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Peter S. Pershan and Mark L. Schlossman
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1 Introduction

The physical properties of liquid surfaces have been an area of scientific interest for the past two centuries and more. In the early nineteenth century the study of capillarity, as exemplified by the study of the rise of liquids either in a small-bore capillary tube or between glass plates, proved important in the pursuit of a general scientific understanding of particle interactions that could not be explained by Newton's theory of gravity (Rowlinson, 2002). In the early development of the mathematical theory of capillarity, in particular by Laplace, it was assumed that the surface of a liquid was without structure and could be treated as an abrupt boundary between liquid and vapor (Laplace, 1807). Although Poisson objected to the assumption of an abrupt interface on fundamental grounds, it was not until the late nineteenth century that van der Waals developed a theory of surface tension that relied upon a diffuse interface (van der Waals, 1893, van der Waals, 1979). This statistical-mechanical theory proved important for the general understanding of non-uniform systems. Also in the late nineteenth century Pockels and Lord Rayleigh noted that measurements of the surface tension of a film of olive oil on water allowed them to deduce that its thickness was about 1 nm, thus setting the size of a molecule of olive oil and enabling deductions of the spatial extent of intermolecular forces of attraction between water and oil (Pockels, 1891, Pockels, 1892, Rayleigh, 1899). Further experiments on molecular films by Langmuir (Langmuir, 1917) allowed observations on the size and shapes of molecules, long before the modern investigative methods of the later twentieth century confirmed them.

Advances in our understanding of all aspects of condensed matter during the twentieth century have taken advantage of contributions over a broad front of parallel research. This becomes obvious on even the most superficial observation of the symbiotic relationship between theoretical developments in areas such as quantum mechanics and statistical physics and the parallel experimental discoveries. This is an ongoing process since the tools that enable new discoveries are continually evolving. Furthermore, recent decades have witnessed major advances in technology that in turn made possible even newer experimental tools that facilitated advances in directions that had previously been impossible. The field of the structure of liquid surfaces, which is the theme of this book, has been one of the beneficiaries of these developments. During this period synchrotron X-ray sources became available and the reliance of X-ray investigations of liquid surfaces on the development of these sources will be explained below (Section 1.7). Although neutron methods share many of the advantages of X-ray techniques, including the added advantage of element-specificity as a result of isotopic substitution, the significantly

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higher incident flux and smaller beam size of synchrotron X-ray sources gives X-rays a decided advantage in many investigations (Thomas, 2004, Schlossman, 2002). Optical methods that can be applied to liquid surfaces have also proven important and will be briefly described in Section 1.6. The combination of X-ray and optical methods has led to a fundamentally new understanding of the structure and chemistry of liquid interfaces.

The principal property that makes X-ray studies of most liquid surfaces different from studies of solid surfaces is that they are horizontal, such as the free surface of water in a wide dish. Similarly, oil and water poured into a wide dish will phase separate and form a mostly horizontal liquid/liquid interface. Since the physics of X-ray scattering generally requires a variable angle of incidence, the study of liquid surfaces with this technique required the development of a mechanism to steer the nominally horizontal synchrotron beam downward. This is in contrast to the study of solids, for which the variable angle of incidence for studying the surface is achieved by reorienting the solid.

The physical systems to be addressed can naturally be separated into three different categories. The first is the interface between bulk liquids and vapor, which is commonly referred to as the free surface. As has just been mentioned, the existing instrumentation for X-ray scattering from solid surfaces could not be applied to the study of free liquid surfaces and new instrumentation needed to be developed. The second category of systems consists of thin liquid films that separate two bulk phases. In this category, the simplest system is a thin wetting layer that coats a solid surface to form a film between bulk solid and vapor. Strictly speaking, some of the wetting-layer phenomena to be discussed below are not really surface problems since the liquid wetting layer can often be described as a thin layer of a bulk liquid; however, it is probably best to discuss these distinctions in the context of experimental studies, as is done in Chapters 3 and 4. The third category consists of buried interfaces, either between two bulk liquids or between a solid surface and a bulk liquid. The liquid/liquid interface can also be studied with the instrumentation developed for free surfaces. The progress in this area of study has been delayed compared with that in the study of free surfaces as a result of technical challenges that will be discussed in Chapters 2 and 4. Similar technical complications needed to be addressed for studies of the buried solid/liquid interface. In principle this interface can take on any orientation and in many, but not all, circumstances the X-ray instrumentation that has been available for the surfaces of bulk solids can be directly applied.

