Liquid Surfaces and Interfaces

Synchrotron X-ray Methods

The availability of synchrotron X-ray sources has radically transformed much of X-ray physics. Subsequent developments described in this book have led to substantial progress in our understanding of molecular ordering at liquid interfaces, with relevance to many areas of science and technology. This practical guide on the subject will enable graduate students and researchers to understand and carry out experimental investigations into the basic physical and chemical properties of liquid surfaces and interfaces.

The book examines the surfaces of bulk liquids, thin wetting films, and buried liquid/liquid interfaces. It discusses experiments on simple and complex fluids, including pure water and organic liquids, liquid crystals, liquid metals, electrified liquid/liquid interfaces, and interfacial monolayers of amphiphiles, nanoparticles, polymers, and biomolecules. A detailed description of the apparatus and techniques required for these experiments is provided, and theoretical approaches to data analysis are described, including approximate methods such as the master formula, the Born approximation, Parratt's algorithm, and the distorted-wave approximation. It is ideal for people working in physics, chemistry, biology, and materials science.

Peter S. Pershan is Frank B. Baird, Jr. Professor of Science in the Physics Department and the School of Engineering and Applied Science at Harvard University. In the early 1980s he helped produce the first synchrotron X-ray reflectometer for study of the horizontal liquid surface. He has since led the liquid surface field in exploration of such diverse liquid surfaces as superfluid helium, water, and liquid metals.

Mark L. Schlossman is a Professor in the Department of Physics at the University of Illinois at Chicago. He built an X-ray reflectometer at the NSLS that subsequently served as a prototype when he helped design the ChemMatCARS instrument featured in this book. His use of both reflectometers led to pioneering studies of the structure of liquid/liquid interfaces.

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Peter S. Pershan and Mark L. Schlossman
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To Pat Pershan whose patient and loving support made my mid-career pursuit of synchrotron experiments possible. She graciously endured over thirty years of lonely days and nights of synchrotron travel in order that this book could be written.

To Mark's wife Binhua Lin whose adventures in X-ray studies of liquid surfaces have made his own studies that much more pleasant, and to their daughter Elizabeth who endured our many dinnertime conversations on the topic.

"This modest-sized volume is a real treasure trove for researchers of liquid surfaces and interfaces. Peter Pershan, a founding father and a prime motive in the field of synchrotron X-ray studies of liquid surfaces, and Mark Schlossman, a leading expert in the field, present an admirable combination of a comprehensive, in-depth, exposition of the experimental methods and their underlying theory and data analysis approaches, with a lucid discussion of selected results obtained using these methods. The book's first part is an invaluable guide for researchers wishing to enter the field. The second part is a broad, insightful and inspiring panorama of the field's major achievements, which is a joy to read, even separately from the first part. Although the selection is, by necessity, personal, it reflects elegantly the authors' wisdom, breadth of view, and 30 years of experience. I have no doubt that this volume will find a place of honor on the bookshelves of all researchers in the field worldwide."

Moshe Deutsch, Bar-Ilan University, Israel

"Anyone interested in learning about the physical properties of liquid surfaces will appreciate this comprehensive treatise that emphasizes synchrotron X-ray scattering methods. The book provides a rigorous approach to scattering theory as well as a practical guide on how to align instruments. Pershan and Schlossman present an excellent summary of our current understanding of the structure and thermal fluctuations observed at liquid interfaces with a wide range of examples extending from simple liquids to Langmuir monolayers. There is no doubt that this will become the standard for many years."

Ben Ocko, Brookhaven National Laboratory

"The liquid state is stable in only a small domain of the space of density, pressure and temperature, yet it plays a dominant role in living and geological processes on earth, and in many manufacturing processes. And every liquid is contained by bounding materials that generate interfaces with properties that are different from those in the contacting phases. It has been realized for two centuries that those interfaces play several important roles in determining phenomena in our world. However, it is only in the last three decades that experimental methodology has advanced to the point that the relationships between the atomic/molecular structure of interfaces and interfacial properties can be studied and interpreted. Profs. Peter Pershan and Mark Schlossman, who are pioneers in the development of the modern experimental tools for the study of liquid interfaces, have written a masterful account of the uses of X-ray reflection and scattering to study liquid interfaces, and of the interpretation of the findings for many such interfaces. Their incisive treatment of the experimental methodology and the analysis of data obtained make this book a "must read" for all physicists and chemists interested in liquid interfacial phenomena. This book will serve several purposes: as an introduction to the field for graduate students, as a reference to the subtleties of interpretation of data for active users of synchrotron radiation for interface studies, and as a thought provoking survey of the many subtle properties of liquid interfaces and the differences and similarities of those properties across classes of liquids and contact media."

