42]. This reduction was speculated to be attributed to the existence of a thin liquid-like surface layer in which the segments of polymer chains possess higher mobility than those within the interior of the film even in a certain temperature range above the bulk $T_g$, i.e., the viscosity of the film is not homogenous in the direction normal to the surface [28, 30, 43, 74, 94, 174]. Therefore, the surface dynamics would be modified accordingly. To test this hypothesis, we have developed a theory for the surface and interfacial dynamics of an inhomogeneous film composed of two layers of different viscosities. Details of the calculation can be found in Appendix. C and Ref. [72].

Following Kawana and Jones [74], we hypothesize the existence of a high mobility surface layer of thickness $h_2 = 10$ nm and viscosities 10, 100, 1000 times less than the bulk.

Figure 3.12: Viscosity vs. temperature obtained from PS films of various molecular weights (black squares) [76,77]. Bulk values are shown in red solid symbols.
Figure 3.13: (a) Experiment (○) and calculated relaxation time constants for a PS film of \( M_W = 123 \text{ kg/mol} \) and total thickness \( d \approx 80 \text{ nm} \) at 150 °C. Single-layer theory is used for film model (1) (black solid line), while bilayer theory is used for hypothesized film models (2)-(4) (other lines as labeled). (b) and (c) are the logarithmic intensity map of \( 1/|\chi_{zz}^{(22)}(q_, \omega)| \) and corresponding mode amplitude for film model (2).

value on a single-layer PS film of fixed total thickness \( d = 80 \text{ nm} \) at 150 °C (Fig. 3.13). Surface tension \( \gamma_2 = 31.4 \times 10^{-3} \text{ N/m} \) is taken from the bulk value and bulk viscosity \( \eta_1 = 3.58 \times 10^5 \text{ Nsec/m}^2 \) is taken from the fitted experimental value using a single-layer model. Since the film is composed of the same substance, it is reasonable to assume a zero interfacial tension \( \gamma_1 = 0 \text{ N/m} \). Many x-ray and neutron reflectivities from single-layer PS films did not reveal less dense layers on surfaces, thus we assume the same mass density throughout the whole film. The relaxation time constants for bilayer film models (2)-(4) in Fig. 3.13a are calculated by numerically searching for purely imaginary poles of \( \chi_{zz}^{(22)}(q_, \omega) \) in the lower complex \( \omega \) plane. A logarithmic intensity map of \( 1/|\chi_{zz}^{(22)}(q_, \omega)| \)
for bilayer film model (2) is shown in Fig. 3.13b, where the dark line corresponds to the solutions of $1/\chi^{(22)}_{zz}(q_{||},-i\Gamma) = 0$. The mode amplitudes of the relaxation time constants of bilayer film model (2) are almost 1 and shown in Fig. 3.13c. If a non-zero interfacial tension is considered, another mode is supposed to exist. However, such a mode vanishes and does not contribute to the surface dynamics, because the PS system in the present study has zero interfacial tension. For the observed mode, the amplitude deviations at low wave vectors are attributed to the precision limit of our numerical computations. Considering the penetration of the velocity fields for the viscous liquid elements (Fig. 2.3) which are engaged in elliptical motions (overall effect of these motions on the surface is capillary waves), the waves with smaller wavelengths are more sensitive to the properties of the region close to surface. Therefore, this region contributes more to the overall dynamics at large wave vectors, where large deviation from the dynamics of supported homogeneous single-layer film (black solid line) is observed as shown in Fig. 3.13a.

If we fix the total film thickness $d$ and viscosities $\eta_2 = 0.1\eta_1$, and vary the top layer thickness $h_2 = 10, 20, 40$ nm, the calculated surface dynamics are shown in Fig. 3.14.

We then fix the thin surface layer viscosity and thickness, $\eta_2 = 0.1\eta_1$ and $h_2=10$ nm,
Figure 3.15: Calculated relaxation time constants from various supported PS films at 150 °C. Blue dashed lines are bilayer calculations for films whose total thickness \(d\) is (a) 80 nm, (b) 60 nm, (c) 40 nm, and (d) 20 nm, while the thin top surface layer thickness and viscosity are fixed, \(h_2=10\) nm and \(\eta_2 = 0.1\eta_1\). Black solid and red dotted lines are single-layer calculations with a non-slip boundary condition for two kinds of films of parameters \(d\) and \(\eta_1\) (black solid lines), \(h_2\) and \(\eta_2\) (red dotted lines) respectively.

Vary the bottom layer thickness \(h_1\) from 70, 50, 30 to 10 nm while keeping its viscosity constantly at \(\eta_1 = 3.58 \times 10^5\) Nsec/m², and compare the surface dynamics to those from supported homogeneous single-layer films of viscosity \(\eta_1\) and thicknesses \(d = 80, 60, 40\) and 20 nm respectively (Fig. 3.15). As the bottom layer thickness decreases, the surface dynamics (blue dashed lines) become more and more deviated from those of the homogeneous single-layer films of the same total thicknesses (black solid lines). However, the contribution from the thin liquid-like surface layer shows prominent effects only when the thickness of this layer is comparable to that of the bottom layer.

Therefore, based on the above bilayer analysis, within a typical resolution of the XPCS experiments in a reflection geometry, we can rule out the possibility of the existence of more than a 10 nm thick surface layer with a viscosity smaller than one tenth of the bulk value. In order to narrow the parameter limits of the possible liquid-like surface layer, surface dynamics have to be measured at high wave vectors where larger deviations from homogeneous single-layer films may be observed if they exist.
3.5.2 Ultra-thin Films ($d \sim R_g$)

So far, we have demonstrated that the surface dynamics of PS ($M_W = 123k$) molten films of thickness ($> 8R_g$) and wavelengths of the order of 100 nm or larger, can be explained in terms of the normal hydrodynamic theory for capillary wave fluctuations on viscous liquid films. However, follow-up XPCS experiments on PS films of thickness comparable to $2R_g$ significantly exhibit different fluctuation relaxation behaviors from those of a simple viscous liquid. This may be attributed to the occurrence of the shear modulus (Eq. 3.17), which presumably arises from the adsorption effect at the substrate. The surface spectrum may then be described in Eq. (3.20). It has to be emphasized that the PS films studied here are not intentionally grafted brushes and the shear modulus is expected to be smaller than for brushes. In fact, directly applying the brush model in Ref. [45] to evaluate the shear modulus yields a value several orders of magnitude larger than the measured values for the spin-cast films in our experiments (Fig. 3.17).

Therefore, in the limit that $\gamma \gg \mu d$, Eq. (3.20) reduces to

$$S(q_\parallel) \approx \frac{k_B T}{\gamma q_\parallel^2 + 3\mu/(q_\parallel^2 d^3)},$$

(3.29)

which is essentially $\tilde{C}(q_\parallel)$, the Fourier transform of the surface height-height correlation function $C(R)$. It then follows that

$$C(R) = \int dq_\parallel S(q_\parallel) e^{iq_\parallel \cdot R} = \frac{B}{2} \ker (q_{l,c} R),$$

(3.30)

where $q_{l,c} = (3\mu/\gamma)^{1/4}d^{-3/4}$, and $\ker(x)$ is the Kelvin function defined through $\ker(x) = \text{Re} [K_0(x\sqrt{i})]$ with $K_0$ being the modified Bessel function of the second kind. For small $x$, $\ker(x)$ is well approximated by $K_0(x)$ (Fig. 3.16). Hence, including the upper wave vector cutoff $q_{\text{max}} = 2\pi/r_0$ to prevent divergence, we have

$$C(R) \approx \frac{B}{2} K_0 \left( q_{l,c} \sqrt{R^2 + r_0^2} \right),$$

(3.31)

which is identical to Eq. (2.42), except that the lower wave cutoff $q_{l,c}$ is determined by the elasticity instead of the gravitational effect or the van der Waals interaction.

PS films of various molecular weights, with corresponding radii of gyration $R_g$ listed in Table. 3.1, were prepared. Film thicknesses were controlled to be $R_g$, $2R_g$, $4R_g$, and thicker.

Although the elasticity manifests itself in Eq. (3.17), the limits imposed by the XPCS experimental setup due to weak scattered intensity at high $q_\parallel$ and beamline temporal instability prevent a precise determination of the shear modulus directly from the
dynamic measurement. However, Eq. (3.20) points out that the shear modulus can also be determined more accurately from static scattering experiments with a much broader $q_{\parallel}$ window. Transverse diffuse scans were measured on each sample at various temperatures (well above the bulk $T_g$) desired for the XPCS measurement. At a small $q_z$ value, the observed intensity with slit widely opened in the direction of out-of-plane ($q_y$) is essentially proportional to the convolution of $\tilde{C}(q_{\parallel})$ and the instrumental resolution function (Section 2.3.3). The transverse scattering data was fitted to the full expression described in Eq. (2.89), with the height-height correlation function $C(R)$ given by Eq. (3.31). In Fig. 3.17, we show the log-log plot of transverse scans for PS (123k) films of thicknesses $2R_g$ and $4R_g$. The fitted lower wave vector cutoff $q_{l,c}$ which is related to the shear modulus of the film is marked by the vertical dash-dot lines. In the lower inset, the shear moduli from $2R_g$ films clearly show values at least three orders of magnitude smaller than those expected for brushes [45]. The error bars were calculated based on repeated measurements. We found that the cutoff position in the rocking scans shows some variations on repeating the measurements, indicating that the films of $M_W > 123k$

Table 3.1: The radius of gyration $R_g$ of PS of different molecular weights.

<table>
<thead>
<tr>
<th>$M_W$ (kg/mol)</th>
<th>65</th>
<th>123</th>
<th>400</th>
<th>650</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_g$ (nm)</td>
<td>6.8</td>
<td>9.4</td>
<td>17.0</td>
<td>21.7</td>
</tr>
</tbody>
</table>
are still in a non-equilibrium state. However, it should not affect the following XPCS dynamic measurements because the process towards final equilibrium occurs on a much slower time scale than the capillary wave relaxation. The broad plateau of the transverse diffuse scattering in the small $q_x$ region is the specular beam, and its width is determined by the instrumental resolution. The peak at the high $q_x$ end is known as the Yoneda peak [182], arising from the enhanced electric field at the surface when either the incident or the exit angle reaches the critical angle value.

The $g_2$ functions from the XPCS measurements are shown in Fig. 3.18 for PS films of $M_W = 123k$ g/mol and various thicknesses. The surface dynamics get slower when the film thickness is decreased from $4R_g$ to $2R_g$. A further decrease in thickness to $1R_g$ yields frozen surface dynamics. Inserting the values of the bulk viscosity and surface tension into Eq. (3.12), we obtain a relaxation time for the $1R_g$ film which should have been observable within the experimental time window. However, the observed $g_2$ of the $1R_g$ film is above unity and shows time-independence for all the wave vectors, indicating
that the surface fluctuations are very highly temporally correlated, a signature of a static surface or at least a surface with extremely slow dynamics. This might be due to the fact that the number of adsorption points per chain should be larger in 1$R_g$ films than 2$R_g$ films, which means there is highly restricted chain mobilities in 1$R_g$ films and the lateral displacement of chains required for surface fluctuations is thermodynamically unfavorable.

In Fig. 3.19a we plot the relaxation time constant $\tau$ vs. in-plane wave vector $q_\parallel$ deduced from $g_2$ for PS (123k) film of thickness $h = 4R_g$. Both viscoelastic (Eq. 3.17) and purely viscous models (Eq. 3.12) are used for the fitting. Surface tension is known from
Figure 3.19: Measured time constant $\tau$ vs. in-plane wave vector $q_{\parallel}$ for PS films of various molecular weights and relative thicknesses at various temperatures. Data in each panel was fitted to both viscoelastic (Eq. 3.17) and viscous (Eq. 3.12) models represented by the solid and dashed lines respectively. In (a) and (c), the two models can not be distinguished.

the static scattering at very high wave vectors, shear modulus (or lower wave vector cut-off) is obtained from the transverse diffuse scattering, and the exact thickness is obtained from reflectivity fitting. Hence viscosity is the only fitting parameter. In Fig. 3.19a, the two fits cannot be easily distinguished from each other, thus the conventional viscous model is sufficient to describe the surface dynamics. However, for the film of $h = 2R_g$, only the viscoelastic model yields a good fit (Fig. 3.19b). More interestingly, when 65k, 4$R_g$ and 400k, 2$R_g$ films are compared, although these two films have a similar thickness, they behave very differently: the latter shows a significant viscoelastic effect (Fig. 3.19d), while the former does not (Fig. 3.19c). Such an effect was also observed in other 2$R_g$ films of different molecular weights, but not in 4$R_g$ films. Therefore, it is not the absolute thickness of the film but rather the ratio of the thickness to $R_g$ and the length scale of the surface waves which determine whether the elastic shear modulus needs to be taken into account in calculating the relaxation time of over-damped capillary waves.

Although the chains in 2$R_g$ films are not purposely grafted, chain segments are
confined and still pinned onto the substrate, forming a Guiselin brush [54]. In order to create surface fluctuations and meanwhile maintain a constant density, lateral chain stretching is required. However, due to the large entropy penalty, the long wavelength mode (lateral displacement at a large length scale) would be suppressed [45, 180], and the elasticity is expected in this regime. This effect does not manifest itself for films of 4R_{g} or larger thickness, partially because for q_{||}d \ll 1, \tau_{\text{nonslip}} \sim 1/d^3, meaning a speed-up of a factor of 8 for surface wave relaxation time when the thickness increases from 2R_{g} to 4R_{g}, so that the 2nd term in the denominator of Eq. (3.17) may be negligible. Furthermore, in a qualitative way the elasticity due to the adsorption of chain segments to the substrate is expected to less effectively modulate the surface dynamics in thicker films. Therefore the capillary wave relaxation becomes less sensitive to the elasticity effect in 4R_{g} within the current experimental time and wave vector windows.

We have also tried to interpret the deviation from the normal viscous model for 2R_{g} films by introducing the van der Waals interactions into the expression of the relaxation time constant, so that

$$\tau_{\text{vdW}}(q_{||}) \approx \frac{\tau_{\text{nonslip}}(q_{||})}{1 + A_{\text{eff}}/(2\pi\gamma d^4 q_{||}^2)}.$$  \hspace{1cm} (3.32)

Although the experiment data can be fitted by Eq. (3.32) mathematically, the obtained
effective Hamaker constant $A_{\text{eff}}$ turned out to be unphysically large ($10^{-19} \sim 10^{-17}$ J), compared with the typical value for PS on silicon oxide, $2.2 \times 10^{-20}$ J [135]. This is consistent with the findings in Ref. [84], where capillary wave spectra of PS films on patterned Si substrates were analyzed and it was found that taking into account only the van der Waals interactions yielded unreasonably large values of $A_{\text{eff}}$. Therefore, this explanation can be safely excluded.

The obtained viscosities from the fits to the viscous model for $4R_g$ films and the viscoelastic model for $2R_g$ films using the values of $\mu$ given by the static $S(q_\parallel)$, are plotted as a function of $M_W$ in Fig. 3.20. A power-law fitting $\eta \sim M_W^{\zeta}$ yields $\zeta = 1.94 \pm 0.15$ and $2.90 \pm 0.16$ for (a) $2R_g$ and (b) $4R_g$ films respectively. In strongly confined polymers, the chains are proposed to reduce interpenetration into each other [9], resulting in less entanglement. However, according to Ref. [73], this confinement-induced entanglement reduction only occurs when the film thickness is much less than $R_g$ and closer to the segment length. Nevertheless, it is interesting to note that the deviation of the scaling factor $\zeta$ from the prediction of the reptation theory for the bulk $3.0 \sim 3.4$ [27, 126], increases as the film thickness becomes smaller with respect to $R_g$.

### 3.6 Surface Dynamics of Spin-cast Films at near $T_g$

Although the glass transition phenomenon in polymer films is always of great interest, we were initially reluctant to perform XPCS measurements at near $T_g$, because it was expected that the viscosity would be tremendously large and that the surface dynamics would be too slow to be resolved. However, a recent upgrade on Sector 8-ID-I significantly improves the coherence and photon flux, making possible XPCS measurements at higher in-plane wave vector $q_\parallel$ values. With some hope of observing slow dynamics at close to $T_g$, we prepared spin-cast PS films of $M_W$ ranging from 11k to 900k g/mol and thickness ranging from 76 nm to 300 nm, but surprisingly, the XPCS results revealed a much more complicated surface dynamic behavior than we had expected.