The remainder of this chapter contains an introduction to the principal features of liquid surfaces and to the X-ray and other experimental methods that have been used to study them. Section 1.7 contains a description of those aspects of X-ray scattering from surfaces that must be understood in order to appreciate the motivation behind the specific instrumentation described in Chapter 2 which has been developed for studying liquid surfaces. The material in Chapter 2 addresses both the physical nature of the instrumentation and the practical procedures that are required both for alignment and for measurement. There are sections dealing with details of spectrometer alignment that are necessary only for specialists, such as beam-line personnel. These can be skipped

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without sacrificing any understanding of the subsequent material in Chapters 3 and 4. Most of Chapter 2 addresses synchrotron instrumentation; however, some mention is made of apparatus developed for laboratory sources.

Although the general theory of X-ray scattering was developed relatively early in the twentieth century, a complete theory of surface scattering is unnecessarily cumbersome for interpretation of experiments. In particular, a number of fruitful approximations can simplify the interpretation of experimental results. These will be discussed in Chapter 3. Chapter 4 contains a discussion of experiments on liquid surfaces and interfaces that have been carried out in recent years. Nearly all of them became possible only as a result of the development of the synchrotron instrumentation. Our hope is that the examples in Chapter 4 will help the reader to envisage possibilities for future research.

1.1 The intrinsic liquid/vapor interface

One of the first features of liquid surfaces that historically attracted serious scientific interest was the shape of the meniscus that forms at liquid/vapor interfaces. The concept of surface tension that is most critical to understanding this was introduced by Young in a seminal paper over 200 years ago (Young *et al.*, 1855, Young, 1805) and for the nearly two centuries since this has been one of the few physical quantities that could be measured experimentally. Although the atomic or molecular nature of matter was already recognized in the early nineteenth century and although people did try to explain the measured surface tensions in terms of atomic effects, the early attempts were handicapped by the general unawareness of the importance of statistical effects. For example, Rayleigh estimated the surface tension by considering how the attractive interactions between constituent particles of a body would raise the energy when a single body is broken into two halves. As we now know, there are entropic as well as energetic contributions to the surface tension and Rayleigh's approach, as well as other contemporaneous approaches, could at best account for only the energetic contribution. A second problem with these earliest efforts to understand the properties of the interface is that they neglected the idea that the transition between the liquid and vapor phases occurred over a finite distance. Young had recognized this in 1816, but he neglected the effect and it remained for Poisson to replace the idea of the interface as a step function by a continuous function with a finite interfacial width (Rowlinson and Widom, 1982). These two ideas, the surface tension, or the free energy of the surface, and the atomic/molecular nature of the spatial transition, or interfacial profile, between the liquid and vapor phases remain to this day among the principal scientific issues regarding liquid surfaces. On the other hand, since reliable calculation of the surface tension ultimately depends upon knowing the atomic/molecular nature of the transition between the liquid and vapor, one might argue that the central issue is knowledge of the structure of the interfacial profile.

The principal modern theoretical approaches to understanding the liquid/vapor interfacial profile are density-functional methods and molecular-dynamics simulations. Most of the details of these methods are well beyond the scope of this book and readers are

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referred to any one of a number of excellent reviews (Leach, 2001, Rowlinson and Widom, 1982, Croxton, 1980, Percus, 1982, Croxton, 1986, Hansen and McDonald, 1986, Percus, 1988, Evans, 1990, Davis, 1995, Benjamin, 1997). There is, however, one issue common to both of these approaches that needs discussion.