Stuart A. Rice, University of Chicago

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Preface

Some time around 1980 a conversation at a summer Gordon conference between one of us (P.P.) and Jens Als-Nielsen motivated Jens to conceive of a mechanism by which the horizontal X-ray beams of the newly developing synchrotron sources could be deflected downward onto the horizontal surface of a freely standing liquid. The liquid-surface scattering instrument that Jens installed at the Hasylab synchrotron in Germany was the basis for the start of a personally rewarding collaboration between these two scientists, involving multiple transatlantic flights between Boston and Hamburg. This collaboration ended only when the NSLS synchrotron was commissioned and Pershan built the first liquid-surface instrument in the United States. In the interim the collaboration carried out the first experiments to demonstrate surface-induced molecular layering (i.e. smectic order) at the surfaces of the isotropic and nematic phases of various liquid-crystal-forming materials and the first synchrotron measurements from the surface of water. Two of Pershan's collaborators at Harvard during this initial period, Ben Ocko and Moshe Deutsch, went on to become prominent leaders in this field.

Mark Schlossman came to Harvard as a postdoctoral fellow soon after the NSLS reflectometer had been commissioned. Afterwards he moved to Chicago and built a separate reflectometer at the NSLS beamline X19C, which was commissioned in 1994. The higher X-ray energies available at the X19C reflectometer allowed him to carry out a series of measurements of the buried liquid/liquid interface. This instrument then served as the prototype for the ChemMatCARS reflectometer, which was commissioned in 2002 at the third-generation X-ray synchrotron source at Argonne National Laboratory. In the nearly three decades since Als-Nielsen's first instrument the field has grown and, as shown in Table 2.1, there are now reflectometers in existence and under development throughout the United States, Europe, and Asia. In view of the fact that multiple researchers use each instrument, the community is growing continually.

The goal of this book is to make the large number of theoretical and experimental techniques that have been developed by the authors and their colleagues during nearly three decades of experiments available to the general community. These techniques have substantially altered our understanding of liquid surfaces. For example, although the basic framework of capillary wave theory that describes thermal fluctuations of liquid surfaces existed more than thirty years ago, the techniques to probe them and their influence on the surface structure did not. This has been remedied by the techniques described herein and their application to a diverse range of liquids such as water, organic solvents, superfluid ^{4}He, and high-temperature liquid metals. As another example, consider the

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experiments on monolayers of organic molecules that Irving Langmuir carried out in the early part of the twentieth century. In the absence of any way to directly probe the molecular structure of these monolayers, Langmuir's interpretations about the size and ordering of these molecules had to rely upon thermodynamic data. While his interpretations were essentially correct, there are numerous aspects of the molecular structure that were learned only from synchrotron X-ray measurements.

The scattering techniques discussed in this book revolutionized our view of molecular ordering in Langmuir monolayers and, generally, of molecular ordering at liquid surfaces and interfaces. X-ray surface scattering from liquids is now being applied to address current scientific and technological issues, such as the development of methods for the directed assembly on the nanoscale of materials with specific functionality and the understanding of interfacial processes that are important for the sustainability of our environment, among many others.

We believe that this book will serve both as a primer for students and as a guidebook for more senior researchers who are preparing to enter the field of liquid surface and interface structures. However, this book is not meant to be an introduction to X-ray physics, and the reader who requires that background may wish to consult Als-Nielsen's and McMorrow's book *Elements of Modern X-ray Physics* or another book at a similar level. The first chapter of this book, which is a general introduction to the research area of liquid surfaces and interfaces, including some comments on its history, might be of general interest to all readers. The second chapter on liquid-surface instrumentation contains both a tutorial on the basics of any liquid-surface instrument and a step-by-step guide to the procedures for aligning the instrument and for careful control of the measurements. The introduction to the second chapter (Section 2.1) describes those sections that contain details that the casual experimenter might choose to skip.