The $g_2$ autocorrelation correlation functions obtained at below bulk $T_g$ ($\sim 100$ °C) from all films of $M_W \geq 30k$ g/mol do not show any relaxation in the experimental wave vector range $10^{-3} \sim 10^{-1}$ nm$^{-1}$, indicating that if they exist the surface dynamics must occur on time scales much slower than those achievable in the experiment ($\sim 10^3$ sec). However, at temperatures $T \geq 106$ °C, we start to observe relaxations. Fig. 3.21 shows the $g_2$ functions obtained from a film of $M_W=129k$ g/mol and thickness $d=160$ nm at
Figure 3.21: The $g_2$ functions obtained at an in-plane wave vector $q_∥ = 1.8 \times 10^{-2}$ nm$^{-1}$ from a PS film of $M_W = 129$ k g/mol and thickness $d = 160$ nm at various temperatures. Solid lines denote the best fits to a single exponential behavior with $\alpha = 1$, and dotted lines are fits to a stretching exponential behavior. The curves are vertically shifted for clarity.

different temperatures. Solid lines are best fits to Eq. (3.27) with $\alpha = 1$ for 101 $\sim$ 111 °C. Surprisingly, a further increase in temperature results in a strongly stretched exponential decay of the $g_2$ function, denoted by the dashed lines corresponding to $\alpha \approx 0.10$ and 0.26 for 116 °C and 122 °C respectively. However, such fittings yield very large parameter uncertainties (error bars can be comparable or even larger than parameters themselves), because it can be clearly seen that neither the baseline nor the initial plateau can be reached for the $g_2$ function, which, on the hand, indicates a highly stretched behavior. Once the temperature is increased to well above $T_g$, the $g_2$ functions switched back to conventional single exponential decay with $\alpha \approx 1$, as shown Section 3.5. This behavior of the $g_2$ functions was observed for all the films of $M_W > 30$ k g/mol. On the other hand, for films of $M_W \leq 30$ k g/mol whose bulk $T_g$ values are obviously $M_W$-dependent and less than those of $M_W > 30$ k g/mol, the stretched exponential behavior was not observed, and only a single exponential decay with $\alpha \approx 1$ was found at any temperature above the bulk $T_g$. The molecular weights investigated in the current study at temperatures are marked as symbols in the $M_W - T$ diagram shown in Fig. 3.22 constructed by the
Figure 3.22: $M_W - T$ diagram constructed from XPCS measurements on the surface dynamics of supported PS films. The experiment points are marked with symbols. Bulk glass transition temperatures shown as the leftmost solid line are obtained from Ref. [104]. The horizontal dashed line indicates $M_C$, the critical molecular weight for entanglement. In glass state (∗) no relaxation was found. Region SI (□) and region SII (□) denote the single exponential behaviors dominated by chain segments of critical entanglement length and full chains, respectively. Region ST (▲) denotes the stretched exponential behavior for the surface dynamics which arises from the dynamics of chain segments of lengths ranging from the critical entanglement length to the full chain length.

XPCS measurement of surface dynamics. Below the bulk glass transition temperatures (obtained from Ref. [104] and represented by the leftmost line) surface dynamics do not exist or they occur on times scales too slow to be measured at present.

The $g_2$ function explicitly indicates the characteristic relaxation time of the thermally excited surface height fluctuations as a function of in-plane wave vector $q_∥$, which is shown in Fig. 3.23 for 160 nm films as an example. As we have demonstrated in Section 3.5 that at temperatures well above bulk $T_g$, the surface dynamics can be very well explained by Eq. (3.12), with the fitted viscosities consistent with the bulk values of the corresponding molecular weight. Fig. 3.23a shows that at 151 °C, a temperature well above the bulk $T_g$, for a fixed film thickness, the surface dynamics in terms of the over-damped capillary waves become solely dependent on the wave vector and the viscosity (hence the molecular weight). As the temperature is decreased to 111 °C near the bulk $T_g$ (Fig. 3.23b), it is very surprising to observe the collapse of the relaxation time constants for all films of $M_W \geq 30$ k g/mol onto almost a single curve, i.e., the surface
dynamics become fairly independent of the molecular weight. However, films of smaller molecular weights, e.g., 11k and 22k g/mol, still show $M_W$-dependent dynamics. While the fitted viscosities at high temperatures are consistent with the bulk values obtained via rheological measurements [113], those of $M_W > 30k$ g/mol at low temperatures (near $T_g$) are orders of magnitude smaller, as shown in Fig. 3.24. It is also interesting to note that the mean value of the $M_W$-independent viscosities for $M_W \geq 30k$ g/mol films at 111 °C intersects the bulk viscosity behavior at $M_W^* \approx 30.7k$ g/mol. This value is very close to the critical molecular weight for entanglement $M_C=31.2k$ g/mol [41]. The same coincidence was also observed at a lower temperature $T = 106$ °C, where the surface dynamics was found about seven times slower than at 111 °C.

Based on the behaviors of the surface dynamics, the $M_W - T$ diagram (Fig. 3.22) can therefore be subdivided into several regions: a glass state, region SI and region SII for $M_W$ independent and dependent single exponential relaxations, and an intermediate
Figure 3.24: Fitted viscosity (○) vs. molecular weight for PS films of an identical thickness 160 nm at 111 °C, compared with bulk viscosity values (♦). Dash-dot line denotes the mean value of the fitted viscosities for $M_W \geq 30k$ g/mol, and red solid line represents the bulk behavior in the entangled regime with a scaling behavior of $\eta \sim M_W^{3.4}$ predicted by the reptation theory [27]. Their intersection is labeled as $M_W^* \approx 30.7k$ g/mol. The symbols in the dashed box in the bottom-right corner show the fitted viscosity values obtained at 151 °C which are consistent with the bulk values.

region ST for stretched exponential relaxation. The coincidence of $M_W^*$ and $M_C$ values may indicate that the mechanism that dominates the surface dynamics in the vicinity of $T_g$ arises from the cooperative motion of segments whose length is equal to the critical entanglement length, so that the apparent viscosity is the same for all films of $M_W \geq M_C$.

As the temperature is increased into region ST, the appearance of the stretched exponential in the $g_2$ function signals the existence of multiple time scales, as the dynamics begin to encompass length scales ranging from the critical entanglement length to the full chain length. At $T \gg T_g$ in region SII, the $g_2$ functions again exhibit single exponential behavior, the relaxation time constants clearly show $M_W$ dependence, and the fitted viscosities are consistent with the bulk values, implying that the full chain dynamics become dominant. On the other hand, for chains with $M_W < M_C$, i.e., chains shorter than the critical entanglement length, the full chain dynamics are always determinant so that no stretched exponential behavior is observed.

In Section 3.5.1 we discussed the surface dynamics at temperatures well above the bulk $T_g$ and excluded the possibility of a thin liquid-like surface layer which was hypothesized to be the determinant factor for the $T_g$ reduction in supported PS films. To test
Figure 3.25: (a) Thickness-scaling plot of $\tau/d$ vs. $q_{||}d$ for films of $M_W=129$ k g/mol and various thicknesses at two temperatures: 111 °C (top-right) and 151 °C (bottom-left). Kim’s data (red ♦) are reprinted from Ref. [76] for PS films of $M_W=123$ k g/mol and various thicknesses at 150 °C. Solid lines represent the best fits to Eq. (3.12). (b) $\tau/d$ vs. $q_{||}d$ for the film of $M_W=290$ k g/mol and $d=160$ nm at 111 °C. The solid line represents the best fits to both the single layer model (3.12) and the bilayer model (with $\eta_2$ and $h_2$ being the fitting parameters), which are indistinguishable from each other. The dotted line denotes another try of the bilayer fitting with $h_2$ fixed at 10 nm and $\eta_2$ the only fitting parameter. The inset shows the bilayer geometry.

This hypothesis again for temperatures very close to $T_g$, we first examined the relaxation time constants for films of different thicknesses but constant $M_W$ in a thickness-scaling plot, i.e., $\tau/d$ vs. $q_{||}d$, as shown in Fig. 3.25a. It is implied in Eq. (3.28) that $\tau/d$ should be only a function of $q_{||}d$ and directly proportional to $\eta/\gamma$ for uniform viscous films. In both single exponential relaxation regions SI and SII, 111 °C and 151 °C for example, the collapse of $\tau/d$ onto a single master curve indicates a homogeneous viscosity throughout the film. Therefore, the faster surface dynamics (as compared to the predictions with bulk viscosities) observed in region SI should arise from the dynamics within the film, instead of from the conjectured low-viscosity surface layer. Otherwise, inhomogeneities
would lead to a failure in the scaling behavior as a function of film thickness. In order to strengthen this point, we performed a bilayer analysis, where the film is treated as a supported bilayer system with a lower-viscosity \( (\eta_2) \) layer of thickness \( h_2 \) sitting on top of another layer of viscosity \( \eta_1 \). Using the theory developed in the Appendix C and Ref. [72] for the surface and interfacial dynamics in viscous bilayer films, a fitting to the bilayer model was performed (solid line in Fig. 3.25b) with total layer film thickness \( d \) fixed at 160 nm and bottom layer viscosity \( \eta_1 \) fixed at the bulk value taken from Ref. [113]. The best fit results in a top layer thickness \( h_2 \) identical to the total film thickness \( d \) and its viscosity identical to the value if the film is treated as a homogenous film (Eq. 3.12). The dotted line denotes another bilayer fitting with thickness \( h_2 \) of the high-mobility surface layer fixed at a value of 10 nm, as claimed by Kawana and Jones [74]. The failure of the bilayer model clearly indicates that, within the current experimental resolution, the possibility of the existence of a thin less viscous layer near the surface can be excluded safely. This may be consistent with the observations of Liu et al. [85], who measured the local chain relaxations near the surface after an imposition of a small deformation and concluded that the mobility at a free surface is not significantly different from that within the film. In addition, in Ref. [46] \( T_g \) on the surface of PS films was measured with a localized shear modulus force microscopy technique and was found identical to the bulk value, as was predicted that the glass transition in confinement should be a collective effect of the whole film [5].

3.7 Dry Brushes

Films in which polymers are purposely tethered in some fashion have attracted enormous interest due to the strong changes in the collective behavior of the chains induced by the stretching of the chains required to accommodate the tethering. It is anticipated that long wavelength modes of the thermally stimulated fluctuations on the surface would be suppressed on a dry (not solvent swollen) brush due to the entropic penalty chains must pay to stretch sufficiently to allow long wavelength fluctuations [45, 154, 180]. The competition between the elastic restoring force at long wavelengths and the surface tension penalty at shorter wavelengths should lead to an energetically preferred wavelength of the order of the equilibrium brush height. Via x-ray longitudinal diffuse scattering, the roughnesses of the air/brush and brush/substrate interfaces of a diblock copolymer brush have been found to be strongly correlated, i.e., the interfacial profiles are con-
Table 3.2: Sample characteristics of polymer brushes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>d (nm)</th>
<th>$M_n$ (kg/mol)</th>
<th>$\sigma$ (chains/nm$^2$)</th>
<th>s (nm)</th>
<th>$R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-9</td>
<td>9 ± 0.2</td>
<td>10 ± 0.5</td>
<td>0.6 ± 0.03</td>
<td>1.4 ± 0.03</td>
<td>2.8 ± 0.1</td>
</tr>
<tr>
<td>PS-26</td>
<td>26 ± 0.2</td>
<td>28 ± 1.4</td>
<td>0.6 ± 0.03</td>
<td>1.3 ± 0.03</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>PS-39</td>
<td>39 ± 0.2</td>
<td>34 ± 1.7</td>
<td>0.6 ± 0.04</td>
<td>1.3 ± 0.03</td>
<td>4.9 ± 0.2</td>
</tr>
<tr>
<td>PS-48</td>
<td>48 ± 0.2</td>
<td>50 ± 2.5</td>
<td>0.6 ± 0.03</td>
<td>1.3 ± 0.03</td>
<td>6.0 ± 0.3</td>
</tr>
<tr>
<td>PnBA-30</td>
<td>30 ± 0.2</td>
<td>25 ± 1.3</td>
<td>0.8 ± 0.04</td>
<td>1.1 ± 0.03</td>
<td>3.6 ± 0.2</td>
</tr>
</tbody>
</table>

[2] Number averaged molecular weights measured using permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized.
[3] Grafting density calculated using $\sigma = N_A \rho_m d / M_n$, where $N_A$ is Avogadro’s constant and $\rho_m$ is the bulk mass density.
[4] Distance between the anchoring points.

formal, indirectly indicating that the surface fluctuations can not occur on large length scales [1]. In order to directly demonstrate the suppression of long wavelength fluctuations, XPCS experiments were performed recently on a series of PS brushes of various thicknesses synthesized by ATRP. The characteristics of the brush samples studied are shown in Table 3.2.

That the fluctuations at the surface are remarkably suppressed can be clearly seen from the comparison in Fig. 3.26, where $g_2$ functions are plotted for a brush and a spin-cast film. The fitting to Eq. (3.27) with $\alpha = 1$ yields a relaxation time constant $\tau \approx 32$ sec for the untethered spin-cast film. In contrast, the $g_2$ function for the brush indicates that no relaxation within the experimental window. If the brush had a surface relaxation with a single exponential shape and a relaxation time of about 30,000 s or smaller, the beginning of the relaxation would be visible within this time window. Thus, if fluctuations exist at the surface for this length length scale, their relaxation time has been increased by at least three orders of magnitude. In addition, there was no relaxation observed at any of the length scales probed, as shown in Fig. 3.27. The suppression of fluctuations was seen for PS brushes of four different thicknesses, as shown in Fig. 3.28. It would be very interesting to test the behavior of much thicker brushes. However, it is not possible to make thicker brushes with chains of molecular weight as well controlled as for the brushes studied here. Data collected at much shorter times for the 26 nm and 48 nm thick PS brushes demonstrated that there is no relaxation on time scales as short...
Figure 3.26: $g_2$ vs. time delay at $q_\parallel = 5.3 \times 10^{-3} \text{ nm}^{-1}$ for a 26 nm thick PS brush and 29 nm thick spin-cast film ($M_n = 65 \text{ g/mol}$) at 170 °C.

Figure 3.27: $g_2$ functions for a 39 nm thick PS brush at 190 °C at various in-plane wave vectors as labeled. Curves are shifted for clarity.
Figure 3.28: $g_2$ at $q_{\parallel} = 3.4 \times 10^{-3}$ nm$^{-1}$ for PS brushes of thickness 48, 39 and 26 nm. $g_2$ for the 9 nm thick PS brush was shown at $q_{\parallel} = 3.1 \times 10^{-3}$ nm$^{-1}$. For the 26 and 48 nm brushes data were collected on much shorter time scales.

Figure 3.29: $g_2$ functions for a 48 nm thick PS brush (top), and for a 30 nm thick PnBA brush (bottom) at various temperatures.
as tenths of a second.

No relaxation was seen for any PS brush at any temperature investigated, as shown in Fig. 3.29, which shows data for the thickest PS brush at temperatures up to 230 °C. The highest temperature is around 130 °C above the $T_g$ of the untethered chains of the same molecular weight in a spin-cast film. A poly($n$-butyl acrylate) (P$n$BA) brush was also synthesized by ATRP, and there was no relaxation observed either, at temperatures up to 170 °C above the $T_g$ of corresponding untethered chains ($\sim -50$ °C).

All of these observations are consistent with the theoretical predictions in Refs. [45, 180] that for brushes of monodisperse tethered chains long wavelength surface modes should be suppressed. The scattering intensity falls off so quickly with respect to $q_{\parallel}^{-2}$ (Eq. 3.26) that even at the state-of-the-art facility on Sector 8-ID-I, it is not currently possible to reach sufficiently large $q_{\parallel}$ values in order to verify if the dynamics predicted to be present for length scales comparable to the brush thickness are indeed there.

A possible concern is that the suppression of the surface fluctuations may be due to some other mechanisms, e.g., the brushes are not truly in the molten state. However, it is very unlikely that the suppression is due to changes in $T_g$ of the film as a whole induced by tethering. The $T_g$ of poly(methyl methacrylate) (PMMA) bushes with high grafting densities has been investigated by spectroscopic ellipsometry [181], and at a thickness of 50 nm, only an elevation of 8 °C in $T_g$ was observed compared to the $T_g$ of untethered chains in a spin-cast PMMA film of the same thickness. This indicates that in the brushes studied here, change in $T_g$ of the film as a whole is not the issue. On the other hand, it was reported that an increase of 25 °C in the $T_g$ was observed using ellipsometry and a localized thermal technique in a 43 nm thick PS film, in which only a small fraction of the chains were end-tethered to the substrate [162]. In there, the grafting density was much lower than in the present study, and it suggests the possibility that films containing larger fractions of tethered chains, i.e., higher grafting density, could show even an increase of film $T_g$ larger than 25 °C.