For example, in the case of molecular-dynamics simulations there are practical limits to the number of particles that current computers can include in a simulation. An unfortunate consequence of this is that many computer simulations do not include the effects of long-wavelength thermally excited fluctuations of the position of the interface, although they are intrinsic to all real liquid surfaces and interfaces (Buff *et al.*, 1965, Lovett *et al.*, 1976, Chacon *et al.*, 2006, Chacon and Tarazona, 2005, Tarazona and Chacon, 2004, Tarazona *et al.*, 2002, Soler *et al.*, 2001). These fluctuations, referred to as capillary fluctuations or capillary waves, are discussed in the following section, and the effects can be incorporated into simulations (Bresme *et al.*, 2008, Chacon *et al.*, 2006, Sedlmeier *et al.*, 2009). In spite of the frequent omission of these long-wavelength fluctuations, simulations determine what are thought to be reasonably accurate representations for what is commonly referred to as the local or intrinsic interfacial profile. Similarly, density-functional theories that do not include the effects of capillary fluctuations also produce what are believed to be reasonably accurate representations of the intrinsic liquid/vapor interfacial profile (Curtin, 1987, Kyrlidis and Brown, 1995, Laird and Haymet, 1992, Tsuyumoto *et al.*, 1998). The problem, which will be explained below, is that if one simply seeks to know the average interfacial profile for a real liquid surface the effect of the macroscopically long-wavelength capillary waves would be to smear the resultant average beyond values that are relevant to the microscopic physics that governs the surface tension. The key issue that needs to be addressed in discussing liquid surfaces is the development of a logical procedure for understanding how these two effects are related. A second issue is understanding how the interactions that govern the properties of a bulk liquid relate to both the surface tension and the intrinsic interfacial profile (Rowlinson and Widom, 1982, Percus and Williams, 1986, Dietrich and Haase, 1995).

One way to think about the interface is to consider a *snapshot of* a molecular model of a free liquid surface at some instant of time. One can define a *local density profile*

$$\langle \rho(\vec{r}_{xy}, z)\rangle_\xi \equiv \frac{1}{A_\xi}\int d^2\vec{r}\,'_{xy}\ \rho(\vec{r}_{xy} - \vec{r}\,'_{xy}, z) = \rho[z - h(\vec{r}_{xy})] \tag{1.1}$$

at a position $\vec{r}_{xy}$ that describes the short-distance *average* of the density over an area $A_\xi \sim \xi^2$ of the order of the square of an atomic-scale correlation length ξ parallel to the surface. For all practical purposes ξ is the same as the bulk correlation length. A *short-distance average* is needed because the granular molecular nature of the surface results in a finite *intrinsic width* σ_{int} for the transition from the value of the density in the bulk of the liquid to that in the vapor. Although we will see that the atomic length scale ξ over which the average is taken is somewhat arbitrary, we will argue below that the physical properties of interest are relatively insensitive to its precise value. Throughout this book we will refer to $\rho[z - h(\vec{r}_{xy})]$ as the *intrinsic profile* relative to a value $h(\vec{r}_{xy})$ that defines a characteristic height along the surface normal, see Fig. 1.1 (Buff *et al.*, 1965,

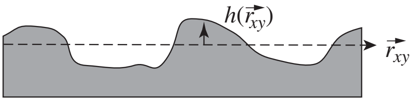

Fig. 1.1 Illustration of the surface height function $h(\vec{r}_{xy})$. This function is defined such that $\langle h(\vec{r}_{xy})\rangle = 0$.