The third chapter treats the various theoretical approximations for practical quantitative interpretation of the measurements. These are particularly important since, as will be explained, the equations obtained from exact theoretical treatments are often unmanageable. Finally, the last chapter is an anthology of a number of the principal experiments that have been carried out during the past three decades. This chapter is not meant to be an exhaustive review of the field, and we hope that the reader recognizes that space and other limitations have prevented us from describing many interesting experiments. This last chapter can probably be read in isolation with only occasional reference to specific issues in the earlier chapters. In particular, the material in this chapter should give the reader some sense of the potential for future research.

The authors would also like to express their appreciation of all of their students and colleagues whose hard work made possible the research reported in this book. Aside from the three who have already been mentioned, namely Jens Als-Nielsen, Ben Ocko, and Moshe Deutsch, some of the people whose efforts made major contributions to the work described in this book include Kyle Alvine, Venkat Balagurusamy, G. Marco Bommarito, Alan Braslau, Wei Bu, Chiu-Hao Chen, Elaine DiMasi, Masa Fukuto, Oleg Gang, Alexey Grigoriev, Ralf Heilmann, Binyang Hou, Patrick Huber, Nouamane Laanait, Ming Li, Binhua Lin, Guangming Luo, Larry Lurio, Olaf Magnussen, Sarka Malkova, Stefan Mechler, Mati Meron, Dragoslav Mitrinović, Konstantin Penanen, Sai Venkatesh Pingali,

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Diego Pontoni, Tom Rabedeau, Mike Regan, Stuart A. Rice, Daniel Schwartz, Stefan Sellner, Oleg Shpyrko, Dennis Synal, Aleksey Tikhonov, Holger Tostmann, P. James Viccaro, and Eyal Yahel. The authors are grateful for the research funding provided over many years by the US National Science Foundation and the Department of Energy, which supported both their individual research groups and the operation of synchrotron facilities for the investigation of liquid surfaces and interfaces.

Finally, it is essential to recognize that the mid-career change that made all of the above possible would never have occurred without the welcome that allowed Peter Pershan to spend the 1978–1979 academic year learning the basics of X-ray physics in Bob Birgeneau's laboratory at MIT.

Tables of widely used symbols

Here we list those symbols that are widely used throughout the book. In some cases where the same symbol is used for different objects the meaning can be easily understood by noting the context in which it appears. Similarly, some symbols that are used only in one place are not listed here. Their meanings also can easily be understood from the local context.

Greek symbols

Symbol	Definition
α_c	Critical angle for total reflection
α_d	Angle measured from the horizontal plane for radiation scattered from the sample into the detector
α_i	Angle of incidence measured from the horizontal plane
$\alpha_\mathrm{i}^\mathrm{Local}$	Local angle of incidence for curved samples
$\alpha_\mathrm{i}^\mathrm{p}$	Provisional value of α_i during alignment of reflectometer
β and $\beta(z)$	Imaginary part of the index of refraction
γ	Surface or interfacial tension
γ_0	Limiting value of γ for a Langmuir monolayer as the surface surfactant concentration approaches zero
$\Gamma_\mathrm{r}(\vec{Q}_{xy}, Q_z; \vec{Q}'_{xy}, Q'_z)$	Resolution function
$\Gamma_\mathrm{r}(Q_z, \vec{Q}_{xy} - \vec{Q}'_{xy})$	Resolution function near specular reflection, $(\lvert\vec{Q}' - \vec{Q}\rvert \ll \lvert\vec{Q}\rvert)$
$\Gamma_\mathrm{r}(Q_z, \vec{r}_{xy})$	Fourier transform of the resolution function
$\delta\nu_\mathrm{s}$	Angle between the vertical and the normal to the surface at some position on a curved sample
$\delta\rho_h(\vec{r}_{xy}, z)$	Deviation of the local electron density from the locally averaged surface $\rho[z - h(\vec{r}_{xy})]$
$\delta\rho(z, \vec{r}_{xy})$	Deviation of the local electron density from the average $\langle\rho(z)\rangle$ that is used in the distorted-wave approximation
$\delta\rho^0(\vec{r}_{xy})$	Integral of $\delta\rho(z, \vec{r}_{xy})$ along the surface normal
$\delta\Phi(Q_z, \vec{r}_{xy})$	Generalization of the surface structure factor to treat inhomogeneous surfaces
$\delta\chi_{3\mathrm{c}}$	Deviation of $\chi_{3\mathrm{c}}$ from the value that leads to $\alpha_\mathrm{i} = 0$
$\delta I(Q_x, Q_z) = I(Q_{x,}0, Q_z) - I(Q_{x,}\delta Q_y, Q_z)$ or $\delta I(\alpha_\mathrm{i}, \alpha_\mathrm{d})$	Background subtracted signal