**Acknowledgements**

The text of this chapter, in part, is a reprint of the material as it appears in

Copyright (2006) by the American Physical Society.


Polymeric Liquid Bilayers

Polymer/polymer interfaces play an important role in the mechanical toughness of polymer blends, adhesion properties in coatings, and co-extrusion of polymers. Interface properties are also critical in many industrial applications, such as optical multi-layers. Polymeric bilayers can also be employed as model systems to study intermixing phenomena across interfaces, wetting and de-wetting mechanisms, entanglement effects, $T_g$ reduction, or van der Waals interactions. In this chapter, we will discuss the static structures and dynamic properties of polymeric bilayers measured via scattering techniques combined with a standing wave geometry.

4.1 Sample Preparation

The samples in this investigation consist of a bilayer of polystyrene (PS) on top of poly(4-bromo styrene) (PBrS, $T_g \approx 142 \degree C$ [158]) supported on a single crystal silicon wafer (PS/PBrS/Si). The chemical structures of PS and PBrS are shown in Fig. 4.1. The PS ($M_W=200k \text{ g/mol}$, $M_W/M_n=1.06$) was purchased from Polymer Source. The PBr$_x$S was obtained by brominating PS ($M_W=350k \text{ g/mol}$, $M_W/M_n=1.06$), resulting in a bromination fraction of $x=0.89$. PBrS was spin-cast from toluene solution directly onto the silicon wafer. PS was spin cast onto a glass slide and floated from deionized water onto the PBrS layer. Samples were annealed at 180 $\degree C$ in an oil-trapped vacuum ($<10^{-3} \text{ Torr}$) for at least 12 hours. For a high degree of bromination, the Flory-Huggins interaction parameter $\chi = 0.064 \pm 0.004$ [16] for PS/PBrS at 180 $\degree C$ is much larger than $\chi_c = 1.04 \times 10^{-3}$ at the critical temperature, indicating the strong incompatibility of our polymers. Strongly incompatible polymers only intermix on a segmental scale, hence
Figure 4.1: Chemical structure of polystyrene and poly(4-bromo styrene).

Figure 4.2: AFM images from bilayers (a) PS(98k)/PBrS(90k)/Si with roughness = 2.3 nm, and (b) PBrS(90k)/PS(98k)/Si with roughness = 8.4 nm after being annealed at 150 °C for 12 hours [67].
their interface widths are several nanometers wide, but remain finite [53, 105]. There are some other advantages of choosing PS/PBrS as the bilayer model. The dynamics of PS single layers have been previously characterized. In addition, the intensity of x-ray scattering is proportional to the electron density contrast, and the bromination of PS provides a very good contrast across the PS/PBrS interface.

Two bilayer geometries were prepared: 100 nm PS on 100 nm PBrS, and 100 nm PS on 200 nm PBrS. Fig. 4.2 shows the AFM images of the surfaces from (a) PS/PBrS and (b) PBrS/PS samples of small molecular weights. When PBrS is on top, the film is subject to a dispersive force driven instability which amplifies the interfacial thermally excited capillary waves at late times [142]. Therefore, to study the structures and dynamics at the wetting interface in equilibrium, bilayers of PS on PBrS are chosen.

4.2 Experiment Techniques

Neutron reflectivity

The PS/PBrS interface was first characterized using neutron reflectivity (NR). The principle of elastic neutron scattering is similar to that of x-ray scattering discussed in Chapter 2, except that neutrons interact with the nucleus instead of the surrounding electrons for x-rays. In order to enhance the neutron scattering contrast, deuterated polystyrene was used. The polymer was spin-cast onto a much larger silicon wafer (5 mm thick, 2 inch in diameter). NR experiments were carried out on POSYII instrument at Intense Pulsed Neutron Source (IPNS), Argonne National Laboratory.

X-ray standing wave

The x-ray experiments were performed in a grazing incidence geometry on Sector 8-ID-I, the same beamline for XPCS experiments from molten PS films. To make the scattering surface sensitive only, the incident angle has to be less than the critical angle \( \alpha_{c,PS} = 0.164^\circ \) for x-rays of energy \( E = 7.7 \) keV of total external reflection for the top PS layer. On the other hand, to probe the interface, x-ray standing wave (XSW) technique in thin film geometry was employed [175,176]. Since the critical angle \( \alpha_{c,PBrS} = 0.191^\circ \) of PBrS is larger than that of PS, when the incident angle falls in between these two critical angles, x-ray resonances can form within the top PS layer as a result of the interference between reflected and refracted x-rays. Therefore, the electric
Figure 4.3: (a) Simulation of the normalized EFI as a function of incident angle $\alpha_i$ and film depth $z$, for x-rays of energy 7.7 keV incident onto a bilayer composed of PS(100 nm)/PBrS(200 nm) on a Si substrate (inset) at 195 °C. (b) EFI as a function of incident angle from the line cut in (a) at the surface ($z = 0$ nm, black solid line), the interface ($z = 100$ nm, blue dashed line), and the substrate ($z = 300$ nm, red dotted line).

Field intensity (EFI) may be strongly enhanced at certain depths within the film. A simulation of the EFI distribution based on Parratt’s exact recursive method (Appendix B) for a PS(100 nm)/PBrS(200 nm)/Si bilayer is displayed in Fig. 4.3a. EFIs at the PS surface, the PS/PBrS interface and the PBrS/Si interface are shown as a function of incident angle $\alpha_i$ in Fig. 4.3b, where it is clear that when $\alpha_i < \alpha_{c,PS}$, only the PS surface is illuminated, and when $\alpha_{c,PS} < \alpha_i < \alpha_{c,PBrS}$, resonant oscillations of the electric field are produced. In particular, at $\alpha_i \approx 0.18^\circ$, the EFI at the interface reaches its maximum, i.e., an antinode occurs, while simultaneously a node is present at the top PS surface. Therefore the scattering arises mainly from the interface. At this moment, the scattering from the bulk has been neglected, because the electron contrast due to thermal density
fluctuations within the bulk is very small compared with that at the surface and the
interface. However, under some circumstances, e.g., when there is no antinode at the
surface or at the interface, the bulk contributions have to be taken into account.

4.3 Interfacial Structure

The interface between two immiscible polymers is not perfectly sharp, because the
unfavorable enthalpy of mixing at the interface is compensated by a gain in the chain
entropy. It has been predicted, using self-consistent field theory [61], that the volume
fraction profile of one component through the interface, $\Phi_A(z)$, takes the hyperbolic
tangent function form,

$$\Phi_A(z) = \frac{1}{2} \left[ 1 + \tanh \left( \frac{z}{w} \right) \right], \quad (4.1)$$

where the intrinsic interface width $w$ is given in terms of the statistical segment length
$a$ and the Flory-Huggins interaction parameter $\chi$ as

$$w = \frac{a}{\sqrt{6\chi}}, \quad (4.2)$$

and that the interfacial tension is given by

$$\gamma_0 = a\rho k_B T \sqrt{\frac{\chi}{6}}, \quad (4.3)$$

where $\rho^{-1}$ is the volume of the monomer repeat unit.

The numerical values of predicted interfacial tensions are typically an order of mag-
nitude smaller than free surface energies. The fundamental reason for the low values of
interfacial energies between two immiscible polymers stems from chain entropy, because
a very sharp interface would excessively restrict the conformational freedom of nearby
chains hence polymer/polymer interfaces are relatively diffuse. As for the interfacial
width, detailed comparison between theory and experimental measurements revealed a
large discrepancy. For example, independent measurements [3, 40] on PS/PMMA inter-
facial width, using neutron reflectivities, produced a result about 70% in excess of the
predicted value. The reason for this is that the self-consistent mean-field theory calcu-
lates only the diffuseness of the intrinsic interface arising from mixing at the molecular
level as described by the configurational statistics of polymer molecules in the interfacial
region. This theory ignores the roughening fluctuations in the plane of the interface due
to thermally excited capillary waves [137, 147]. Experimental probes such as neutron and
x-ray scattering typically average over the intrinsic diffuseness and roughness due to the capillary waves, yielding a total interfacial roughness $\sigma$ as [144]

$$\sigma^2 = \sigma_0^2 + \sigma_c^2,$$

(4.4)

where $\sigma_0$ and $\sigma_c$ denote the contributions from diffusivity (intrinsic width) and capillary waves, respectively. As shown in Ref. [95] and noted in Ref. [144], the contributions to the interfacial width from the measured roughness can significantly exceed the intrinsic diffusivity, even in the case of diverging diffusivity. The capillary wave contribution depends on the thickness of the top layer, because the spectrum of wavelengths present may be modified by van der Waals forces across the film. Another factor which controls the width and energy of the interface is the molecular weight of the polymers involved; the original calculation was done in the limit of infinite molecular weight, but the results are expected to be modified by having samples with finite molecular weight due to chain end effects.

### 4.3.1 Neutron Reflectivity

The interfacial mixing of incompatible polymers comes to equilibrium after the formation of a small interfacial region. The kinetics of interface formation depend on $\chi$ and have been studied in the past for dPS/PBrS bilayers as a function of bromination [53]. The time dependence of the growth of the interfacial roughness for other polymer pairs as dPS/PMMA [143, 145] also follows the same kinetic behavior. First there is a fast increase in interfacial width with time, which follows a power law dependence with exponent 0.25 ($\sim t^{0.25}$) as predicted theoretically [116], followed by a long period of much slower logarithmic growth. In the limit of a large degree of immiscibility, a narrow intrinsic interface may come into equilibrium quite rapidly. On the other hand, the broadening of the interface by capillary waves will take much longer, as the growth of these waves requires hydrodynamic flow of the polymer melts [145].

In order to check for the equilibrium formation of an interface for the bilayer system, neutron reflectivity experiments were performed as a function of annealing time on a dPS(200k)/PBrS(350k) bilayer. The fitted parameters are shown in Table 4.1. Since a hyperbolic tangent profile is assumed across the interface, the interfacial roughness due to diffuseness is obtained through the relation, $w = 1.253\sigma_0$, where the intrinsic width $w$ is given by Eq. (4.2). A value of $\chi_{PS/PBrS} = 0.064 \pm 0.004$ at 180 °C [16] gives $\sigma_0 = 0.9$ nm.
Table 4.1: Neutron reflectivity results and calculation of a PS/PBrS film.

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>dPS Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C, 12 h</td>
<td>95.7 ± 1.0</td>
<td>0.6 ± 0.3</td>
</tr>
<tr>
<td>180 °C, 38 h</td>
<td>95.3 ± 1.0</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Annealing condition</th>
<th>PBrS Thickness (nm)</th>
<th>Interfacial roughness</th>
<th>Capillary wave</th>
<th>Self-consistent</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C, 12 h</td>
<td>115.8±5.0</td>
<td>2.3±0.7</td>
<td>0.90±0.03</td>
<td>1.1±0.6×10^{-3}</td>
</tr>
<tr>
<td>180 °C, 38 h</td>
<td>116.0±5.0</td>
<td>2.8±0.8</td>
<td>0.90±0.03</td>
<td>1.1±0.6×10^{-3}</td>
</tr>
</tbody>
</table>
Since the layers in the present study are quite thick, so that van der Waals cut-off in the capillary wave spectrum may be neglected, it is the instrumental resolution that determines the largest measurable wavelength of the fluctuations that contribute to the interfacial capillary wave roughness. We may therefore replace the lower wave vector cutoff in the capillary wave roughness expression (Eq. 2.40) by the in-plane wave vector resolution \( \Delta q_x \), i.e., \( q_{l,c} = \Delta q_x \approx q_z \Delta \alpha_d \), where \( \Delta \alpha_d \) is the full width of the angular resolution in the plane of incidence [14]. With the knowledge of the capillary wave roughness from the square difference (Eq. 4.4) of the measured total roughness \( \sigma \) and the calculated intrinsic roughness \( \sigma_0 \), Eq. (2.40) gives a value of interfacial tension \( 1.1 \pm 0.6 \times 10^{-3} \text{ N/m} \). However, by Eq. (4.3) the self-consistent theory predicts that the interfacial tension is \( \gamma_0 = 2.00 \pm 0.06 \times 10^{-3} \text{ N/m} \), which is obviously larger than capillary wave calculations. The origin of this discrepancy is not clear yet. There exists a large uncertainty in the interfacial tension obtained from Eq. (2.40) since the logarithmic cut-off at small \( q_\parallel \) can not be determined precisely. However, the values used here are in a reasonable agreement with a previous measurement in similar system [184].

4.3.2 Static X-ray Diffuse Scattering

The theory of x-ray diffuse scattering from multi-layers has been discussed in detail in Section 2.3.2. In the limit that \( \alpha_f \gg \alpha_e \) and under grazing incidence geometry, neglecting the instrumental resolution effect (because a CCD detector of high spatial resolution was used), the diffuse scattering cross section of the \( j \)th \((j = 1, 2)\) interface may be approximately written as

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{diff},j} \approx Ar_e^2 |\Delta \rho_j|^2 S_j(q_\parallel) \sum_{m,n=0}^3 \widetilde{G}_{j+1}^m \widetilde{G}_{j+1}^{n*},
\]

where \( S_j(q_\parallel) \approx k_B T/(\gamma_j q_\parallel^2) \) is given in Eq. (3.26), and \( \widetilde{G} \) is defined as described in Section 2.3.2.

To measure the surface tension of the top PS layer, an incident angle of 0.14°, below \( \alpha_{e,PS} = 0.164° \), was used. At this incident angle, the EFI penetration depth is 8.6 nm (Eq. B.8), and only the structure of the top surface region is measured.

At \( \alpha_i = 0.18° \), as shown in Fig. 4.3, the standing wave has a node at the top surface and simultaneously has an antinode at the PS/PBrS interface. Consequently, if resolution could be neglected, the scattering is due nearly entirely to the buried interface. To verify the theoretically predicted distribution of the EFI through the film, measurements
Figure 4.4: (a) Measured diffuse x-ray intensity from a bilayer of PS(200k, 95 nm)/PBrS(350k, 100 nm) at 175.6 °C. (b) Comparison of the measured and predicted diffuse scattering intensities as a function of incident angle $\alpha_i$. The circles are experimental data integrated over the rectangular box in (a) with a fixed average outgoing angle $\alpha_f = 0.98 \pm 0.05^\circ$ and outgoing azimuthal angle $\chi = 0.068 \pm 0.005^\circ$. The solid and dotted lines are the theoretical calculations respectively for the total diffuse intensity, and for the PS/PBrS interface only.

were made of the diffuse scattering intensity at fixed exit angle $\alpha_f$, while varying the incident angle $\alpha_i$. The intensity was calculated for an outgoing angle relative to the surface of $\alpha_f = 0.98 \pm 0.05^\circ$ and outgoing azimuthal angle of $\chi = 0.068 \pm 0.005^\circ$. In Fig. 4.4a, the experimental data integrated over the rectangular box (50 pixel × 100 pixel) which has the angular ranges specified above, are shown as circular symbols in Fig. 4.4b. The calculated diffuse scattering for the entire sample is shown as the solid line. The parameters for the layer thicknesses were taken from the fit to the specular reflectivity. The dotted line represents the theoretical calculation for the diffuse scattering just from the PS(200k, 95 nm)/PBrS(350k, 100 nm) interface. This accounts for 80% of the expected
Table 4.2: Surface and interfacial tension of a supported bilayer composed of PS(200k, 95 nm)/PBrS(350k, 100 nm).