Lovett *et al*., 1976). For a relatively simple interface $h(\vec{r}_{xy})$ might be taken as the Gibbs dividing surface that has been the staple of liquid-surface discussions for many years (Adamson and Gast, 1997); however, in principle it can be defined relative to any particular characteristic feature such as, for example, the position where the value of $\rho[z - h(\vec{r}_{xy})]$ is equal to the mean of the electron densities of the bulk phases on either side of the interface.

Before proceeding further it is important to recognize that when speaking about "density" one needs to be clear about whether one is referring to atomic number density, mass density, electron density, or some other density. The density that is commonly employed for computer simulations of liquids is the atomic number density. However, it is obvious that if one does simulations of liquids of asymmetric molecules, such as water, the local mass or electron density depends not only on the molecular centroid but also on the molecular orientation. Again this is one reason for the *average*. While the theoretical description of such a surface might not be intractable, the methods for experimentally sorting out these subtle differences are not trivial. In addition the experimenter has the complementary problem of determining how to relate measured quantities to the different densities. We will show below that X-rays directly probe the electron density of interfaces and unless otherwise stated explicitly we will reserve the word "density" to denote electron density. In general the atomic number density that is often the most convenient for molecular simulations can easily be related to the electron density.

The most important difference between liquid and solid surfaces is the effect that long-wavelength thermal fluctuations, or capillary waves, have on the location of the local profile, $h(\vec{r}_{xy})$. More will be said about capillary waves in Section 1.3. In view of the fact that the length scales for these capillary fluctuations, ξ_g, are considerably larger than the atomic length scales ξ that are employed in defining the intrinsic profiles $\rho[z - h(\vec{r}_{xy})]$ capillary waves have only a minor effect on $\rho[z - h(\vec{r}_{xy})]$. Typically ξ is of the order of at most several atomic diameters, while the capillary length scales ξ_g extend to millimeter lengths. Consequently, all of the microscopic fluctuations that are important for determination of the intrinsic profile, and related quantities such as the surface tension, occur on length scales that are considerably smaller than the capillary length scales. The fact that capillary effects are not completely negligible will be considered next.

A representation of the macroscopic average electron density profile $\langle\rho(z)\rangle$ for an area larger than $\sim\xi^2$ is obtained by averaging $\rho[z - h(\vec{r}_{xy})]$ over the ensemble distribution of $\{h(\vec{r}_{xy})\}$. Assuming that capillary fluctuations can be described by Gaussian statistics, $\langle\rho(z)\rangle$ can be approximated by the convolution of the intrinsic profile $\rho[z - h(\vec{r}_{xy})]$ with

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a Gaussian distribution that depends on the mean square average, over some length that will be elaborated below, of the long-wavelength contributions to $\langle h^2(\vec{r}_{xy})\rangle$,

$$\langle\rho(z)\rangle = \int dh(\vec{r}_{xy})\rho[z - h(\vec{r}_{xy})]\left\{\frac{1}{\sqrt{2\pi\sigma_{\text{cap}}^2}}\exp\left[-[\delta h(\vec{r}_{xy})]^2/\left(2\sigma_{\text{cap}}^2\right)\right]\right\}, \tag{1.2}$$

where

$$\sigma_{\text{cap}}^2 = \langle[\delta h(\vec{r}_{xy})]^2\rangle = \langle[h(\vec{r}_{xy}) - \langle h(\vec{r}_{xy})\rangle]^2\rangle = \langle h^2(\vec{r}_{xy})\rangle - \langle h(\vec{r}_{xy})\rangle^2. \tag{1.3}$$

The notation is simplified by defining the height function such that $\langle h(\vec{r}_{xy})\rangle = 0$, allowing $\sigma_{\text{cap}}^2 \to \langle h^2(\vec{r}_{xy})\rangle$, as illustrated in Fig. 1.1. There are two issues that need to be addressed in connection with this. The first is that of how to define the proper way to experimentally distinguish between the macroscopic profile $\langle\rho(z)\rangle$ and the intrinsic profile $\rho[z - h(\vec{r}_{xy})]$. This is ubiquitous both for liquid and for solid surfaces; however, in Section 1.3 we will demonstrate that liquid surfaces present a problem that does not occur for solids.