(*cont.*)

Symbol	Definition
δx	Difference between the position along the x-axis where the beam strikes the sample and the center of the sample
$\delta^2(\vec{Q}_{xy})$	Two-dimensional delta-function
$\Delta\alpha_{\mathrm{d}}^{\mathrm{res}}$, $\Delta\theta_{\mathrm{d}}^{\mathrm{res}}$, $\Delta\Omega^{\mathrm{res}}$	Angular resolution on the detector arm
$\Delta\alpha_{\mathrm{i}}^{\mathrm{Local}}$	Spread in the local angle of incidence on a curved sample due to the height of the incident beam
$\Delta\theta_{\mathrm{Darwin}}$	Darwin width
$\Delta Q_x^{\mathrm{res}}$, $\Delta Q_y^{\mathrm{res}}$	Projection of $\Delta^2\vec{Q}_{xy}^{\mathrm{res}}$ on the x- and y-axes
$\Delta Q_{xy}^{\mathrm{res}}$	Radius of the circular resolution function
$\Delta^2\vec{Q}_{xy}^{\mathrm{res}}$	Two-dimensional resolution in Q-space
$\Delta\omega_{\mathfrak{z}}$	Frequency band width of the fluctuations in the electronic polarizability
ε and $\varepsilon(z)$	Dielectric constant (relative permittivity) of bulk material or layer and its z dependence across a liquid interface
ζ and $\zeta(z)$	Real part of $1 - n$, where n is the X-ray index of refraction
$\zeta(z, \vec{k}_{xy})$	Self-consistent solution for the Fourier component of the scattered wave from an inhomogeneous surface. Result from the DWA
$\zeta_0^{\pm}(z, \vec{k}_{xy})$	Amplitude of the asymptotic solutions (i.e. at $\|z\| \to \infty$) for a plane wave incident on a flat surface. Used in the DWA
$\zeta_{\mathrm{off\text{-}spec}}(z, \vec{k}_{xy})$	Solution for $\zeta(z, \vec{k}_{xy})$ away from the specular reflection
η	Capillary exponent ($\eta = Q_z^2 k_{\mathrm{B}}T/(2\pi\gamma)$, or angle of deviation of $\vec{k}_{\mathrm{syn}}$ from the horizontal (Chapter 2 only)
$\theta(z)$	Heaviside step function
θ_{B}	Bragg angle
θ_{d}	Angle between the vertical planes containing $\vec{k}_{\mathrm{i}}(\alpha_{\mathrm{i}})$ and $\vec{k}_{\mathrm{s}}(\alpha_{\mathrm{d}}, \theta_{\mathrm{d}})$
θ_{s}	Angle of rotation about a vertical axis through the center of the sample stage
$\hat{\theta}_{\mathrm{track}}$	Unit vector defining the rotation axis of the θ_{track} circle
$2\theta_{\mathrm{track}}$	Angle between the vertical planes containing $\vec{k}_{\mathrm{syn}}$ and $\vec{k}_{\mathrm{i}}(\alpha_{\mathrm{i}})$
$\theta_{3\mathrm{c}}$	Rotation angle for the $\theta_{3\mathrm{c}}$ circle
$\Theta(\vec{Q}_{xy}, Q_z, T)$	Capillary function
κ	Ratio of the electron density of the film to that of the bulk
λ	Wavelength
Λ	Evanescent decay length for the amplitude of the electromagnetic field
μ	Chemical potential
μ_ℓ	Linear absorption coefficient
ξ	Atomic-scale correlation length
ξ_Φ	Coherence length for the surface structure factor of inhomogeneous surfaces
ξ_{c}	Critical correlation length
ξ_{g}	Capillary length at the interface between two bulk phases
$\xi_{\mathrm{vdW}}(w)$	Capillary length due to van der Waals forces within a thin film of thickness w
ξ_{X}	X-ray coherence length
$\xi_{\mathrm{t,X}}$	X-ray coherence length transverse to the beam direction