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>Surface/Interfacial Tension (N/m)</th>
<th>Surface Tension (N/m) (Exp.)</th>
<th>Interfacial Tension (N/m) (Cal.)</th>
<th>Interfacial Tension (N/m) (Exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>175.6</td>
<td>9.3±0.9</td>
<td>20±2×10^{-3}</td>
<td>2.00±0.06×10^{-3}</td>
<td>2.2±0.3×10^{-3}</td>
</tr>
<tr>
<td>195.2</td>
<td>8.4±0.8</td>
<td>22±2×10^{-3}</td>
<td>2.10±0.06×10^{-3}</td>
<td>2.6±0.4×10^{-3}</td>
</tr>
<tr>
<td>204.9</td>
<td>8.7±0.9</td>
<td>25±3×10^{-3}</td>
<td>2.10±0.06×10^{-3}</td>
<td>2.9±0.4×10^{-3}</td>
</tr>
<tr>
<td>214.7</td>
<td>8.9±0.9</td>
<td>24±2×10^{-3}</td>
<td>2.20±0.07×10^{-3}</td>
<td>2.7±0.4×10^{-3}</td>
</tr>
<tr>
<td>224.4</td>
<td>8.1±0.8</td>
<td>19±2×10^{-3}</td>
<td>2.20±0.07×10^{-3}</td>
<td>2.3±0.3×10^{-3}</td>
</tr>
</tbody>
</table>

scattering at \( \alpha_i = 0.18^\circ \) and would account for nearly 100% of the scattering if resolution effects were not included. As can be seen, the experimental data show similar peaks as in the model, located at the same positions and of approximately the same magnitude. Both the data and simulations have been arbitrarily normalized to unity at \( \alpha_i = 0.16^\circ \). Therefore, the fits are only sensitive to the ratio of the surface to interface roughness, not to the absolute value of roughness. The only adjustable parameter, beyond an overall scale factor, was the ratio of the surface tension of the top vacuum/PS to the interfacial tension of the buried PS/PBrS. Knowing the surface tension of the vacuum/PS surface from the surface diffuse scattering data taken at \( \alpha_i = 0.14^\circ \), the interfacial tension of the buried interface can be determined. In Table 4.2, the experimental results and the calculated values from the self-consistent theory (Eq. 4.3) are shown for comparison.

The neutron prediction for the interfacial tension is over a factor of two lower than the x-ray value, which may result from the imprecise limits on the logarithmic term involving an instrumental resolution used to relate the interfacial tension to the total roughness. If, on the other hand, these limits are correct, it may indicate a much smaller value of the interdiffusion of PS and PBrS than expected, since x-ray method only sees roughness while the neutron measurement see both roughness and interdiffusion. The x-ray result is slightly higher but still within a factor of 15% of the value predicted by the self-consistent theory.

### 4.4 Surface and Interfacial Dynamics

It has been reported that immiscible polymer blends can have viscosities lower than either of their components [58], which may be ascribed to the interfacial slip as indicated by a recent multi-layer co-extrusion experiment [183]. Due to weak entanglement be-
tween dissimilar polymers at an interface [105], poor adhesion usually is present at the
interface of immiscible polymers [23]. Dissipation within the interfacial regions can only
be indirectly studied by bulk rheological measurements. In the current study, XPCS was
combined with standing wave technique, providing a direct way to resolve the dynamics
at the buried interface. Its ability to reach nanometer scale spatial resolution provides a
significant advance in knowledge over multi-layer co-extrusion methods, and can provide
test of theoretical models which address hydrodynamic modes of viscoelastic polymer
films and interface slip [59,114].

For a liquid that exhibits multiple over-damped relaxation modes, the intermediate
scattering function \( f(q_{\parallel}, t) \) in the normalized intensity-intensity correlation function \( g_2 \)
(Eq. 2.103) is often expressed as a sum over exponentials (Appendix C),

\[
f(q_{\parallel}, t) = \sum_m a_m e^{-t/\tau_m},
\]

where \( \tau_m \) are relaxation time constants, and \( a_m \) are their amplitudes with \( \sum_m a_m = 1 \).

Measured \( g_2 \) functions at \( q_{\parallel} = 4.3 \times 10^{-3} \) nm\(^{-1} \) from a PS(200k, 100 nm)/PBrS(350k,
200 nm)/Si bilayer are shown in Fig. 4.5(b and d). For comparison, the \( g_2 \) functions mea-
sured from a PS single layer film of equivalent thickness 100 nm are shown in Fig. 4.5(a
and c). The PS single layer surface dynamics at \( T \gg T_g \) are well described by a sin-
gle exponential relaxation of the form \( f(q_{\parallel}) = e^{-t/\tau} \), as shown in Section 3.5.1. In the
bilayer film, the vacuum/PS (top) interface shows two distinct decay modes, while the
PS/PBrS (bottom) interface shows only one single decay mode. The \( g_2 \) functions of the
bottom interface were fitted to a single exponential form, while the \( g_2 \) functions of the
top interface were fitted to a double exponential form,

\[
f(q_{\parallel}, t) = ae^{-t/\tau_1} + (1-a)e^{-t/\tau_2}.
\]

The presence of two modes demonstrates that there is coupling between the top and
bottom interface due to hydrodynamic flows throughout the film. It is possible to observe
this coupling since the bilayer thickness \( d \) is not too larger than experimental \( q_{\parallel}^{-1} \) values.

In Fig. 4.6 the relaxation time constants extracted from the measured \( g_2 \) functions
are displayed, along with models for the dependence of the relaxation times on the
wave vector. The corresponding relaxation time for a PS single layer film is also shown
for comparison. The fast mode \( \tau_1 \) from the top surface of the bilayer is faster than
the relaxation for the corresponding PS single layer and the \( q_{\parallel} \)-dependence is weaker.
Figure 4.5: $g_2$ functions from PS single and PS/PBrS bilayer films measured at $q_{\parallel} = 4.3 \times 10^{-3}$ nm$^{-1}$. (a) PS single layer at 176 °C; (b) PS/PBrS bilayer at 176 °C: (▲) top and (♦) bottom; (c) and (d) are single and bilayer data at 205 °C. Solids lines indicate the single and double exponential fits described in the text.

The slow mode $\tau_2$ from the bilayer top surface and single mode $\tau$ from the bilayer PS/PBrS interface are nearly identical and exhibit a flat $q_{\parallel}$ dependence. Measurements were also made on a bilayer of PS(100 nm)/PBrS(100 nm)/Si, the dynamic behavior of which was identical to PS(100 nm)/PBrS(200 nm)/Si. The temperature and thickness dependence of the bottom interface $\tau$'s are shown in Fig. 4.7. The dynamics speed up systematically with temperature, as expected, since the viscosity decreases. The relaxation time constant is nearly independent of $q_{\parallel}$ and PBrS thickness, which indicates that $\tau$ of the bottom interface indeed shows the dynamics of the interfacial region only, as it is not sensitive to the thickness changes of the bottom PBrS layer.

The dynamics of a PS single layer on Si substrate are well described by Eq. (3.12), where the boundary condition at the bottom is zero velocity, while the top surface
Figure 4.6: $\tau$ vs. $q_{||}$ at 195 °C. PS(100 nm)/PBrS(200 nm) bilayer: ($\triangle$) top fast mode $\tau_1$, (○) top slow mode $\tau_2$, (◇) bottom $\tau$. Corresponding single layer: (□) 100 nm PS. Theoretical models: (red solid) single layer fit with non-slip boundary condition, (blue dashed) bilayer model with low viscosity interface, (green dash-dot-dot) single layer calculation for the top PS layer with perfect slip boundary condition.

Figure 4.7: Temperature and thickness dependence of the relaxation time constants of the bottom interface at 195 °C for PS(100 nm)/PBrS(100 nm) (○) and PS(100 nm)/PBrS(200 nm) (△), and at 225 °C for PS(100 nm)/PBrS(100 nm) (▽) and PS(100 nm)/PBrS(200 nm) (□). Solid lines denote the averages of $\tau$ values.
boundary condition is that the viscous stress within the fluid is balanced by the surface tension. However, when the PS layer is placed on PBrS instead of Si, the fast mode $\tau_1$ becomes faster than the PS single layer, as shown in Fig. 4.6. The change in dynamics is of the same magnitude as would be expected from changing the lower interface boundary condition of the PS layer from non-slippage to perfect slippage, which would lead to Eq. (3.15), shown as the green dash-dot-dot line in Fig. 4.6. The actual experiment data falls intermediate between non-slip and slip conditions.

The capillary wave dynamics were not observed for PBrS single layer film of thickness 100 nm, as the dynamics of this film were too slow on the experimental time scale, presumably owing to its high viscosity. Thus in the analysis using the bilayer model, PBrS was effectively treated as an immobile substrate for the purpose of boundary conditions applied. This assumption is justified in Fig. 4.7, where the relaxation time constant is dependent on temperature but not on PBrS thickness. When modeling the bilayer, a thin mixed layer is placed between the liquid-like PS and solid-like PBrS layers to account for the interface. Its viscosity is approximated as uniform. A value of $2.6 \times 10^{-3}$ N/m at 195 °C (Table 4.2) was used for the interfacial tension between the mixed layer and the PS layer. This value was obtained from the static diffuse x-ray scattering, which also provides a value of 6.6 nm for the mixed layer thickness (assuming the width is $2.35\sigma$ with $\sigma$ being the Gaussian roughness). A non-slip boundary condition is assumed at the interface between the mixed layer and the solid PBrS layer.

At the vacuum/PS interface surface tension balances the viscous stress. At the interface between the PS layer and the mixed layer, the velocity is continuous and the viscous stress difference is balanced by the interfacial tension. The viscoelastic properties of polymer layers are taken into account by a frequency-dependent viscosity $\eta(\omega) \approx \eta + i\mu/\omega$ (Section 3.1). For the thick spin-cast PS layer, the effect of shear modulus is negligible. However, for the thin mixed layer, the addition of elasticity significantly modified the dynamics. The over-damped relaxation time constants can be numerically obtained via searching for poles of the susceptibility (Appendix C). The magnitudes of viscosity and shear modulus of the mixed layer were varied using nonlinear least-square regression to obtain the best fit to the measured relaxation time constants of the top surface ($\tau_1$ and $\tau_2$) and bottom interface ($\tau$) simultaneously, the result of which is shown as the blue dashed lines in Fig. 4.6 with fitted viscosity and shear modulus given by $\eta \sim 327$ Nsec/m$^2$ and $\mu \sim 18$ N/m$^2$ respectively. The best fitted viscosity is only around 2% of that of
the PS layer. Therefore, if we only consider the dynamics of the PS fast mode (\(\tau_1\)), the mixed layer imbues a finite slip length to the PS/PBrS interface. The dynamics of the top slow mode (\(\tau_2\)), which is nearly identical to that of the mixed layer, shows almost no dependence on the wave vector, which can not be explained by a pure viscous model for thin films. However, the introduction of the shear modulus term produces a flattening of the spectrum. The obtained \(\mu\) value from the fits was of the same magnitude of the shear modulus for bulk PS at comparable time scales [51].

While the model described above does give a good fit to the data, it is clear that it approximates the actual interfacial region by a uniform layer, which is unlikely correct. An interfacial tension is not applicable over length scales comparable to the thickness of the interface. Nevertheless, the present results provide a significant improvement over previous rheological results. Here, not only the existence of the slip between PS/PBrS has been proved, but the thickness, viscosity, interfacial tension, and shear modulus of the mixed region have been estimated. As discussed in Chapter 3, the reduction of \(T_g\) on Si supported PS films was proposed by some arguments to be ascribed to the existence of a thin low-viscosity layer on the surface. It seems reasonable to speculate that the low viscosity in the mixed region is similar to the cause of the reduced \(T_g\). However, a recent experiment research has been performed [124], by selectively placing fluorescent dyes, on measuring the \(T_g\) reduction of ultra-thin PS capping layers on top of another immiscible polymer layer, such as PMMA and poly(2-vinylpyridine) (P2VP), and the reduction of \(T_g\) was found to be less prominent than that of single PS layers on silicon, although there exists a thin mixed layer with much less viscosity. Therefore, the reduction of \(T_g\) is not likely to arise from the argument of thin liquid-like layers. Instead it is more likely to be related to the cooperative segmental mobility, which can be strongly affected by the substrates underneath. This is consistent with our XPCS result from single PS films near \(T_g\) (Section 3.6). Finally, it is noted that experiments on the mobility of gold nanoparticles at the polymer-polymer interface in a bilayer system of PtBA/PtBA [101] have also shown anomalously high mobility, which may be similarly related to a region of reduced viscosity as was found here.

Acknowledgements

The text of this chapter, in part, is a reprint of the material as it appears in

A perfectly homogeneous medium with uniform density throughout does not give rise to any scattering for any non-zero wave vector \( q \), except at the unobservable \( q = 0 \). However, in a liquid, inhomogeneities in density due to thermal motions of atoms and molecules always exist, leading to the so-called “thermal density fluctuations”. Such density fluctuations occur at all length scales, i.e., a difference may exist for the total number of scatters found in a region of a certain volume when compared with another region of the same volume, no matter what this volume is. Scattering intensities are then produced from these density fluctuations at all \( q \) values. The fluctuation dissipation theorem predicts that in the limit of \( q \to 0 \) the bulk scattering structure factor for an x-ray scattering experiment is related to the isothermal compressibility \( \kappa_T \) and the electron density fluctuation \( \delta \rho \) via \cite{122,123}

\[
S(q \to 0) = (r_e \delta \rho)^2 k_B T \kappa_T,
\]

(5.1)

where \( r_e \) is the Thompson scattering length, \( k_B \) is Boltzmann constant, and \( T \) is the temperature. The temperature dependence of the diffuse scattering changes slope at \( T_g \), which allows the compressibility to serve as an indicator of the glass transition.

DWBA theory has been previously discussed in Section 2.3.2 for the calculation of the surface diffuse scattering in general for a multi-layer film. The predicted surface structure factor corresponding to the capillary wave fluctuations on liquid surfaces shows a good agreement with measured surface fluctuations of a polymer melt over a considerably large range of length scales. In addition to the surface contributions to the diffuse...
scattering, under some circumstances, a large source of scattering to be considered is induced by thermal density fluctuations in the interior of the liquid film. So far, there is no reported measurement of the structure factor corresponding to the density fluctuations within thin liquid films. In order to extract the bulk structure factor in thin films from the total diffuse scattering, the DWBA theory is extended in this chapter to be able to separate the surface and bulk contributions, and the theoretical calculations are compared with the experimental diffuse scattering results from supported single layer thin polystyrene films.

5.1 Bulk Scattering Theory for Thin Films

Take vacuum/film/substrate as a model system, the scattering geometry of which is illustrated in Fig. 5.1. Following Section 2.3.2, the unperturbed eigenstate of an ideal system with smooth interfaces for a normalized plane wave $\phi = e^{ik \cdot r}$ incident from $z > 0$ onto the surface at an average height $z = 0$ can be expressed as

$$
\psi_i = \begin{cases} 
  e^{i(k^i_\| \cdot r^i_\| + k^i_{z,1} z)} + R_1(\alpha_i) e^{i(k^i_\| \cdot r^i_\| - k^i_{z,1} z)}, & 0 < z \\
  T_2(\alpha_i) e^{i(k^i_\| \cdot r^i_\| + k^i_{z,2} z)} + R_2(\alpha_i) e^{i(k^i_\| \cdot r^i_\| - k^i_{z,2} z)}, & -\Delta < z < 0 \\
  T_3(\alpha_i) e^{i(k^i_\| \cdot r^i_\| + k^i_{z,3} z)}, & z < -\Delta
\end{cases}
$$

(5.2)
where $R$ and $T$ are Fresnel reflectivity and transmittivity coefficients calculated in Appendix B, and $k_{i,j}^z (j = 2, 3)$ is $z$-component of the transmitted wave vector in the $j$th medium given by

$$k_{i,j}^z = \left[(k_{i,1}^z)^2 - 4\pi r_e \rho_j \right]^{\frac{1}{2}}, \quad (5.3)$$

where $\rho_2 = \rho_f$ and $\rho_3 = \rho_s$ are the electron densities of the film and substrate respectively.

We may also define another eigenstate for the same ideal system, which is a time reversed state

$$\tilde{\psi}_f = \begin{cases} e^{i(k_f^z r_1 + k_{i,1}^z z)} + R_1^*(\alpha_f) e^{i(k_f^z r_1 - k_{i,1}^z z)}, & 0 < z \\ T_2^*(\alpha_f) e^{i(k_f^z r_1 + k_{i,2}^z z)} + R_2^*(\alpha_f) e^{i(k_f^z r_1 - k_{i,2}^z z)}, & -\Delta < z < 0 \\ T_3^*(\alpha_f) e^{i(k_f^z r_1 - k_{i,2}^z z)}, & z < -\Delta \end{cases} \quad (5.4)$$

The basic assumption in DWBA is to split the the scattering potential $V$ into a small perturbation term $\delta V$ superimposed onto an unperturbed potential $V$ of an ideal system. For the system considered in Fig. 5.1, $V$ corresponds to a film of uniform density having smooth surfaces, and $\delta V$ is the perturbation expressed as

$$\delta V = \delta V_{S_1} + \delta V_{S_2} + \delta V_{\text{bulk}}, \quad (5.5)$$

where $\delta V_{S_1}$, $\delta V_{S_2}$, and $\delta V_{\text{bulk}}$ denote the contributions from the two surfaces and the bulk, respectively. The solid substrate in a real experiment can be made extremely smooth, so that the diffuse scattering arising from $\delta V_{S_2}$ may be neglected for simplicity.

