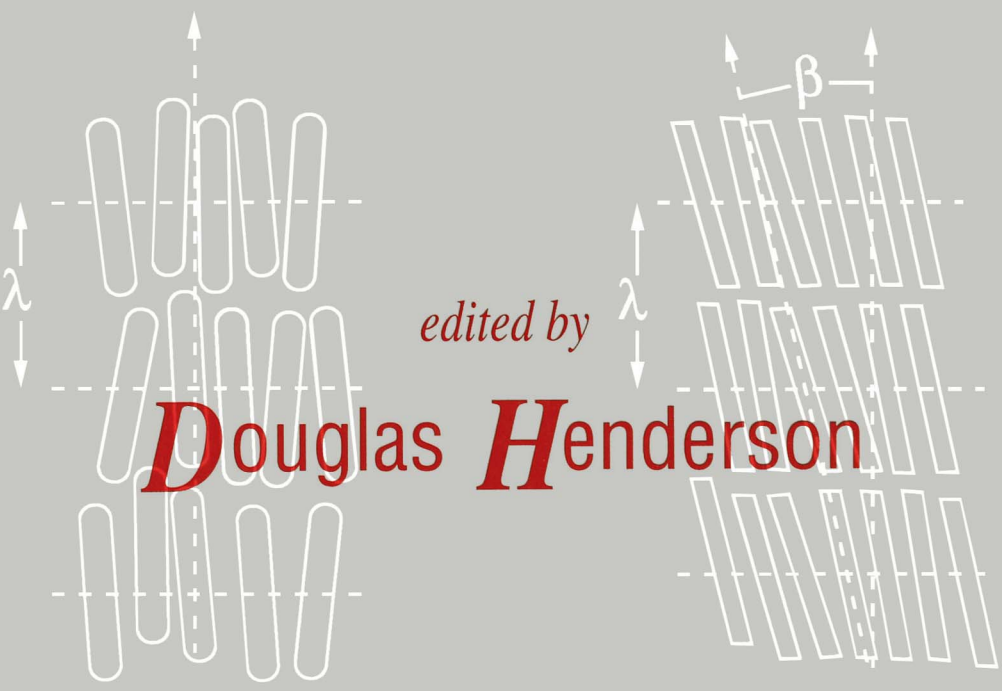


**F**undamentals  
*of*  
**I**nhomogeneous  
**F**luids



*edited by*

**D**ouglas **H**enderson

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***Utah Supercomputing Institute/IBM Partnership  
and University of Utah  
Salt Lake City, Utah***



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## *Preface*

Around 1960 Joe Hirschfelder wrote an essay outlining what he felt were the three unsolved problems in theoretical chemistry. I think that he called them bottlenecks. One of the bottlenecks was the lack of a satisfactory theory of liquids. If a theoretical physicist were to have made in 1960 a similar list of bottlenecks in theoretical physics, the list would undoubtedly have been different. However, it is quite likely that the need for a satisfactory theory of liquids would have appeared on this list also.

In any case, the past quarter century has seen a dramatic increase in our understanding of homogeneous or bulk liquids. However, our understanding of inhomogeneous liquids (liquids near interfaces or confined liquids) is less satisfactory. Since the feature that distinguishes a liquid from a dense gas is the presence of an interface, one might argue that even our understanding of homogeneous liquids is incomplete without an understanding of inhomogeneous fluids. It is for this reason that many of us who worked earlier on the theory of homogeneous liquids have turned our attention to inhomogeneous liquids. Indeed, van der Waals, after developing his theory of liquids, almost immediately turned his attention to interfaces.

A further reason for an interest in inhomogeneous liquids is that many of the technological processes that involve liquids occur at interfaces. A

few examples that come to mind are corrosion, oil recovery, and colloidal stability.

I have used the term inhomogeneous fluids rather than inhomogeneous liquids in the title so as to include such interesting and important topics as the wetting of a surface by a gas. Furthermore, the distinction between a liquid and a dense gas is somewhat artificial. Also, in lattice models, there is a reciprocity between the liquid and vapor phases. This reciprocity is mirrored, at least approximately, in the real world.

There has been considerable progress in the past decade in the development of the theory of inhomogeneous fluids. Thus, it seems timely to bring out a book outlining this progress. The emphasis here is on theory, although experimental work is referred to in the book. In fact, one chapter is devoted to wetting experiments.