Symbol	Definition
ξ_{2D}	Two-dimensional correlation length for nanoparticles and other multi-molecule objects on a liquid surface
$\xi_{\parallel}, \xi_{\perp}$	Parallel and perpendicular correlation lengths for nematic and smectic liquid crystals
Π	Surface pressure
$\rho(z)$	Intrinsic electron-density profile
$\langle\rho(z)\rangle$	Electron-density profile averaged over a macroscopic region of the interface
ρ_∞	Electron density in the bulk phase
ρ_{m}	Mass density
ρ_{vap}	Electron density in the vapor above the liquid surface
σ	Root-mean-square width of an interface due to the combination of the intrinsic and capillary widths
$\bar{\sigma}$	$\sigma_j^2 = \sigma_0^2 + j\,\bar{\sigma}^2$, where $j = 0, 1, 2, \ldots$ in the distorted-crystal model
σ_{ab}	Same as σ except that for a thin film there can be three or more different values, i.e. $ab = \{11, 22 \text{ and } 12\}$
σ_{cap}	Root-mean-square average, over an appropriate length scale, of interfacial height fluctuations due to thermal capillary waves
$\sigma_{\mathrm{cap,macro}}$	Root-mean-square average, over a macroscopic length scale, of interfacial height fluctuations due to thermal capillary waves
σ_{int}	Intrinsic width of locally averaged surface
σ_j	Gaussian width of the jth layer in the distorted-crystal model
σ_{sub}	Roughness of a solid surface (substrate) that supports a thin liquid film
$\vec{\tau}$	Reciprocal-lattice vector of the steering crystal
$\vec{\tau}(\alpha_{\mathrm{i}})$	Reciprocal-lattice vector of the steering crystal when tilted to produce an X-ray beam with angle of incidence α_{i}
$\tau_0 = \lvert\vec{\tau}\rvert$	Magnitude of the reciprocal-lattice vector of the steering crystal
$\Upsilon(z)$	Operator for wave equation that is used to develop the DWA
$\Upsilon_k(z)$	Two-dimensional Fourier transform of $\Upsilon(z)$
ϕ_{3c}	Rotation angle for the ϕ_{3c} circle
φ_x and φ_z	Angles by which the atomic planes of the steering crystal deviate from the plane of the surface of its face (also known as the miscut)
$\phi_0(z, \vec{r}_{xy})$	The zeroth-order approximation for the amplitude of the general solution to the DWA for a homogeneous surface
$\phi(\vec{r}_{xy})$ and $\phi(Q_{xy})$	Spatial correlation and its Fourier transform for domains on a liquid surface
$\Phi(Q_z)$	Intrinsic surface structure factor
$\Phi_{\mathrm{eff}}(Q_z)$	Effective surface structure factor
$\Phi_{\mathrm{eff}}(\vec{Q}_{xy}, Q_z)$	$\lvert\Phi_{\mathrm{eff}}(Q_z)\rvert^2 S^0_{\chi_1,\chi_1}(\vec{Q}_{xy})$
$\chi(\omega)$ and $\chi(\omega_3; \omega_2, \omega_1)$	Linear and non-linear optical response of a material
χ_{f}	Reduced electron density for a film separating vacuum from a material of bulk electron density χ_∞
$\chi_0(z)$	Reduced electron-density profile as used for the DWA
$\chi_1(z, \vec{r}_{xy})$	Deviation between the local value of the reduced electron density and the average density, as used for the DWA
$\chi_1^0(\vec{r}_{xy})$	Integration of $\chi_1(z, \vec{r}_{xy})$ along the z-axis

(*cont.*)

Symbol	Definition
χ_{3c}	Rotation angle for the χ_{3c} circle that tilts the steering crystal
χ_{3c}^0	The value of χ_{3c} that brings $\vec{k}_i(\alpha_i)$ to the horizontal on aligning with a *bt* stage
χ_∞	Bulk value of the reduced electron density as used in the DWA; $\chi_\infty = \lim_{z\to-\infty}[\chi_0(z)]$
ω	Angular frequency (optical or X-ray)
ϖ	Van der Waals molecular interaction parameter
Ω	Solid angle