For an ergodic system, the ensemble average of the bulk density fluctuation is zero. Given that the surface and bulk fluctuations are independent of each other, the total differential cross section for the diffuse scattering may be approximately written as

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{diff}} = \left(\frac{d\sigma}{d\Omega}\right)_{\text{surf}} + \left(\frac{d\sigma}{d\Omega}\right)_{\text{bulk}} \approx \frac{\left|\langle \delta V_{S_1}^{i-f} \rangle \right|^2}{16\pi^2} - \frac{\left|\langle \delta V_{S_1}^{i-f} \rangle / \psi_i \rangle \right|^2}{16\pi^2} + \frac{\left|\delta V_{\text{bulk}}^{i-f} \right|^2}{16\pi^2}, \quad (5.6)$$

where $\delta V_{S_1/\text{bulk}}^{i-f} \equiv \left\langle \tilde{\psi}_f \mid \delta V_{S_1/\text{bulk}} \mid \psi_i \right\rangle$ denotes the transition matrix for scattering between the initial and final states. Hence, according to the definition of the differential cross section in Section 2.1.2, the measured diffuse scattering intensity by a detector that subtends a solid angle $d\Omega$ after normalization over the incident flux $\Phi_0$ and beam cross section area $A_0$ is written as

$$I_{\text{diff}} = \frac{I_{\text{det}}}{\Phi_0 A_0} = \frac{1}{A_0} \left(\frac{d\sigma}{d\Omega}\right)_{\text{diff}}. \quad (5.7)$$
The contribution to the diffuse scattering in Eq. (5.6) from the surface perturbation due to the capillary wave fluctuations has been previously calculated in Section 3.4, and is given, again, by

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{surf}} = A r_e^2 \rho_f^2 |E_i(0)|^2 |E_f(0)|^2 S_c(q),
\]

(5.8)

where \( E_i(0) \) and \( E_f(0) \) are the amplitudes of the electric field that would be created at the surface \( z = 0 \) if the beam were incident at either the angle of incidence or detection respectively, and \( S_c(q) \) is the capillary wave structure factor given in Eq. (3.25).

To calculate the bulk scattering term, a large detector angle of measurements is assumed, so that \( T_2(\alpha_f) \approx 1 \) and \( R_2(\alpha_f) \approx 0 \). With the knowledge that \( \delta V_{\text{bulk}} = 4\pi r_e \delta \rho_f \), the bulk differential cross section may be written as

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{bulk}} = r_e^2 \int_A \int_A dq_i \langle \delta \rho_f(r) \delta \rho_f^*(r') \rangle e^{i q_i \cdot (r - r')} F(z) F^*(z'),
\]

(5.9)

where

\[
F(z) = T_2(\alpha_i) e^{-i(k_i z - k_i z')} + R_2(\alpha_i) e^{-i(k_f z + k_f z')},
\]

(5.10)

\( q_i = k_i - k_f \), and \( \langle \delta \rho_f(r) \delta \rho_f^*(r') \rangle \) is the bulk density fluctuation correlation function within the film. Through the definition of the structure factor \( S(K) \) for bulk density fluctuations [122,155], we may have

\[
\langle \delta \rho_f(r) \delta \rho_f^*(r') \rangle = \frac{N}{(2\pi)^3 V} \int dK S(K) e^{iK \cdot (r - r')},
\]

(5.11)

where \( N \) is the total number of electrons in a volume \( V \) of the sample. The differential cross section for bulk scattering in films is

\[
\left( \frac{d\sigma}{d\Omega} \right)_{\text{bulk}} = \frac{Ar_e^2 N}{2\pi V} \int_{-\infty}^{\infty} dK_z S(q_\parallel, K_z) W(K_z, k_{i,z,2}, k_{f,z,2}),
\]

(5.12)

where

\[
W(K_z, k_{i,z,2}, k_{f,z,2}) = \int_{-\Delta}^{0} \int_{-\Delta}^{0} dz' F(z) F^*(z') e^{iK_z(z-z')}.
\]

(5.13)

Therefore, plugging Eq. (5.12) to Eq. (5.7) leads to the bulk diffuse scattering intensity

\[
I_{\text{bulk}} = \frac{r_e^2 \rho_f}{2\pi \sin \alpha_i} \int_{-\infty}^{\infty} dK_z S(q_\parallel, K_z) W(K_z, k_{i,z,2}, k_{f,z,2}).
\]

(5.14)
Figure 5.2: Calculated $W(K_z, k_{z,2}^i(\alpha_i), k_{z,2}^f(\alpha_f))$ as a function of $K_z$ and the incident angle $\alpha_i$ for a 105 nm PS film on a silicon substrate. $q_z = (k_{z,1}^f - k_{z,1}^i)$ is fixed at 1.2 nm$^{-1}$.

Fig. 5.2 displays the calculated $W(K_z, k_{z,2}^i, k_{z,2}^f)$ as a function of incident angle $\alpha_i$ for a 105 nm PS film. Two peaks can be found at values $K_z = \left| k_{z,2}^f + k_{z,2}^i \right|$ and $K_z = \left| k_{z,2}^f - k_{z,2}^i \right|$. As the film thickness $\Delta$ approaches zero, these two peaks become two discrete delta functions. In the current experiment, the incident angle varies from below the critical angle of PS to just above that of silicon, and it is much smaller than the detector angle. Therefore, $k_{z,2}^i$ may be neglected compared to $k_{z,2}^f$, and the two peaks effectively appear at very close to each other along the $K_z$ axis, so that $S(q_{\parallel}, K_z) \approx S(q_{\parallel}, k_{z,2}^f)$ can approximately hold for a smooth function $S(q_{\parallel}, K_z)$. Then Eq. (5.14) can be rewritten as

$$I_{\text{bulk}} \approx \frac{r_e^2 \rho_f}{2\pi \sin \alpha_i} \overline{S}(q_{\parallel}, k_{z,2}^f) \int_{-\infty}^{\infty} dK_z W(K_z, k_{z,2}^i, k_{z,2}^f),$$

(5.15)

where notation $\overline{S}(q_{\parallel}, k_{z,2}^f)$ is used for the bulk structure factor in order to distinguish
Figure 5.3: Comparison of the bulk $S(q)$ (line) and calculated $\tilde{S}(q)$ (∇) at a fixed incident angle $\alpha_i = 0.225^\circ$ using Eq. (5.17) for a 20 nm PS film. The inset shows the percentage error in the calculation at fixed incident angle $\alpha_i=0.173^\circ$, 0.193°, 0.225° corresponding to the production of standing wave antinodes in the PS films of thicknesses 105 nm, 38 nm, and 20 nm respectively.

It can be seen that the calculated $\tilde{S}(q)$ is almost the same as $S(q)$. The relative error is within 6% for a 20 nm film and less than 1% as the film thickness increases to 100 nm. At high $q$ values, the difference is insignificant irrespective of the film thickness. In particular, the error in $\tilde{S}(q)$ is even less when a standing wave is produced in the film.
interior. Therefore, by measuring the diffuse scattering as a function of the exit angle for a fixed incident angle that corresponds to the production of standing wave antinodes within the film, the structure factor arising from the polymer bulk density fluctuations can be extracted using Eq. (5.16).

5.2 Experiments and Results

Silicon supported spin-cast PS films of $M_W = 129k$ g/mol and various thicknesses were measured on Sector 8-ID-I at the APS. The experimental geometry and procedure are very similar to those described in Section 4.3.2. The incident angle $\alpha_i$ was varied from $0.14^\circ$ to $0.25^\circ$ and the diffuse scattering intensities were collected by a CCD fixed at a proper position in order to collect a wide range of $q$ while keeping a sufficiently good resolution.

The CCD images corresponding to the angles where the most intense standing wave antinodes exist within the film were chosen, and the surface scattering contributions due to the capillary wave fluctuations were subtracted properly according to Eq. (5.8). $\tilde{S}(q)$ calculated following Eq. (5.16) for different films at various temperatures are shown in Fig. 5.4. The smooth solid lines are the fittings of the data with a polynomial. The overall normalization of the extracted $\tilde{S}(q)$ from the intensity of a single CCD image can change due to the fluctuations in the scattering and also the effect of the drifting of the incident flux. However, both shortcomings can be eliminated by first fitting the extracted $\tilde{S}(q)$ from a single image with a polynomial and then fitting the constant parameter of the polynomial to the data for the whole range of $\alpha_i$. The fitted results of the diffuse scattering intensity as a function of the incident angle for 20 nm, 38 nm, 70 nm, and 105 nm thick films at 160 °C are shown in Fig. 5.5. The properly normalized $\tilde{S}(q)$ after fitting the whole range of data for 20 nm, 38 nm, and 105 nm thick PS films at different temperatures is shown in Fig. 5.4a-c. In Fig. 5.4d, the extracted $\tilde{S}(q)$ values for different film thicknesses at 160 °C are shown together for comparison. $S(0)$ corresponding to the bulk PS is marked in order to show that our results from thick films agree quite well with the known $S(0)$ value of the bulk PS.

Apart from the extraction of the bulk structure factor, another outcome of these results is the measurement of the isothermal compressibility of thin PS films, which may be calculated from $S(0)$ as indicated in Eq. (5.1). Under a small $q$ approximation to the
Figure 5.4: (a)-(c) $\tilde{S}(q)$ values extracted from diffuse scattering intensities for different film thicknesses at various temperatures using Eq. (5.16). (d) The polynomial fits of the $\tilde{S}(q)$ for different film thicknesses at 160 °C are plotted together to show the change in nature of $\tilde{S}(q)$ at low $q$ values as a function of film thickness. The expected $S(0)$ value for bulk PS is marked for reference.
Figure 5.5: Diffuse scattering at a fixed wave vector with $q_{\parallel} = 2.515 \text{ nm}^{-1}$ and $q_z = 0.616 \text{ nm}^{-1}$ as a function of incident angle for different PS film thicknesses at $160^\circ \text{C}$. Symbols are experimental data and solid lines are the fits of the total diffuse scattering from the surface and the bulk density fluctuations within the film.
Figure 5.6: (a) Extrapolated bulk $S(0)$ as a function of temperature for different film thicknesses. The intercept of the solid lines indicates the $T_g (101 \pm 8) ^\circ C$ of a 105 nm PS film. (b) Comparison of the obtained compressibility values with the bulk values (solid line). The inset shows the compressibility at 160 $^\circ C$ as a function of film thickness after a normalization to the bulk compressibility value. Red solid line is just a guide to eyes.
bulk density fluctuations, the bulk structure factor may be written as [122,123]

\[
S(q) = S(0)e^{Bq^2},
\]

(5.18)

where \( B \) is an empirical constant. Although this approximation works quite well for bulk PS, it can be seen clearly in Fig. 5.4 that this approximation fails for very thin films. We observed an increase instead of an exponential decay in \( S(q) \) at the low \( q \) region in thin films. To the best of our knowledge, this unusual rise in \( S(q) \) at low \( q \) values for thin films was not observed experimentally before. However, a recent molecular-dynamics (MD) simulation for confined thin polymer films shows the same behavior in \( S(q) \) at low \( q \) values [171]. Unfortunately, the cause of this behavior is still not clear.

Since there is no theory to account for the rise in \( S(q) \) as \( q \to 0 \), we were unable to extrapolate the bulk structure factor curves for thin PS films. It is also not possible to push our experiments to near \( q = 0 \) as the surface scattering will be predominant there. Therefore, we tentatively approximate \( S(0) \) by extrapolating the fitted polynomial and plotted it as a function of temperature for different thicknesses, as shown in Fig. 5.6a. The intercept of the two solid lines for thick films indicates the glass transition temperature \( T_g \) at about 101 ± 8 °C for a 105 nm film. The compressibility \( \kappa_T \) obtained via Eq. (5.1) is shown in Fig. 5.6b. We know that by this process of measurements, some errors are unavoidably introduced into the calculations of the compressibility without knowing the explicit nature of \( S(q) \) at low \( q \) values for thin films. However, the \( \kappa_T \) values for the thickest film is within 8% of the known compressibility value of the bulk PS. In addition, it is clear from the inset, in a qualitative manner, that the compressibility shows a significant increase as the film thickness decreases.

Acknowledgements

The text of this chapter, in part, is a reprint of the material as it appears in

6

Scattering Study of Lipid Bilayers

6.1 Introduction to Lipid Bilayer Membranes

The physical and chemical properties of fluid interfaces are of crucial importance in the field of biomaterials. Lipids are a major constituent of the biological membranes that serve as the outer boundary of cells and organelles, and thus can transport nutrients into and metabolic wastes out of the cell, prevent unwanted materials into the extracellular milieu from entering the cell, prevent loss of needed metabolites, and maintain the proper ionic composition and osmotic pressure of the cytosol [86]. Significant evidence collected over the past decade challenges the textbook model of the cell membrane as a two-dimensional, featureless “solvent” lipid bilayer allowing free diffusion of integral proteins (as well as lipids) to occur and with no in-plane structure of its own. For animal cell plasma membranes, in particular, the molecular diversity of the membrane constituents, e.g., the presence of sphingolipids and cholesterol, points to the possibility of ordered phases co-existing with fluid phase at physiological temperatures. Such in-plane structure may have important consequences in many membrane-mediated biological functions including protein trafficking, cell surface signaling, and membrane fusion [149,150]. However, direct evidence for such phase separation in cellular membranes has been difficult to obtain using standard light-based microscopies in part because of the molecular complexity, small dimensions, and rapid dynamics. To this end, model systems with reduced number of components were designed to mimic real biological membranes. Among those models, solid-supported lipid bilayers are the most commonly used experimental cell surface model. Their ability to retain the intrinsic “fluid” property to self-heal local defects while achieving excellent mechanical stability offers distinct advantages over freestand-
ing, solvent-free lipid bilayers or spherical lipid vesicles suspensions [128], and thus has allowed us to gain considerable progresses over the last two decades.

It is now generally accepted that sphingolipids, cholesterol, and saturated phospholipids phase separate from more fluid-like unsaturated phospholipids in lipid bilayers and make laterally mobile, dense liquid-ordered micro-domains, referred to as “rafts”, as a result of the molecular packing requirements and phase behavior of lipid mixtures [10]. It has been suggested that, sphingolipids, a major constituent of rafts, associate laterally with one another, probably through weak interactions between the carbohydrate heads of the glycosphingolipids. The head groups occupy larger excluded areas in the plane of the leaflet than do their predominantly saturated acyl chains. Cone-like rigid cholesterol molecules are thus allowed to be tightly intercalated into the intermolecular free volume between the associating sphingolipids. As a result, the close-packed sphingolipid-cholesterol clusters behave as rafts within the leaflet, and phase separate from the fluid-like regions occupied by unsaturated phosphatidylcholine molecules. It is also proposed that raft domains preferentially include or exclude proteins. Although accumulating evidence favors the existence of some kinds of rafts, but important details regarding size and composition in different biological contexts remain to be elucidated [70]. Among the most pressing issues are the size, in-plane structure and dynamics of rafts and the molecular determinants of the these characteristics.

A striking feature in the phase behavior derived from the model system studies is the observation of larger variations in the sizes of these raft-like micro-domains observed from nominally comparable lipid mixtures and at comparable temperatures. For instance, in giant unilamellar vesicles (GUV), the use of confocal microscopy and other fluorescence imaging methods, have revealed micrometer scale (2-10 \( \mu m \)) domains. By contrast, raft-like micro-domains in supported bilayers appear to be in the sub-micron or even nanoscale dimensions. These discrepancies raise the question of possible incompleteness in the phase separation and the preponderance of metastable or kinetically arrested phase separation in supported bilayers and possibly real biomembranes. Furthermore, the fraction variation of cholesterol drastically mediates the raft structures. For instance, Fig. 6.1 shows the AFM images of supported bilayers of mixtures of 1,2-Dioleoyl-\( sn \)-Glycero-3-Phosphocholine (DOPC) and egg sphingomyelin (SM) with various cholesterol (CH) concentrations at a temperature between the melting temperatures of DOPC (\( T_m = -15 \, ^\circ C \)) and SM (\( T_m = 38 \, ^\circ C \)) [121]. It can be seen that at low CH
Figure 6.1: AFM images reprinted from Ref. [121] showing phase separations in supported DOPC/SM (1:1) bilayers with (A) no CH, (B) 10 mol% CH, (C) 25 mol% CH, (D) 30 mol% CH, and (E) 50 mol% CH. The size of each image is $5 \times 5 \, \mu m^2$, the scale bar is $1 \, \mu m$, and the $z$-scale (normal to the paper) is $10 \, nm$ visible as a gray scale in which low height (DOPC enriched liquid-disordered phase) is black and high height (SM enriched liquid-ordered phase) is white.

concentrations, bilayers have a similar appearance, except that the average domain size grows slightly larger with an increase of CH concentration. At 25 mol% CH, the domain size grows up to $1 \, \mu m$, and less irregular shapes are observed. However, at 30 mol% CH, a percolation structure appears, which has been proposed to be biologically functional [172]. At higher CH concentrations where the percolation threshold is passed, the domain structure becomes macroscopic, and the surface height contrast between the liquid-disordered and liquid-ordered phases becomes obviously smaller than at low CH concentrations, which is believed to be ascribed to the CH saturation in both SM and DOPC molecules.