For example, the simplest type of interface has $\langle\rho(z)\rangle$ as a monotonic function of z that progresses from zero, or nearly zero, in the vapor far above the liquid/vapor interface to the bulk density ρ_∞ on the liquid side of the interface. This type of interface might be represented by a model of the form

$$\langle\rho(z)\rangle = (\rho_\infty/2)(1 + \text{erf}[-z/(\sigma\sqrt{2})]), \tag{1.4}$$

where erf stands for the error function (Mathews and Walker, 1970), σ describes the width of the interface, and

$$d\langle\rho(z)\rangle/dz = (\rho_\infty/(\sigma\sqrt{2\pi}))\exp[-z^2/(2\sigma^2)]. \tag{1.5}$$

If the intrinsic profile also has a similar Gaussian shape with an *intrinsic* width σ_{int} the convolution in Eq. (1.2) between the intrinsic profile and the effect of capillary fluctuations produces a total interfacial width of

$$\sigma^2 = \sigma_{\text{int}}^2 + \sigma_{\text{cap}}^2. \tag{1.6}$$

The problem with liquid surfaces that will be explained in Section 1.3 is that the value of σ_{cap}^2 increases logarithmically with the size of the area over which the capillary fluctuations are averaged. We will show below that when σ_{cap}^2 is properly defined the profile given by Eq. (1.4) with the width in Eq. (1.6) is a very good representation of the experimentally measured surface of water and a number of other interfaces. On the other hand, there are different interfaces for which this profile is not adequate.

To summarize, within this book we will treat the liquid surface, and all interfaces, in terms of an *intrinsic density profile* $\rho[z - h(\vec{r}_{xy})]$ that represents a local average over a surface area that is large enough to yield a well-defined profile but still small enough that the effects of long-wavelength capillary fluctuations can be neglected. The statistical properties of $h(\vec{r}_{xy})$ and its correlation functions will be governed by capillary fluctuations.

1.2 Surface-induced order

1.2.1 Surface layering

Density-functional theory and molecular-dynamics simulations predict that well-defined atomic layers will form at the interface between an atomic liquid and an atomically flat solid surface. At this interface $\rho(z)$ has the form of decaying oscillations with a period that is close to the atomic size. The length scale for the decay is typically of the order of the bulk-liquid correlation length (Curtin, 1987, Kyrlidis and Brown, 1995, Laird and Haymet, 1992, Tsuyumoto *et al.*, 1998). Although oscillations in the bulk structure factor are ubiquitous for nearly all liquids, this is not usually sufficient to induce atomic layering at the free surface of simple liquids such as H_2O (Sedlmeier *et al.*, 2009, McCoustra, 2008) and rare gases (Chapela *et al.*, 1977) because, as demonstrated by computer simulations, the atomic-scale randomness in the atomic positions at the liquid free surface smears out oscillations in the structure factor. The implication is that the intrinsic width of the surface must be sufficiently narrow in order to induce surface layering (Soler *et al.*, 2001). Of course "narrow" is a relative term and it is not surprising that layering will appear at the surfaces of more complex systems such as liquid crystals for which molecular lengths exceeding 20 Å are large compared with the intrinsic width of the surface (Pershan, 1989, Pershan, 1988, Pershan, 1987, Pershan and Als-Nielsen, 1984, Swislow *et al.*, 1991). Similar layering is also found in microemulsions (Zhou *et al.*, 1992). It is surprising that layering is predicted and observed at the free surfaces of liquid metals (Rice, 1987, D'Evelyn and Rice, 1983a, D'Evelyn and Rice, 1983b, Regan *et al.*, 1996, Magnussen *et al.*, 1995). According to Rice the fact that a bulk liquid metal exists as a coexisting Fermi liquid of conduction electrons and an atomic liquid of positive ions has a profound effect on the local surface structure. Atoms escape the surface to the vapor only as neutral atoms; therefore, atom–atom interactions at the surface and in the bulk liquid are dramatically different. On one side of the surface the interactions are metallic and on the other side, in the vapor, they are van der Waals. Rice argued that the effect of this is that short-length-scale fluctuations in surface positions of individual atoms are partially suppressed and on this local scale the intrinsic interfacial width is sufficiently narrow to induce layering.