Roman symbols

Symbol	Definition
a	A measure of the atomic/molecular size diameter, the nearest-neighbor distance or the unit-cell parameter
$a(w)$	Van der Waals interaction parameter that couples height fluctuations on the top and bottom interfaces of a thin film
$a_\perp$	Nearest-neighbor distance between long alkane chains perpendicular to the chain axis
A	Area of the liquid surface
$A_\xi \sim \xi^2$	Two-dimensional area of the order of the square of the bulk correlation length ξ
A_0	Cross-sectional area of the X-ray beam
A_f	Surface area illuminated by the X-ray beam, i.e. the X-ray footprint
$A_{q_{xy}}$	Area in reciprocal space per surface mode
A_x	Area per molecule in a Langmuir monolayer as obtained from GID
A_A	Surface area per liquid atom (or molecule)
A_LT	Area of Langmuir trough accessible to amphiphiles
$b,\ b_\perp$	Unit-cell parameter and unit-cell parameter perpendicular to the chain axis
$b_\mathrm{h}, b_\mathrm{w}$	Height and width of the X-ray beam
$b_\mathrm{w,s}(\theta_\mathrm{d})$	Effective width of X-ray footprint on the liquid surface as viewed from angle θ_d away from the plane of incidence
bh	Vertical translation of the steering goniometer base (see Table 2.2)
bt	Base tilt angle
by	Horizontal *y*-translation of steering goniometer base
$C(\vec{r}_{xy})$	Local radius of curvature of the sample surface at position $\vec{r}_{xy}$
d	Layer thickness
$\frac{d\sigma}{d\Omega}, \frac{d\sigma}{d^2\vec{Q}_{xy}}$	Differential scattering cross section

Symbol	Definition
D	Diameter of nanoparticle
$\mathbf{E}$	Time-independent amplitude of the sum of the incident, reflected, and transmitted X-ray electric-field vectors as used in the Parratt discussion
$\vec{E}(\vec{r})$, $\vec{E}^{\mathrm{i}}(\vec{r})$, $\vec{E}^{\mathrm{s}}(\vec{r})$, $\vec{E}^{\mathrm{t}}(\vec{r})$	X-ray electric field vector (incident, scattered, transmitted beams) when fluctuations are neglected
$E_j^-(z)$, $E_j^+(z)$	Amplitude of electric field in layer j that propagates away from (−) or towards (+) the upper phase, as used in the Parratt method
$\mathcal{E}_0(t)$ and $\mathcal{E}_{\mathrm{S}}(t)$	Complex time-dependent fluctuating incident and scattered X-ray electric field
f', f''	Real and imaginary parts of the anomalous dispersion correction to the atomic scattering factor
$\mathcal{F}(w)$	Van der Waals energy per unit area for a thin film as a function of the film thickness w
$\mathcal{F}_{\mathrm{S}}(w)$	Surface free energy density for a wetting film
$g(\vec{r}_{xy}) = S_{\mathrm{hh}}(0) - S_{\mathrm{hh}}(\vec{r}_{xy})$	Height–height correlation function
$g_{ij}(\vec{r}_{xy})$	Height–height correlation function for two interfaces, $\{i, j\} = (11), (12), (22)$
$G(z, z' : \vec{k}_{xy})$	Green's function for the DWA solution to an inhomogeneous surface
h_{i}	Opening height of slit i
$h(\vec{r}_{xy})$ and $h(\vec{q}_{xy})$	Height and Fourier transform of a locally averaged surface
$h_{\mathrm{sub}}(\vec{q}_{xy})$	Fourier transform of the rigid height variations for a solid surface
$H(\vec{r}_{xy}, Q_z)$ and $H(\vec{Q}_{xy}, Q_z)$	Exponential of the height–height correlation function and its Fourier transform
$H_2(\vec{Q}_{xy}, Q_z)$	$H(\vec{Q}_{xy}, Q_z)$ for two surfaces
$H_{\mathrm{EE}}(\vec{Q}_{xy}, Q_z)$	Electric field correlation function
ih, ir	Translation and rotation of input arm (input height and input rotation)
$\mathbf{I}_{j-1,j}$	Interface matrix used in the Parratt method
$I(\vec{Q}_{xy}, Q_z)$	Scattered intensity
$I(t)$	Time-dependent intensity of the X-ray field
$I_0(\alpha_{\mathrm{i}})$ or I_0	Intensity incident on the sample (at angle of incidence α_{i})
k_0	Amplitude of X-ray wave vector
$\vec{k}_{\mathrm{i}}$ (or $\vec{k}_{\mathrm{i}}(\alpha_{\mathrm{i}})$), $\vec{k}_{\mathrm{s}}$, $\vec{k}_{\mathrm{t}}$	Incident, scattered, and transmitted wave vectors
$k_{\mathrm{f},z}$, $k_{\mathrm{b},z}$	z-components of wave vectors (internal and below a thin film)
$\vec{k}_{\mathrm{syn}}$	Wave vector from the synchrotron
$\Bbbk$	Bending rigidity of liquid surface
$l,\ L$	Various lengths
ℓ	Molecular chain length
ℓ_{abs}	X-ray absorption (decay) length
my	Transverse displacement of the steering crystal
$\mathbf{M}$ or M_{ij}	Matrix product as used in the Parratt method
n and $n(z)$	X-ray index of refraction of bulk material and at position z along the surface normal
n_{liq} and n_{vap}	Number density of liquid and vapor phases