The goal of the present study is to investigate the structures and fluctuations of lipid bilayers consisting of co-existing phases using both static and time-resolved x-ray and neutron scattering techniques. Particularly interesting will be to examine the effect of the lipid rafts with combinations of cholesterol and integral proteins on the lipid bilayer structures and their dynamic behaviors.
6.2 Sample Preparation

Supported membranes are usually prepared by direct deposition of lipid mono-layers or bilayers onto solid or polymer surfaces to yield macroscopically large areas. Bilayer depositions can occur by four methods: successive transfer of lipid mono-layers from the air/water interface using Langmuir-Blodgett (LB) technique, fusion of lipid vesicles from suspensions, spontaneous spreading of a single bilayer, and solvent exchange method from alcohols to aqueous buffers [107,129,161], among which the second method was employed to make bilayer samples used in the current study.

1,2-Dioleoyl-sn-Glycero-3-Phosphocholine (DOPC), egg sphingomyelin (SM), 1,2-Dilauroyl-sn-Glycero-3-Phosphocholine (DLPC), deuterated 1,2-Distearoyl-sn-Glycero-3-Phosphocholine (DSPC), and cholesterol (CH) were purchased from Avanti Polar Lipids. All lipids were > 99% pure. Fig. 6.2 shows the chemical structures of these...
lipid molecules.

To make lipid bilayers used for x-ray scattering experiments, DOPC, SM and CH from chloroform stock were dissolved at predetermined molar concentrations in glass vials. The lipid mixtures were then dried under nitrogen stream followed by 1 hour storage under high vacuum. The thoroughly dried mixtures were then reconstituted with Millipore deionized water at a 2 mg/mL concentration, and allowed to sit overnight in refrigeration. Upon usage, the solution was extruded using warmed syringes 21 times through the filter unit on an extruder containing a 100 nm pore membrane filter kept at 60 °C. The extruded lipid mixtures were then placed in a plastic curvet and phosphate buffered saline was added at 1:1 ratio, ending in a 1 mg/mL solution of ~100 nm vesicles which was kept at 60 °C until fusion. 100 µL solution was dropped on a plastic Petri dish. A polished silicon substrate of thickness 1 mm and effective surface area 50×8 mm² was treated in a piranha etch followed by a plasma cleaning process, rinsed with Millipore water, placed face down on top of the drop, and kept for 2 min in order to allow the vesicles to adsorb and fuse onto the silicon surface. The dish was then immersed in a large dish filled with Millipore water. The sample was then picked with tweezers and moved back and forth through the water to rinse off any extra lipid, leaving only the bilayer attached to the silicon substrate. The sample was then placed in a fluid cell (Fig. 6.3) to be used for x-ray scattering experiments.

In neutron scattering experiments, because of the much larger cross section area of
a typical neutron beam and the ability of neutrons to penetrate through quartz with negligible absorption, a thick quartz of 3" in diameter was used. The Melcor fluid cell unit used for neutron experiments consists of two identical pieces of quartz aligned in parallel and spaced by a thin layer of deuterated water (D$_2$O). Because of the large scattering length density of D$_2$O, this thin D$_2$O layer effectively acts as the sub-phase, i.e., neutrons were incident through the quartz, and reflected by the hanging lipid bilayers immersed in D$_2$O. Bilayers of 70% DLPC mixed with 30% DSPC were made by the same vesicle fusion method.

6.3 X-ray Reflectivity

X-ray reflectivity experiments were performed on Sector 1-BM-C at the Advanced Photon Source, Argonne National Laboratory. The scattering setup is very similar to Fig. 3.6. Because x-rays have to pass through the water buffer which has a strong absorption cross section, in order to minimize the loss of photons, x-ray energy was tuned to as high as 20.016 keV. To avoid radiation damage during the reflectivity scans, samples were translated to a fresh area after about every one minute.

Reflectivities from supported bilayers of mixtures of 1:1, 2:1, 1:2 and 1:4 DOPC:SM and various CH concentrations at room temperature were normalized to the Fresnel reflectivity (Eq. B.10) of the silicon substrate in order to eliminate the trivial $q_z^{-4}$ dependence and enhance the visibility of the interference fringes. They are shown in Figs. 6.4(a)-6.7(a) in comparison with the reflectivity from a pure DOPC bilayer.

To get the bilayer structure information, in terms of the electron density profile, in the direction normal to the bilayer plane, both box model and non-box model (non-parametric cubic beta spline method) were used in the fitting process. In the box model, the bilayer structure can be divided into multiple parallel slabs (herein called the “box model”), each described by three parameters: thickness, roughness and in-plane averaged refraction index. Parratt’s exact recursive method (Appendix B) is employed to reconstruct the reflectivity. The structural parameters may then be obtained by fitting to the experimental reflectivity using a constrained nonlinear least-square method. On the contrary, in the cubic beta spline method [57,109–111], the electron density is treated as a continuous profile expressed as the sum of a series of cubic spline basis functions. The coefficients in the series are determined by a constrained nonlinear least-square fitting. This method works particularly well for those fuzzy and aperiodic structures, such as the
Figure 6.4: (a) X-ray reflectivities from 1:1 DOPC:SM bilayers with various CH concentrations. Pure DOPC bilayer data is also shown for comparison. Black solid lines are fits with the cubic beta spline model. Orange dotted line is the fit for pure DOPC using a box model of 4 slabs, and cyan dashed lines are fits for other bilayers using a box model of 5 slabs. For clarity, the curves are consecutively multiplied by $10^{-2}$ from top to bottom. (b) Corresponding scattering length density profiles. Black lines represent the cubic beta spline model, and lines of other colors represent the box model results with smeared and unsmeared profiles. Curves are consecutively shifted down by $10^{-5}$ Å$^{-2}$. 
Figure 6.5: (a) X-ray reflectivities from 2:1 DOPC:SM bilayers with various CH concentrations. Lines represent the fits to the same models as used in Fig. 6.4. (b) Corresponding scattering length density profiles.
Figure 6.6: (a) X-ray reflectivities from 1:2 DOPC:SM bilayers with various CH concentrations. Lines represent the fits to the same models as used in Fig. 6.4. (b) Corresponding scattering length density profiles.
Figure 6.7: (a) X-ray reflectivities from 1:4 DOPC:SM bilayers with various CH concentrations. Lines represent the fits to the same models as used in Fig. 6.4. (b) Corresponding scattering length density profiles.
biological membranes in the current study. In the box model, the bilayer of pure DOPC can be represented by a stack of 4 slabs: water cushion, inner head groups, hydrocarbon tails, and outer head groups, as illustrated in Fig. 6.8a. This 4-slab box model has been shown to work properly for bilayers of pure lipids in Ref. [97], which is the first report on x-ray reflectivity measurement from single lipid bilayer membrane at a lipid/water interface. For bilayers of DOPC and SM mixtures showing phase separations, because the saturated hydrocarbon tails of SM molecules tend to pack closely resulting in their head groups sticking out of the fluid phase composed of other unsaturated DOPC molecules, a box model of 5 or more slabs has to be employed. However, more slabs mean that a lot more unknown parameters are to be involved, and that the physical meanings of these slabs become less clear. A 5-slab box model shown in Fig. 6.8b would be sufficient to fit the experimental reflectivity data.

The fitted scattering length density (SLD) profiles, defined as the product of the Thompson constant $r_e$ and the electron density $\rho$, are shown in parallel with corresponding reflectivities in Fig. 6.4b-6.7b. Both box model and cubic beta spline method can fit the reflectivity almost equally well, and yield similar overall SLD profiles. However, a close inspection indicates that the fitted SLD profiles show disagreement to some extent. In fact, a lot more SLD profiles able to fit the reflectivity data as well were found. This is known as the famous phase problem of scattering. To justify the validity and physics of each profile, a preliminary understanding of the system has to be taken into account. At this moment, however, this would not help solve the problem for the not-well-defined aperiodic bilayers, since the fitted profiles only display subtle variations that occur locally at length scales smaller the resolution of the reflectivity experiment $2\pi/\text{max}[q_z] \approx 9$ Å. Figs. 6.4-6.7 show some of the most reasonable fitted results. To
help clarify the bilayer structures, the SLD profiles obtained from the box model are also plotted before smearing.

It is known that the presence of CH condenses phospholipid bilayers, increases their thickness, and at high enough concentrations eliminates the phase transition. CH is thought to cause these effects by intercalating between acyl chains of phospholipids, possibly due to its inverted cone shape and amphipathic nature [130]. CH squeezes its hydrophobic core into the hydrocarbon region of the phospholipid with the OH group protruding into the polar head groups. This intercalation would order the bilayer acyl chains and reduce their ability to tilt, causing the bilayer to thicken. Similarly, CH may also intercalate between sphingolipids. For 1:1 and 2:1 DOPC:SM bilayers (Figs. 6.4 and 6.5), although the shapes of the continuous SLD profiles look similar for all CH concentrations, the unsmeared profiles from the box model results clearly indicates an expansion of the bilayer thickness in the presence of CH. This is consistent with the shift of the position of the first minimum in the reflectivity. However, this thickening effect is not observed in 1:2 and 1:4 DOPC:SM bilayers of higher SM concentrations. It is also clear that the reflectivity data display a significant transition with the increase of CH concentration: 40–50% in 2:1 DOPC:SM bilayers, and 30–40% for 1:1, 1:2, and 1:4 DOPC:SM bilayers. However, simply judging from the SLD profile obtained from reflectivity, which represents the average over the plane of the bilayer, it is impossible to tell what really happens at those critical CH concentrations. To extract the in-plane information of the lipid molecular arrangements, especially the structure of the raft-like domains, we turned to the help of surface x-ray diffuse scattering techniques. Unfortunately, this attempt did not work out quite well, because x-ray diffuse scattering signals are usually orders of magnitude weaker than the reflectivity, and in addition they are diminished in the presence of the water buffer due to the absorption and background scattering of the water molecules.

6.4 Neutron Diffuse Scattering

There have been some successful experiments of neutron reflectivity measurements on single supported lipid bilayer membranes at the lipid/water interfaces. However, as far as we know, there was no attempt of using neutron diffuse scattering to measure the in-plane structures of these systems. In order to test the capability of this technique, a neutron diffuse scattering experiment was carried out on a time-of-flight (TOF) scattering
Figure 6.9: Neutron TOF intensity map (background subtracted) of the diffuse scattering from a bilayer of a mixture of 7:3 DLPC and DSPC lipids. The counting duration is approximately 9.25 hours. Red box indicates the region used for data reduction.

Figure 6.10: Scattering structure factor calculated from Fig. 6.9.
instrument — SPEAR at the Manual Lujan Jr. Neutron Scattering Center on a bilayer of a binary mixture of DLPC and DSPC molecules, which ought to be phase separated to form raft-like domains [119]. To enhance the SLD contrast between the binary lipid components, partially deuterated DSPC lipids were used, because for neutrons there is a very large SLD difference between deuterium and hydrogen nuclei. Fig. 6.9 is the TOF intensity map measured for a duration of 9.25 hours from the surface of a 7:3 DLPC:DSPC bilayer. Although deuterated DSPC was used to increase the contrast and the counting duration was more than 9 hours, the average count per pixel was still as weak as ∼3, which would lead to enormously large statistical uncertainties. A specific software was developed for SPEAR to reduce the diffuse TOF data to the scattering structure factor as a function of $q_z$ and $q_x$, which is shown in Fig. 6.10. It can be seen the achievable maximum in-plane wave vector transfer is only $\sim 10^{-2}$ Å$^{-1}$, which is far from sufficient to probe nanoscale domains. In addition, the in-plane wave vector transfer window is only about $2.5 \times 10^{-3}$ Å$^{-1}$ at a fixed $q_z$. Due to these drawbacks, the attempt to investigate in-plane raft-like domains in a single supported bilayer using neutron diffuse scattering did not work out.

Acknowledgements

The text of this chapter, in full, is based on the preliminary work accomplished in collaboration with A. Szmodis and A. Parikh in University of California at Davis. Sector 1-BM-C at the Advanced Photon Source, and SPEAR at the Manual Lujan Jr. Neutron Scattering Center, Los Alamos National Laboratory are acknowledged for providing facilities.
Conclusions and Prospects

In this thesis the surface and interfacial structures and dynamics of various polymeric liquid systems have been studied, mainly by x-ray scattering techniques, including conventional x-ray reflectivity, transverse diffuse scattering, and the newly developed x-ray photon correlation spectroscopy (XPCS).

In Chapter 3, using XPCS, we found that the surface dynamics on thick \((d \gg R_g)\), supported, spin-cast molten polystyrene (PS) films are well explained by capillary wave theory in the over-damped region, and that the viscosity obtained at temperatures well above the bulk \(T_g\) agrees with the bulk PS values. As the thickness of the films approaches the dimension of the polymer chains, \(2R_g\) for example, an elasticity effect appears to affect the surface dynamics, and this can be ascribed to the adsorption of polymer chain segments onto the substrate, which may effectively lead to the formation of a brush. This elasticity effect was also observed as a lower wave vector cutoff in the static spectrum measured by transverse diffuse scattering. However, in a real PS brush with all the chains intentionally tethered to the substrate and stretched normal to the surface, we did not observe any surface dynamics on any accessible length scales \((600 - 3000 \text{ nm})\), even at temperatures more than 130 °C above the bulk \(T_g\). This indicates that the thermal energy may not be large enough to excite surface waves on certain length scales, so that all surface fluctuations are fully suppressed. As a possible research direction in the future, brushes of lower grafting densities may be studied in order to investigate the transition region from completely suppressed to over-damped surface dynamics.

We have also discovered rich surface dynamic behaviors in supported spin-cast PS films at temperatures near above and well above the bulk \(T_g\), and have constructed a
“phase” diagram accordingly. For films of molecular weight larger than the critical molecular weight for entanglement, i.e. $M_W > M_C$, the surface dynamics were found to be single exponential relaxations, dependent of $M_W$ well above the bulk $T_g$, but independent of $M_W$ close to $T_g$, whereas in an intermediate temperature range they behave as a stretched exponential relaxation. On the other hand, for films of $M_W \leq M_C$, only the $M_W$-dependent single exponential relaxation was observed at any temperature above $T_g$. These complicated surface dynamics are believed to arise from the internal dynamics of the polymer segments whose length varies with temperature for $M_W > M_C$.

In addition, the existence of a high-mobility surface layer speculated to be behind the reduction of $T_g$ in supported thin PS films, can be clearly excluded by the thickness-scaling and bilayer dynamics analysis.

In Chapter 4, the x-ray standing wave technique has been applied for the first time in combination with x-ray diffuse scattering and XPCS to measure interfacial structures and dynamics of bilayer films, e.g. PS/PBrS films. The interfacial tension of this system was determined nondestructively. Dynamic studies reveal that both the surface and interfacial relaxations are independent of the bottom PBrS layer thickness, and therefore the existence of a low-viscosity interface between the two immiscible polymer layers is confirmed. As a possible research direction in the future, a bilayer of PBrS on top of PS may be studied in terms of the kinetic development of the dewetting behavior.

Apart from surface capillary wave contributions to the total diffuse scattering, thermal density fluctuations within in the film are another source of scattering. Therefore, in Chapter 5, with the DWBA theory, we have developed a technique to separate these two contributions. The experimental results from thin films reveal a rise in the bulk structure factor in the small $q$ region. Although the cause of this behavior is still not understood, it is consistent with molecular-dynamics simulations for confined thin liquid polymer films.