1.2.2 In-plane surface order

Some of the earliest X-ray experiments on liquid surfaces were motivated by a desire to understand the nature of phase transitions that had been detected in Langmuir monolayers on the surface of water (Dutta *et al.*, 1987, Grayer-Wolf *et al.*, 1987,

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Helm *et al.*, 1987, Kjær *et al.*, 1987, Kaganer *et al.*, 1999). Langmuir monolayers are commonly formed from insoluble amphiphilic molecules such as lipids that contain a hydrophilic part (usually polar) and a hydrophobic part (typically alkyl chains). These competing interactions lead to molecular segregation at the water/vapor interface. Insoluble monolayers have been studied extensively using a Langmuir trough in which the surface tension γ can be measured as a function of the macroscopic area of the trough, A_{LT}, which is accessible to the amphiphiles. In view of the insoluble nature of the amphiphiles, the surface tension γ from this type of measurement is basically synonymous with the two-dimensional (2D) surface pressure $\Pi = \gamma_0 - \gamma$, where γ_0 is the tension of the bare interface (Adamson and Gast, 1997). Measurements of such Π–A_{LT} isotherms are similar to the traditional pressure–volume isotherms by which means the early phase properties of three-dimensional (3D) phases were first studied. The literature for much of the twentieth century contains many reports of phase transitions in Langmuir monolayers. Unfortunately, in the absence of X-ray measurements the microscopic nature of these transitions was largely not understood.

The development in the mid 1970s of synchrotron X-ray facilities that produced X-ray beams of high intensity, small size, and very small angular divergence provided a major new tool for the study of 2D phase transitions on solid surfaces (Marra *et al.*, 1979, Dosch, 1992). We discuss below how this method was later adapted for liquid surfaces. The possibilities opened by synchrotron X-ray sources can be understood by comparing the number of illuminated unit cells in a 3D crystal of a size that was typically studied at that time using a conventional laboratory X-ray source with the greatly reduced number of unit cells at the surface that are illuminated by synchrotron X-ray sources of much higher intensity. For example, a typical 3D molecular crystal of volume 1 mm^3 with a unit cell of the order of 100 Å^3 has approximately 10^{19} unit cells. Studies of surfaces with a technique known as grazing-incidence diffraction (GID, Section 3.1) may utilize an X-ray beam of dimensions 0.05 mm × 1 mm (height × width) incident at a small, or grazing, angle from the surface $\alpha_{\mathrm{i}} \approx 0.1^\circ$ that will illuminate a surface area of ~30 mm^2 because the small angle of incidence leads to the beam spreading over the surface. If the 2D unit cell has an area of 10 Å^2 then 3×10^{14} unit cells will be illuminated by synchrotron X-rays, which is about five orders of magnitude smaller than the number of unit cells in the 3D crystal which would be illuminated by a conventional laboratory source. The synchrotron X-ray intensity is, however, at least five orders of magnitude larger than that of conventional laboratory sources, suggesting that the diffracted intensity from a surface is measurable.

One complication is the presence of background scattering from atoms that are not at the surface. Fortunately, by taking advantage of the high collimation and small beam size of the synchrotron the GID method significantly reduces background scattering from the bulk material below the surface. As explained in Section 1.7, X-rays at grazing incidence below a critical angle α_{c} penetrate into the bulk material by only a few tens of ångström units. As a result, diffuse scattering from the bulk material below the surface is also very weak. The viability of the GID technique is now well established (Dosch, 1992).