(cont.)

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Symbol	Definition
n_{A}	Surface number density of surfactant molecules
$\hat{n}$	Director (direction of molecular alignment in nematic liquid crystals)
N_{A}	Number of capillary surface modes per unit area or number of molecules in a Langmuir monolayer
oh, or	Vertical translation and rotations for the sample arm (output height and output rotation)
$P(s)$	Interfacial Patterson function
$P^{\mathrm{M}}(s)$	Modified interfacial Patterson function (filtered to include the effects of the finite range of data)
$\mathbf{P}_j$	Propagation matrix used in the Parratt method
$\mathcal{P}$	Optical-frequency polarization density in response to $\mathcal{E}$
$\vec{q}$	Wave vector
$q_{\mathscr{k}}$	Elastic wave number due to surface rigidity
q_{g}	Inverse capillary length due to gravity
$q_{\text{in-plane}}$	Wave vector for in-plane periodicity of 2D surface order
$q_{\max}$	Maximum allowed wave-vector amplitude for capillary waves, analogous to the Debye cutoff wave vector for phonons in crystals
$\vec{q}_{xy}$	Capillary wave vector
$q_{\mathrm{vdW}}(w)$	Van der Waals cutoff for short-wavelength capillary waves in a thin film of thickness w
$\vec{Q}$	Wave-vector transfer for scattered radiation
Q_{c}	Critical wave vector transfer for total reflection
$\vec{Q}_{xy}$	Projection of $\vec{Q}$ onto the plane of the surface
$r(\alpha_{\mathrm{i}})$ or $r(\vec{k}_{xy})$	Reflection coefficient for a flat surface
$r(0f)$, $t(0f)$, $r(fb)$, $t(fb)$	Reflection coefficients needed to describe the reflectivity from a thin film
r_{e}	Classical radius of the electron ($\approx 2.818 \times 10^{-15}$ m)
r_{i}	Amplitude of reflection from a thin film
$\vec{r}_{xy}$	Position vector in the plane of the surface
r_{A}	Atomic or molecular radius
$R(Q_z)$ and $R(\alpha_{\mathrm{i}})$	Reflection amplitude
$R(Q_z, \hbar\omega)$	Energy-dependent reflection amplitude
$R_{\mathrm{F}}(Q_z)$ and $R_{\mathrm{F}}(\alpha_{\mathrm{i}})$	Fresnel reflectivity
$R^{\mathrm{BS}}(Q_z)$	Background-subtracted reflectivity
sh	Sample height
sy	y-translation of sample stage
$S_{\chi_1,\chi_1}(z', z'' : \vec{k}_{s,xy} - \vec{k}_{i,xy})$	Spectral density for the reduced form of the surface inhomogeneity $\chi_1(z, \vec{r}_{xy})$
$S^0_{\chi_1,\chi_1}(\vec{k}_{xy})$	Spectral density of the reduced form of $\chi_1^0(\vec{r}_{xy}) \sim \delta\rho^0(\vec{r}_{xy})$
$S_{\mathrm{hh}}(\vec{r}_{xy})$ and $S_{\mathrm{hh}}(\vec{q}_{xy})$	Spectral density and correlation function for height fluctuations
S_{s}, S_{b}	entropy per molecule of the surface and bulk phases
$S^{\mathrm{ex}}_{\mathrm{A}}$	Excess entropy per molecule at the surface relative to the bulk
$S_{\mathrm{EE}}(\vec{r}_{\mathrm{t}})$, $S_{\mathrm{EE}}(\vec{r}_{xy})$	Electric-field correlation function in the plane transverse to the X-ray wave vector ($S_{\mathrm{EE}}(\vec{r}_{\mathrm{t}})$) and in the plane of the surface ($S_{\mathrm{EE}}(\vec{r}_{xy})$)