Finally, in Chapter 6, we have also attempted, for the first time, to probe the structures of raft-like domains formed in single supported bilayers composed of phase-separated lipids using x-ray and neutron scattering techniques. The x-ray reflectivity results clearly reveal that the structure of bilayers of DOPC and SM lipid mixtures abruptly changes as the amount of cholesterol is increased beyond a critical concentration. However, due to the phase problem, a direct understanding from the fitted electron density profile is unlikely. Attempts to directly view the in-plane structures of these bi-
layers using x-ray and neutron diffuse scattering techniques did not work out due to some shortcomings, e.g., the large photon absorption of the water buffer for x-ray measurements and weak neutron counting rate for neutron measurements. However, with the increase of the neutron flux anticipated when the Spallation Neutron Source comes alive, neutron diffuse scattering from these single supported lipid bilayers may become possible. Alternatively, for x-ray scattering measurements, saturated vapor may be a possible substitution for the water buffer so that the absorption and parasitic scattering of the water would be significantly diminished.

We have demonstrated only a small portion of possible applications of scattering techniques to investigate polymeric liquid surfaces. There remains a vast number of phenomena in polymer surface science that can be studied by scattering. For example, the self-assembling of diblock copolymers in thin films is of great interest nowadays. The kinetics of the self-assembling process that may occur at both the surface and within the film can be studied by combining x-ray scattering and standing wave techniques. More excitingly, with the new generation of x-ray sources (XFEL and ERL) coming soon, providing orders of magnitude more intensity and almost perfect coherence, the dream of capturing instantaneous structures of liquid surfaces, i.e., time-resolved x-ray holography of liquid surfaces, may come to reality one day.
Appendix A

Green’s Function

The Green’s function can be obtained by solving the Helmholtz equation that defines the Green’s function,

\[(\nabla^2 + k^2)r G(r) = \delta^3(r).\] (A.1)

In terms of their Fourier transformation, the Green’s function and the \(\delta\) function can be written as

\[G(r) = \int dK \tilde{G}(K)e^{-iKr},\] (A.2)

\[\text{and} \quad \delta^3(r) = \frac{1}{(2\pi)^3} \int dK e^{-iKr}.\] (A.3)

It then follows from Eq. (A.1) that

\[\tilde{G}(K) = -\frac{1}{(2\pi)^3} \frac{1}{K^2 - \frac{k^2}{2}}.\] (A.4)

Hence,

\[G(r) = -\frac{1}{(2\pi)^3} \int dK \frac{e^{-iKr}}{K^2 - \frac{k^2}{2}}\]

\[= -\frac{1}{(2\pi)^3} \int_{0}^{2\pi} d\varphi_K \int_{0}^{\pi} d\theta_K \sin \theta_K \int_{0}^{\infty} dKK^2 e^{-iKr} \cos \theta_K\]

\[= -\frac{1}{(2\pi)^2 (ir)} \int_{-\infty}^{\infty} dK \frac{K e^{iKr}}{(K + k)(K - k)}.\] (A.5)

There are two first order poles on the real axis in the complex plane. The integral can then be calculated using complex analysis [179]. Since \(r > 0\), according to Jordan’s lemma, we can choose the upper plane for the contour integral, so that the contour \(C\)
is composed of \( C_2 \) plus the real axis (Fig. A.1). Instead of distorting the contour on the real axis slightly down to avoid the integral through the poles, we shift the positions of the poles by a small amount \( i\beta \). The offsets are infinitesimal, so that this trick makes no difference to the evaluation of the contour integral. The Green’s function is then rewritten as

\[
G(r) = \lim_{\beta \to 0} -\frac{1}{(2\pi)^2} \oint_C dK \frac{K e^{iKr}}{[K + (k + i\beta)][K - (k + i\beta)]}. \tag{A.6}
\]

The way how \( \beta \) approaches zero carries a physical meaning, as we will see below. \( K = k + i\beta \) is the only pole encircled by the contour when \( \beta \to 0^+ \), and \( K = -(k + i\beta) \) when \( \beta \to 0^- \). Therefore, using the residue theorem, we have two Green’s functions

\[
G^+(r) = -\frac{1}{4\pi} \frac{e^{ikr}}{r}, \tag{A.7}
\]

and

\[
G^-(r) = -\frac{1}{4\pi} \frac{e^{-ikr}}{r}, \tag{A.8}
\]

which represent the outgoing and incoming waves respectively in a scattering process.
Appendix B

Parratt’s Recursion

Parratt’s recursive method to calculate the exact reflectivity was named after Parratt [108], and was discussed later in detail in many books [2, 25, 33, 82, 122, 151, 164, 168] and articles [6, 32, 127, 185] on x-ray and neutron scattering.

Fresnel reflectivity

To begin with, consider a single smooth surface, and suppose medium 1 is vacuum, as shown in Fig. B.1. The wave function in each medium is given by

\[ \psi_1(r) = e^{ik_1 \cdot r} + r_{1,2} e^{ik'_1 \cdot r} \]  
\[ \psi_2(r) = t_{1,2} e^{ik_2 \cdot r}, \]  

where \( r_{1,2} \) and \( t_{1,2} \) are introduced respectively as the amplitude reflectivity and transmittivity when the wave travels from medium 1 to medium 2.

Bearing in mind that \( k_1 = |k_1| = |k'| \) and \( k_2 = n_2 k_1 \), by imposing the boundary conditions that the wave function and its first derivative must be continuous at the interface, we have Snell’s law,

\[ \cos \alpha_1 = n_2 \cos \alpha_2, \]  

and the Fresnel equations,

\[ r_{1,2} = \frac{k_{z,1} - k_{z,2}}{k_{z,1} + k_{z,2}}, \]  

and \[ t_{1,2} = \frac{2k_{z,1}}{k_{z,1} + k_{z,2}}. \]
Snell’s law indicates that the in-plane component of the wave vector is invariant across the interface, i.e., $k_{x,1} = k_{x,2}$. Since $\text{Re}[n_2] < 1$, there exists total external reflection, with the critical angle given by $\alpha_c \approx \sqrt{2\delta_2}$. Due to absorption, $k_{z,2}$ has an imaginary component so that $r_{1,2}$ and $t_{1,2}$ are complex. Therefore, the wave function in medium 2 ($z \leq 0$) can be written as,

$$\psi_2(x, z) = t_2 e^{i(k_{x,2}x - \text{Re}[k_{z,2}]z)} e^{\text{Im}[k_{z,2}]z}.$$  \hspace{1cm} (B.6)

At small angles, $k_{z,2}$ is found to be

$$k_{z,2} = \sqrt{k_2^2 - k_{x,2}^2} \approx k_1 \sqrt{(\alpha_1^2 - \alpha_c^2) + i2\beta_2} = \frac{k_1}{\sqrt{2}} \left[ \left( \sqrt{\Theta^2 + 4\beta_2^2 + \Theta} \right)^{\frac{1}{2}} + i \left( \sqrt{\Theta^2 + 4\beta_2^2 - \Theta} \right)^{\frac{1}{2}} \right]$$ \hspace{1cm} (B.7)

where $\Theta = \alpha_1^2 - \alpha_c^2$. When $\alpha_1 < \alpha_c$, $\Theta < 0$. So $\text{Im}[k_{z,2}]$ is quite large, and the penetrated wave damps exponentially fast into the medium, called an evanescent wave. The field penetration depth $\Lambda$ is usually characterized as the depth where the wave amplitude is reduced to $1/e$ of its original value, so that

$$\Lambda \equiv \frac{1}{\text{Im}[k_{z,2}]} = \frac{\sqrt{2}}{k_1} \left( \sqrt{\Theta^2 + 4\beta_2^2 - \Theta} \right)^{-\frac{1}{2}}.$$ \hspace{1cm} (B.8)

Fresnel reflectivity is defined as the modulus square of the amplitude reflectivity,

$$R_F \equiv |r_{1,2}|^2 = \left| \frac{k_{z,1} - k_{z,2}}{k_{z,1} + k_{z,2}} \right|^2.$$ \hspace{1cm} (B.9)

When $\alpha_1 \gg \alpha_c$, from Eq. (B.7), $k_{z,2} \approx k_{z,1} \left[ 1 - \alpha_c^2/(2\alpha_1^2) \right]$. Therefore,

$$R_F \approx \left( \frac{\alpha_c}{2\alpha_1} \right)^4 \approx \frac{16\pi r^2 \rho_2^2}{q_z^2}.$$ \hspace{1cm} (B.10)
This is the expression of Fresnel reflectivity with multiple scattering events neglected, i.e., the Born approximation. To calculate the exact reflectivity, Eq. (B.9) has to be used.

**Reflectivity from a multi-layer**

We now apply the above discussions to a multi-layered system. A rough interface can always be subdivided into many slices, each of which has a very small finite thickness and two smooth surfaces. How the slicing process should be performed depends on the model chosen to describe the electron density profile at the interface, for example, error function or hyperbolic tangent function. For an interface with a roughness value comparable to the thicknesses of nearby layers, an effective-density model is usually adopted [164]. Therefore, for convenience and a general purpose, we will only deal with sharp interfaces without roughnesses.

Suppose there are \( N \) interfaces, the position of each denoted by \( z_j \), where \( j = 1, 2, \ldots, N \) from top to bottom. The wave function in the whole space is written as,

\[
\psi_j(\mathbf{r}) = T_je^{ik_j \cdot \mathbf{r}} + R_je^{ik'_j \cdot \mathbf{r}}, \quad \text{with} \quad j = 1, 2, \ldots, N+1. \tag{B.11}
\]

Here the \( j \)th layer denotes the layer just above the \( j \)th interface, and the \((N + 1)\)th layer is the bottommost layer underneath the \( N \)th interface. We cannot simply use Eqs. (B.4) and (B.5), because the transmitted and the reflected waves in each layer will be transmitted and reflected again into the layer itself and the layers nearby, i.e., multiple scattering events have to be taken into account. As shown in Fig. B.2, the total amplitude reflectivity from the \( j \)th interface is given by

\[
R_j = r_{j,j+1} + t_{j,j+1}t_{j+1,j}P_{j+1}^2 \sum_{m=0}^{\infty} (r_{j+1,j}R_{j+1}P_{j+1}^2)^m,
\]

where \( r_{j,j+1} \) and \( t_{j,j+1} \) are the Fresnel amplitude reflectivity and transmittivity respectively at the \( j \)th interface. They can be calculated from Eqs. (B.4) and (B.5). \( P_{j+1} = e^{ik_{z,j+1}(z_j-z_{j+1})} \) accounts for the phase lag due to the wave bounces in the \( j+1 \) layer. In deriving Eq. (B.12), we have applied identities \( r_{j,j+1} = -r_{j+1,j} \) and \( r_{j,j+1}^2 + t_{j,j+1}t_{j+1,j} = 1 \).

Because the \((N + 1)\) layer is infinitely thick, we may write \( R_{N+1} = 0 \). Therefore, Eq. (B.12) may be recursively performed until \( R_1 \) is obtained. Since the amplitude of the
incident beam can always be normalized to one, i.e., \( T_1 = 1 \), the final reflectivity from this multi-layered system is then given by \( R = |R_1|^2 \). Applying the boundary condition to the \((j-1)\)th interface, we may have

\[
T_j = T_{j-1} e^{i(k_{z,j-1}-k_{z,j})z_{j-1}} + R_{j-1} e^{-i(k_{z,j-1}+k_{z,j})z_{j-1}} - R_j e^{-2k_{z,j}z_{j-1}}.
\]  

(B.13)

With the knowledge of \( R_j \) and \( T_1 = 1 \), we can then recursively obtain the amplitude transmittivity \( T_j \) in each layer. Eventually, the complete wave function may be constructed as a function of depth \( z \) throughout the multi-layered system. Parratt’s recursive method will be extremely tedious in the presence of a large number of interfaces, and thus is usually calculated with computers nowadays.
Appendix C

Surface and Interfacial Dynamics of Liquid Bilayers

Consider a liquid bilayer film on a solid substrate (Fig. C.1) with bottom layer thickness $h_1$ and top layer thickness $h_2 = d - h_1$. For clarity, we use subscript and superscript, 1 and 2, to represent the parameters related to the bottom and top layers, and the interface and free surface respectively. For example, the dynamic viscosity and the mass density of the top layer II are denoted by $\eta_2$ and $\rho_2$. The surface and interfacial tensions are $\gamma_2$ and $\gamma_1$ respectively. We assume small periodic externally applied pressure perturbations on the interface and the free surface of the form $P_z^{(1)} e^{i(kx - \omega t)}$ and $P_z^{(2)} e^{i(kx - \omega t)}$ respectively, with $u_z^{(1)}$ and $u_z^{(2)}$ being the vertical displacements of the reactive fluctuations. The media are supposed to be uniform throughout each layer so that the mass density profile is composed of step functions on which are superimposed surface and interfacial fluctuations with small amplitudes.

Navier-Stokes equation

We start with the linearized Navier-Stokes equation for incompressible liquids [68,80]

$$\partial_t \mathbf{v} = -\frac{1}{\rho} \nabla p + \nu \nabla^2 \mathbf{v}, \quad (C.1)$$

where $\mathbf{v}$ and $p$ are velocity field and pressure, and $\nu = \eta/\rho$ is the kinematic viscosity of the liquid. In the following calculations, a frequency independent viscosity will be used. However, to take into account the elasticity effect of a viscoelastic liquid, one can explicitly substitute $\nu$ by a frequency dependent kinematic viscosity. In Eq. (C.1) the
gravitational potential is effectively treated as part of the pressure. We then try to look for solutions for the velocity and pressure in the form of monochromatic plane waves propagating along the $x$ direction,

$$v^{(j)}(r, t) = (V_x^{(j)}(z)e_x + V_z^{(j)}(z)e_z)e^{i(kx - \omega t)},$$  \hspace{1cm} (C.2a)  

$$p^{(j)}(r, t) = P^{(j)}(z)e^{i(kx - \omega t)},$$ \hspace{1cm} (C.2b) 

where the superscript $j = 1, 2$ denotes the solutions in region I and II respectively.

**Region I, II and boundary condition at $z = 0$**

Jäckle derived the velocity and pressure fields within a uniform single-layer film [68]. In a similar way for a bilayer film, applying the monochromatic plane wave assumption, Eqs. (C.2), as well as the equation of continuity, $\nabla \cdot \mathbf{v} = 0$, in terms of velocity amplitudes

$$ikV_x^{(j)} + \partial_z V_z^{(j)} = 0,$$ \hspace{1cm} (C.3)

Eq. (C.1) leads to the preliminary solutions of the Navier-Stokes equation in region I and II:

$$V_z^{(j)}(z) = A_k^{(j)} \cosh(kz) + B_k^{(j)} \sinh(kz) + ik\widehat{B}_j \cosh(\kappa_j z) + ik\widehat{C}_j \sinh(\kappa_j z),$$ \hspace{1cm} (C.4a)  

$$V_x^{(j)}(z) = \frac{i}{k} \partial_z V_z^{(j)}(z),$$ \hspace{1cm} (C.4b)  

$$\frac{P^{(j)}(z)}{\rho_j} = \frac{i\nu_j}{k} (\kappa_j^2 - \partial_z^2) V_x^{(j)}(z),$$ \hspace{1cm} (C.4c)  

where $\kappa_j = \sqrt{k^2 - i\omega/\nu_j}$, and $A_k^{(j)}, B_k^{(j)}, \widehat{B}_j$ and $\widehat{C}_j$ are constants to be determined by the boundary conditions at $z = 0, h_1,$ and $d$. 