1.3 Capillary waves on the liquid surface

Aside from its horizontal orientation, the principal difference between liquid and solid surfaces is the thermally induced capillary height fluctuations of the liquid surface. The effect that these fluctuations have on the scattering from liquid surfaces will be deferred to Section 3.7; however, their principal physical properties will be discussed here.

Plausible assumptions regarding the manner in which the physical properties of capillary waves can be related to the microscopic character of a liquid can be developed using the concepts of hydrodynamics (Buff *et al.*, 1965, Lovett *et al.*, 1976, Forster, 1975, Martin *et al.*, 1972). Consider a macroscopic liquid volume containing of the order of Avogadro's number of molecules described by a corresponding number of independent variables. Either classically or quantum mechanically there is the same number of equations of motion as there is of variables, and also there is the same number of characteristic frequencies, which for the most part are atomic in character. In any large many-body system it is rare to find modes with characteristic frequencies that approach zero; however, there are a few as a result of macroscopic conservation laws. For example, the characteristic frequencies ω for sound waves and thermal excitations approach zero as their wave vectors q approach zero; i.e. $\omega \sim |\vec{q}|$ for sound waves and $\omega \sim iq^2$ for diffusive thermal fluctuations. Long-wavelength capillary waves on the liquid surface, such as the long-wavelength fluctuations in $h(\vec{r}_{xy})$, are another set of modes that have the property that their characteristic frequencies become small as their wavelengths λ increase, or as the magnitudes of their wave vectors, $|\vec{q}| = 2\pi/\lambda$, decrease.

Assume that at any instant of time the displacement of the liquid surface along the surface normal (the z-direction) is $h(\vec{r}_{xy})$. For a surface of area $A = L^2$ the amplitude of a surface mode of wave vector $\vec{q}_{n,m} = 2\pi/[L(n\hat{x} + m\hat{y})]$ can then be written as

$$h_{n,m} = \int_A d^2\vec{r}_{xy}\, h(\vec{r}_{xy}) \exp[-i\vec{q}_{n,m} \cdot \vec{r}_{xy}], \tag{1.7}$$

where

$$h(\vec{r}_{xy}) = L^{-2} \sum_{n,m} h_{n,m} \exp[i\vec{q}_{n,m} \cdot \vec{r}_{n,m}]. \tag{1.8}$$

For an interface between a liquid with average mass density ρ_{m} and a vapor with negligible density, the surface gravitational energy density (per unit area) u_{g} associated with the displacement $h(\vec{r}_{xy})$, namely

$$u_{\mathrm{g}} = \frac{1}{L^2} \int_A d^2\vec{r}_{xy} \int^{h(\vec{r}_{xy})} \rho_{\mathrm{m}} g z\, dz = \frac{1}{2L^2}\, \rho_{\mathrm{m}} g \int_A d^2\vec{r}_{xy}\, h^2(\vec{r}_{xy}), \tag{1.9}$$

can be expressed as a sum over the surface modes

$$\begin{aligned} u_{\mathrm{g}} &= \frac{1}{2L^6} \rho_{\mathrm{m}} g \int_A d^2\vec{r}_{xy} \sum_{n',m'} h_{n',m'} \sum_{n,m} h_{n,m} \exp[i\vec{r}_{xy} \cdot (\vec{q}_{n,m} + \vec{q}_{n',m'})] \\ &= \frac{1}{2L^4} \rho_{\mathrm{m}} g \sum_{n,m} |h_{n,m}|^2, \end{aligned} \tag{1.10}$$

where g is the gravitational acceleration and we have used the fact that, since $h(\vec{r}_{xy})$ is real, $h_{-n,-m} = h^*_{n,m}$. In the case of an interface between two fluids ρ_{m} would represent the difference in mass density between the two fluids.