Symbol	Definition
S_1, S_2, S_3	Slits
$t(\alpha_\mathrm{i})$ and $t(\vec{k}_{xy})$	Transmission coefficient for a flat surface
t_i	Amplitude of transmission through a thin film
u	The energy per unit area associated with fluctuations in height of liquid surfaces
u_g	Gravitational energy density per unit area associated with thermal height fluctuations
u_st	Surface tension energy density per unit area associated with thermal height fluctuations
V_SS and V_eff	Hamaker constants
w	Film thickness
w_i	Opening width of slit i
W	Debye–Waller factor, defined here as $2W = Q_z^2\sigma_\mathrm{cap}^2$
$W(\vec{k}_{xy})$	Wronskian used in the DWA
$\mathcal{W}$	Van der Waals interaction
$\mathcal{W}_{ST}$	Short-range contribution to the substrate–liquid interaction energy
$\hat{x}, \hat{y}, \hat{z}$	Unit coordinate vectors in the reference frame with $\hat{y} \cdot \vec{k}_\mathrm{i}(\alpha_\mathrm{i}) = 0$
$x_\mathrm{s}, y_\mathrm{s}, z_\mathrm{s}$	Displacements of sample stage
$\hat{x}_\mathrm{syn}, \hat{y}_\mathrm{syn}, \hat{z}_\mathrm{syn}$	Unit coordinate vectors in the synchrotron reference frame with $\hat{y}_\mathrm{syn} \cdot \vec{k}_\mathrm{syn} = 0$
yt	y-translation of the reflectometer
$Y(Q_z)$	Filter function that accounts for the finite range of data when evaluating the Patterson function
$\mathfrak{z}(t)$	Fluctuating electric polarizability
$\mathcal{Z}(\vec{q}_{xy}, w)$	Response function of the free surface to roughness at the liquid/solid interface

Special formatting

Symbol	Definition
$(\mathcal{T})^\mathrm{p}$	Provisional value for a variable, $\mathcal{T} = \alpha_\mathrm{i}, sh, \chi_{3\mathrm{c}}$, etc., at an early stage in the alignment
$(\mathcal{T})_\mathrm{nom}$	Nominal value of a reflectometer variable, $\mathcal{T} = \alpha_\mathrm{i}, sh, \chi_{3\mathrm{c}}$, etc., as calculated by the software code of the reflectometer
$\#C$	Number of chemical components for a thermodynamic system
$\#F$	Number of degrees of freedom for a thermodynamic system
$\#P_\mathrm{S}, \#P_\mathrm{B}$	Numbers of surface and bulk phases for a thermodynamic system
$\#\delta P_\mathrm{S}$	Difference between the number of thermodynamic interface phases and the number of distinct interfaces
$\#S$	Number of distinct interfaces for a thermodynamic system

Abbreviations

Symbol	Definition
1D, 2D, 3D	One-dimensional, two-dimensional, three-dimensional
APS	Advanced Photon Source
DCM	Distorted-crystal model
DWA	Distorted-wave approximation
erf	Error function
GID	Grazing-incidence diffraction
LM	Langmuir monolayer
MCA	Multi-channel analyzer
NN	Nearest neighbors in a 2D lattice
NNN	Next-nearest neighbors in a 2D lattice
PSD (1D, 2D)	Position-sensitive detector (1D line detector, 2D area detector)
SCA	Single-channel analyzer
UHV	Ultra-high vacuum