Figure C.1: Geometry and notations of a supported bilayer film. Bottom layer and top layer are denoted by region I and II respectively.
The non-slip boundary condition at \( z = 0 \) reads \( V_x^{(1)}|_{z=0} = V_z^{(1)}|_{z=0} = 0 \), yielding \( A_k^{(1)} = -i k \hat{B}_1 \) and \( B_k^{(1)} = -i \kappa_1 \hat{C}_1 \). If the \( xz \) and \( zz \) components of the stress tensor in regions I and II are denoted as

\[
\sigma_{xz}^{(j)} = \hat{\sigma}_{xz}^{(j)} e^{j(kx - \omega t)} = \eta_j \left( \partial_x v_x^{(j)} + \partial_z v_z^{(j)} \right), \quad \text{(C.5a)}
\]
\[
\sigma_{zz}^{(j)} = \hat{\sigma}_{zz}^{(j)} e^{j(kx - \omega t)} = -p^{(j)} + 2 \eta_j \partial_z v_z^{(j)}, \quad \text{(C.5b)}
\]

then Eqs. (C.4) and (C.5a) can be combined into compact matrix expressions:

\[
X = BZ, \quad \text{region I}, \quad \text{(C.6a)}
\]
\[
W = AY, \quad \text{region II}, \quad \text{(C.6b)}
\]

where \( X \) and \( Z \), \( W \) and \( Y \) are defined for region I and II respectively as

\[
X = \begin{bmatrix} V_x^{(1)} \\ V_z^{(1)} \\ P^{(1)}/\rho_1 \\ \hat{\sigma}^{(1)}_{xz} \end{bmatrix}, \quad Z = \begin{bmatrix} \hat{B}_1 \\ \hat{C}_1 \end{bmatrix}, \quad \text{(C.7a)}
\]
\[
W = \begin{bmatrix} V_x^{(2)} \\ V_z^{(2)} \\ P^{(2)}/\rho_2 \\ \hat{\sigma}^{(2)}_{xz} \end{bmatrix}, \quad Y = \begin{bmatrix} A_k^{(2)} \\ B_k^{(2)} \\ \hat{B}_2 \\ \hat{C}_2 \end{bmatrix}, \quad \text{(C.7b)}
\]

and the matrices \( B \) and \( A \) are defined as

\[
B = \begin{bmatrix} k \sinh(kz) - \kappa_1 \sinh(\kappa_1 z) & \kappa_1 \cosh(kz) - \kappa_1 \cosh(\kappa_1 z) \\ -ik \cosh(kz) + ik \cosh(\kappa_1 z) & -i \kappa_1 \sinh(kz) + ik \sinh(\kappa_1 z) \\ \omega \sinh(kz) & \omega(\kappa_1/k) \cosh(kz) \\ 2\eta_1 k^2 \cosh(kz) - \eta_1 (k^2 + \kappa_1^2) \cosh(\kappa_1 z) & 2\eta_1 k \kappa_1 \sinh(kz) - \eta_1 (k^2 + \kappa_1^2) \sinh(\kappa_1 z) \end{bmatrix}, \quad \text{(C.8a)}
\]
\[
A = \begin{bmatrix} i \sinh(kz) & i \cosh(kz) & -\kappa_2 \sinh(\kappa_2 z) & -\kappa_2 \cosh(\kappa_2 z) \\ \cosh(kz) & \sinh(kz) & ik \cosh(\kappa_2 z) & ik \sinh(\kappa_2 z) \\ (i\omega/k) \sinh(kz) & (i\omega/k) \cosh(kz) & 0 & 0 \\ 2ik\eta_2 \cosh(kz) & 2ik\eta_2 \sinh(kz) & -\eta_2 (k^2 + \kappa_2^2) \cosh(\kappa_2 z) & -\eta_2 (k^2 + \kappa_2^2) \sinh(\kappa_2 z) \end{bmatrix}. \quad \text{(C.8b)}
\]
Hence, the hydrodynamic problem reduces to the problem of solving for coefficients \( Y \) and \( Z \) via the other two boundary conditions at \( z = h_1 \) and \( d \).

**Interfacial boundary condition at \( z = h_1 \)**

If the bilayer system is composed of two immiscible liquids, the interfacial boundary condition in equilibrium is that the velocities of the liquids on both sides at the interface must be equal and that the forces which each exerts on the other must be equal and opposite [80]:

\[
\begin{align*}
V_x^{(2)} &= V_x^{(1)}, \\
\tilde{\sigma}_{xz}^{(2)} &= \tilde{\sigma}_{xz}^{(1)}, \\
\tilde{\sigma}_{zz}^{(2)} - \tilde{\sigma}_{zz}^{(1)} &= (\gamma_1 k^2 + g(\rho_1 - \rho_2))U_z^{(1)} - P_z^{(1)},
\end{align*}
\]

where \( U_z^{(1)} \) is the amplitude of the vertical displacement of interfacial fluctuations evaluated by \( u_z^{(1)} = \frac{i}{\omega} v_z^{(1)} \big|_{z=h_1} \). Here in writing the boundary condition Eq. (C.9c), the gravitational potential has to be included explicitly. Again with the equation of continuity Eq. (C.3) in both layers, one can rewrite the interfacial boundary condition in a matrix form

\[
W \big|_{z=h_1} = TX \big|_{z=h_1} + U,
\]

where \( U \) and \( T \) are defined as following,

\[
U = \begin{bmatrix} 0 & 0 & \frac{P_z^{(1)}}{\rho_2} & 0 \end{bmatrix}^T,
\]

\[
T = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ \frac{2ik(\eta_1-\eta_2)}{\rho_2} & -i(\gamma_1 k^2 + g(\rho_1 - \rho_2)) & \frac{\rho_1}{\rho_2} & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}.
\]

By combining Eqs. (C.6) and (C.10), one can relate the components of \( Y \) (for region II) and \( Z \) (for region I),

\[
Y_k = \sum_{l=1}^{2} C_{kl} Z_l + \frac{P_z^{(1)}}{\rho_2} A_{k3}^{-1} \big|_{z=h_1},
\]

where the intermediate matrix \( C \) is given by

\[
C = \left( A^{-1} TB \right) \big|_{z=h_1}.
\]
Surface boundary condition at $z = d$

The boundary condition at the free surface reads

\[ \sigma_{zz}^{(2)} = \eta_2 (\partial_z V_{x}^{(2)} + ik V_{z}^{(2)}) = 0, \quad (C.14a) \]
\[ \sigma_{zz}^{(2)} = -P^{(2)} + 2\eta_2 \partial_z V_{z}^{(2)} = -\left(\gamma_2 k^2 + g\rho_2\right) U_{z}^{(2)} + P_{z,0}^{(2)}. \quad (C.14b) \]

With the equation of continuity Eq. (C.3) and the vertical surface displacement $u_{z}^{(2)} = \frac{\dot{\imath}}{\omega} v_{z}^{(2)} \big|_{z=d}$, one can rewrite Eqs. (C.14) as

\[ \textbf{DY} = 0, \quad (C.15a) \]
\[ \textbf{EY} = \frac{P_{z,0}^{(2)}}{\rho_2}, \quad (C.15b) \]

where

\[ D = \begin{bmatrix} 2k \cosh(kd) \\ 2k \sinh(kd) \\ i(k^2 + \kappa_2^2) \cosh(\kappa_2 d) \\ i(k^2 + \kappa_2^2) \sinh(\kappa_2 d) \end{bmatrix}^T, \quad (C.16a) \]
\[ E = \begin{bmatrix} (2\nu_2 k - \frac{\dot{\imath}}{\kappa}) \sinh(kd) + \frac{i(\gamma_2 k^2 + g\rho_2)}{\rho_2 \omega} \cosh(kd) \\ (2\nu_2 k - \frac{\dot{\imath}}{\kappa}) \cosh(kd) + \frac{i(\gamma_2 k^2 + g\rho_2)}{\rho_2 \omega} \sinh(kd) \\ 2i\nu_2 k\kappa_2 \sinh(\kappa_2 d) - \frac{2i(\gamma_2 k^2 + g\rho_2)}{\rho_2 \omega} \cosh(\kappa_2 d) \\ 2i\nu_2 k\kappa_2 \cosh(\kappa_2 d) - \frac{2i(\gamma_2 k^2 + g\rho_2)}{\rho_2 \omega} \sinh(\kappa_2 d) \end{bmatrix}. \quad (C.16b) \]

Applying Eq. (C.12), one can easily transform the surface boundary condition Eqs. (C.15) into expressions in terms of $\textbf{Z}$, i.e.,

\[ \sum_{l=1}^{2} P_l Z_l = -\frac{P_{z,0}^{(1)}}{\rho_2} P_0, \quad (C.17a) \]
\[ \sum_{l=1}^{2} Q_l Z_l = \frac{P_{z,0}^{(2)}}{\rho_2} - \frac{P_{z,0}^{(1)}}{\rho_2} Q_0, \quad (C.17b) \]

where $P$, $Q$, $P_0$ and $Q_0$ are defined by

\[ P_l = \sum_{j=1}^{4} D_j C_{jl}, \quad P_0 = \sum_{j=1}^{4} D_j A_{j3}^{-1} \big|_{z=h_1}, \quad (C.18a) \]
\[ Q_l = \sum_{j=1}^{4} E_j C_{jl}, \quad Q_0 = \sum_{j=1}^{4} E_j A_{j3}^{-1} \big|_{z=h_1}. \quad (C.18b) \]
Surface and interfacial dynamic susceptibilities

Solving the linear equations (C.17) for \( Z \) yields

\[
Z_1 = \frac{(P_2Q_0 - P_0Q_2)(P_{z,0}^{(1)}/\rho_2) - P_2(P_{z,0}^{(2)}/\rho_2)}{P_1Q_2 - P_2Q_1},
\]

\[
Z_2 = \frac{(P_0Q_1 - P_1Q_0)(P_{z,0}^{(1)}/\rho_2) + P_1(P_{z,0}^{(2)}/\rho_2)}{P_1Q_2 - P_2Q_1}.
\]

Therefore together with the relation Eq. (C.12) we finally obtain the complete monochromatic plane wave solutions. It then follows that the amplitudes of the vertical interfacial and surface fluctuations are

\[
U^{(1)}_z = \frac{i}{\omega} V^{(1)}_z \bigg|_{z = h_1} = \frac{i}{\omega} \sum_{k=1}^{2} N_k Z_k
\]

\[
= \frac{i}{\rho_2\omega} \frac{P_0 [Q, N] - Q_0 [P, N]P_{z,0}^{(1)} + [P, N]P_{z,0}^{(2)}}{[P, Q]},
\]

\[
U^{(2)}_z = \frac{i}{\omega} V^{(2)}_z \bigg|_{z = d} = \frac{i}{\omega} \sum_{k=1}^{4} R_k Y_k = \frac{i}{\omega} \left( \sum_{l=1}^{2} M_l Z_l + \frac{P_{z,0}^{(1)}}{\rho_2} M_0 \right)
\]

\[
= \frac{i}{\rho_2\omega} \left[ [M, P, Q]P_{z,0}^{(1)} + [P, M]P_{z,0}^{(2)} \right],
\]

where \( N, R, M \) and \( M_0 \) are defined as

\[
N = \begin{bmatrix}
-i(k\cosh(kh_1) - k\cosh(\kappa_1h_1)) \\
-i(\kappa_1\sinh(kh_1) - k\sinh(\kappa_1h_1))
\end{bmatrix}^T,
\]

\[
R = \begin{bmatrix}
\cosh(kd) \\
\sinh(kd) \\
-ik\cosh(\kappa_2d) \\
-ik\sinh(\kappa_2d)
\end{bmatrix}^T,
\]

\[
M_l = \sum_{k=1}^{4} R_k C_{kl}, \quad M_0 = \sum_{k=1}^{4} R_k A_{k3}^{-1} \bigg|_{z = h_1}.
\]

The bracket notations in Eqs. (C.20) are defined by

\[
[P, Q] = P_1Q_2 - P_2Q_1,
\]

\[
[M, P, Q] = \sum_{i,j,k=0}^{2} \epsilon_{ijk} M_i P_j Q_k,
\]
where $\epsilon_{ijk}$ is the Levi-Civita symbol. It is noted that each of the interfacial and surface fluctuations is affected by both of the external pressure fields. Rewriting Eqs. (C.20) as $U_z^{(i)} = \sum_j \chi_{zz}^{(ij)} P_z^{(j)}$, one therefore applies the linear response theory and obtains the self and cross dynamic susceptibilities for the interface and the free surface

$$X_{zz} = \frac{i}{\rho_2 \omega [P, Q]} \begin{bmatrix} P_0[Q, N] - Q_0[P, N] & [P, N] \\ [M, P, Q] & [P, M] \end{bmatrix}.$$  \hfill (C.23)

**Discussions**

According to the generalized fluctuation dissipation theorem [78] for classical fluids, the imaginary part of the dynamic susceptibility determines the thermal fluctuation power spectrum

$$S_{zz}^{(ij)}(k, \omega) = \int dt \langle u_z^{(ij)}(k, t) u_z^{(ij)}(-k, 0) \rangle e^{i\omega t} = 2k_B T \frac{\text{Im} \chi_{zz}^{(ij)}(k, \omega)}{\omega}. \hfill (C.24)$$

In general, the frequency-dependent part of the susceptibility of a linear and causal physical process is in the form of $1/(\omega^2 - \omega_0^2 + i\omega \Gamma)$, where $\omega_0$ and $\Gamma$ are defined as the propagation frequency and the damping rate respectively. If $\Gamma$ is small compared to $\omega_0$, the power spectrum has a sharp peak at $\omega = \omega_0$, the peak width being $\Delta \omega_{\text{FWHM}} \approx \Gamma$. More generally, for a system with multiple responses, e.g., a supported liquid bilayer film, the frequencies and damping rates can be straightforwardly resolved by looking for the poles of $\chi_{zz}^{(ij)}(k, \omega)$ in the lower half of the complex $\omega$ plane. In particular, propagating modes are usually suppressed on highly viscous polymeric liquids, and only those over-damped modes characterized by $\Gamma_m$ exist. Hence, when evaluated at imaginary frequencies, the susceptibility turns out to be completely real, and exhibits non-zero simple poles $\omega_m = -i\Gamma_m$ ($\tau_m = 1/\Gamma_m$ are capillary wave relaxation time constants) which are the collection of positive solutions for $1/\chi_{zz}^{(ij)}(k, -i\Gamma) = 0$. It follows that the intermediate scattering function, i.e., the Fourier transform of the surface or interfacial fluctuation spectrum in time representation, is given as the sum of the over-damped modes at these poles,

$$S_{zz}^{(ij)}(k, t) = S_{zz}^{(ij)}(k) \sum_m a_m(k) e^{-\Gamma_m(k)t}, \hfill (C.25)$$

where $S_{zz}^{(ij)}(k) = k_B T \chi_{zz}^{(ij)}(k, 0)$ is the total power of the spectrum; and $a_m$ are the mode amplitudes,

$$a_m(k) = \frac{\text{Residue}[\chi_{zz}^{(ij)}(k, -i\Gamma_m)]}{\chi_{zz}^{(ij)}(k, 0)\Gamma_m}, \hfill (C.26)$$
with the total amplitudes $\sum_m a_m = 1$. The mean vertical height fluctuation correlation is then obtained as

$$\langle u^i_z u^j_z \rangle = \int \frac{d^2k}{(2\pi)^2} S^{(ij)}_{zz}(k).$$

(C.27)

When $i = j$, Eq. (C.27) is the square of the roughness $\sigma_i$. At small $q_z$ in a diffuse x-ray or neutron scattering experiment, the diffuse scattering cross section is simply a linear combination of $S^{(ij)}_{zz}(k)$ [32, 63]. Surface and interface sensitive XPCS is particularly focused on the measurement of the time-dependence of these height-height correlations, and thus provides information about the surface and interfacial fluctuation dynamics.

Because the fluctuations of the surface and the interface are coupled hydrodynamically, any of the four susceptibility elements in Eq. (C.23) contains information about the capillary wave modes, except that the mode amplitudes differ from one component to the other. For a specific bilayer system, all the modes are not necessarily apparent in the scattering experiments. The explicit analytical expressions of the bilayer susceptibilities and over-damped relaxation time constants by $\chi^{(22)}_{zz}(k, \omega)$ are derived approximately, and agree quite well with the numerical calculations\(^1\). However, the following discussions on bilayer models will be mainly based on exact numerical calculations. In a more general sense, the bilayer theory discussed above can be extended straightforwardly to the surface and interfacial dynamics of multilayer films with one boundary condition and one Navier-Stokes equation for each additional layer. Also, the environment above the top layer does not have to be vacuum or air as in the present discussions. In cases that films are submerged in other liquids, the top surface needs to be reinterpreted as an interface with an accordingly modified boundary condition taking into account the interfacial tension, environment viscosity and external pressures. Such a calculation has been performed for a bound membrane surrounded in an incompressible liquid [136].

We have derived the dynamics of capillary waves using the fluctuation dissipation theorem. An alternative approach to calculating the relaxation times of capillary waves is to assume a sinusoidally modulated surface as an initial condition and a trial time dependent solution for the surface amplitude which is an exponential relaxation. Such a method was used, for example, by Herminghaus [62]. This approach is simpler if only the relaxation times are required, but it is not obvious how to extend it to obtain more detailed information such as relative amplitudes of relaxation modes or the dynamics in situations which are not well described by a single exponential relaxation.

---

\(^1\)Codes for analytical expressions are available at http://sinhagroup.ucsd.edu/bilayer/supplement.html.
Bibliography