The limiting case of $A \to \infty$ is treated by introducing

$$\begin{aligned} h(\vec{q}_{xy}) &= \int d^2\vec{r}_{xy}\, h(\vec{r}_{xy}) \exp[-i\vec{q}_{xy} \cdot \vec{r}_{xy}], \\ h(\vec{r}_{xy}) &= \frac{1}{(2\pi)^2} \int d^2\vec{q}_{xy}\, h(\vec{q}_{xy}) \exp[i\vec{q}_{xy} \cdot \vec{r}_{xy}], \end{aligned} \tag{1.11}$$

where the number of modes per unit area, N_{A}, within a range $d^2\vec{q}_{xy}$ is equal to

$$\frac{dN_{\mathrm{A}}}{d^2\vec{q}_{xy}}\, d^2\vec{q}_{xy} = \frac{1}{(2\pi)^2}\, d^2\vec{q}_{xy}. \tag{1.12}$$

On substitution of Eq. (1.11) into Eq. (1.9) the surface gravitational energy density associated with surface fluctuations is then given by

$$\begin{aligned} u_{\mathrm{g}} &= \frac{1}{(2\pi)^2} \lim_{A\to\infty} \int d^2\vec{q}_{xy} \left\{ \frac{\rho_{\mathrm{m}} g}{2A} |h(\vec{q}_{xy})|^2 \right\} \\ &= \lim_{A\to\infty} \int \frac{dN_{\mathrm{A}}}{d^2\vec{q}_{xy}}\, d^2\vec{q}_{xy} \left\{ \frac{\rho_{\mathrm{m}} g}{2A} |h(\vec{q}_{xy})|^2 \right\}, \end{aligned} \tag{1.13}$$

where

$$u_{\mathrm{g}}(\vec{q}_{xy}) = \frac{\rho_{\mathrm{m}} g}{2A} |h(\vec{q}_{xy})|^2 \tag{1.14}$$

is the gravitational energy per mode.

The full expression for the potential-energy density of a surface fluctuation is the sum of the gravitational term plus the excess surface energy density u_{st} due to the increased surface area accompanying $h(\vec{r}_{xy})$. Taking γ to be the surface tension (Safran, 1994),

$$\begin{aligned} u_{\mathrm{st}} &= \lim_{A\to\infty} \frac{\gamma}{A} \int d^2\vec{r}_{xy} \left\{ \sqrt{1 + |\vec{\nabla}_{xy} h(\vec{r}_{xy})|^2} - 1 \right\} \\ &\approx \lim_{A\to\infty} \frac{\gamma}{2A} \int d^2\vec{r}_{xy} |\vec{\nabla}_{xy} h(\vec{r}_{xy})|^2, \end{aligned} \tag{1.15}$$

where the approximation is valid for small displacements, i.e. $|\vec{\nabla}_{xy} h(\vec{r}_{xy})| \ll 1$. The "$-1$" in the integrand arises from subtraction of the energy of the flat surface. The total potential energy can be written as the integral of the potential energy per mode, $u(\vec{q}_{xy}) = u_{\mathrm{g}}(\vec{q}_{xy}) + u_{\mathrm{st}}(\vec{q}_{xy})$, as

$$u = \lim_{A\to\infty} \int \frac{dN_{\mathrm{A}}}{d^2\vec{q}_{xy}}\, d^2\vec{q}_{xy} \left\{ \frac{\rho_{\mathrm{m}} g}{2A} |h(\vec{q}_{xy})|^2 + \frac{\gamma}{2A} |\vec{q}_{xy} h(\vec{q}_{xy})|^2 \right\}, \tag{1.16}$$

with the energy per mode

$$u(\vec{q}_{xy}) = \frac{\rho_{\mathrm{m}} g}{2A} |h(\vec{q}_{xy})|^2 + \frac{\gamma}{2A} |\vec{q}_{xy} h(\vec{q}_{xy})|^2. \tag{1.17}$$