The book is divided into thirteen chapters, each written by a recognized expert. Rowlinson begins with a historical introduction written with the insight that only he can provide. Jim Henderson discusses exact sum rules for inhomogeneous fluids, many of which he derived. Evans and I outline the two main theoretical tools in the theory of inhomogeneous fluids, density functional, and integral equation techniques, respectively. Jan-covici discusses his exact solutions for two-dimensional homogeneous plasmas, and Blum and I discuss the recent progress, mostly based on integral equations, in the theory of interfacial electrochemistry.

Franck discusses wetting experiments—the viewpoint of an experimentalist is complementary and of interest. The theory of wetting (the modern theory of adsorption) is also described in some of the other chapters (see the chapters of Jim Henderson and Evans, in particular). Lozada-Cassou describes confined liquids, mostly electrolytes, largely using the integral equations he has obtained.

Next, phase transitions (mostly first-order) are considered. Haymet discusses freezing with an emphasis on quantum systems. His view is that a solid is a highly inhomogeneous fluid. Although this likely would not be a useful basis for solid-state theory, it seems useful as a description of solids in equilibrium with a liquid and provides the first really useful theory of freezing. Oxtoby discusses homogeneous nucleation in liquid–vapor and solid–liquid transitions. Marko completes this trilogy with a discussion of liquid crystal transitions. The treatment of these three chapters uses the density functional approach discussed by Evans.

The final two chapters are those of Dawson and Mundy on self-organizing liquids and of Davis on kinetic phenomena in inhomogeneous fluids using a modified Enskog theory. Unfortunately an author who was invited to write a chapter on computer simulations did not submit his manuscript. Its lack is compensated for by the fact that many of the authors in this

volume make references to and comparisons with computer simulations in their own chapters.

I want to thank the chapter authors, who made many suggestions that improved this volume. I hesitate to single out any of them, but Tony Haymet and Jim Henderson were especially helpful. Much of the organization of the book was done while I was a visiting professor at the Scuola Normale Superiore in Pisa, Italy, in the spring of 1989. I am grateful to this institution and to Dr. Alessandro Tani for many kindnesses.

Lastly I want to thank my wife, Rose-Marie. The production of a book goes through three phases: initial excitement at the enterprise, frustration with the delays and necessary drudgeries, and finally relief that the business is finished. I am grateful for her bemused tolerance as I passed through these phases.

*Douglas Henderson*



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## *Contributors*

**L. Blum, Ph.D.** Professor of Physics, Department of Physics, University of Puerto Rico, Rio Pedras, Puerto Rico

**H. Ted Davis, Ph.D.** Professor and Head, Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota

**K. A. Dawson, Ph.D.** Assistant Professor, Department of Chemistry, University of California, Berkeley, California

**R. Evans, Ph.D.** H. H. Wills Physics Laboratory, University of Bristol, Bristol, England

**Carl Franck** Associate Professor of Physics, Laboratory of Atomic and Solid State Physics, and Materials Science Center, Cornell University, Ithaca, New York

**A. D. J. Haymet, Ph.D.** Department of Chemistry, University of Sydney, Sydney, N.S.W., Australia

**Douglas Henderson, Ph.D.** Research Scientist, Utah Supercomputing Institute/IBM Partnership, and Adjunct Professor, Department of Chemistry, University of Utah, Salt Lake City, Utah

**J. R. Henderson, Ph.D.** School of Chemistry, University of Leeds, Leeds, England

**B. Jancovici, D.Sc.** Professor, Laboratoire de Physique Théorique, Université de Paris-Sud, Orsay, France

**Marcelo Lozada-Cassou, Ph.D.** Professor, Department of Physics, Universidad Autónoma Metropolitana-Iztapalapa, Mexico City, Mexico

**J. F. Marko, Ph.D.** James Franck Institute, University of Chicago, Chicago, Illinois

**Christopher J. Mundy, B.S.** Research Assistant, Department of Chemistry, University of California, Berkeley, California

**David W. Oxtoby, Ph.D.** Professor of Chemistry, Department of Chemistry, James Franck Institute, University of Chicago, Chicago, Illinois

**J. S. Rowlinson** Dr. Lee's Professor of Chemistry, Physical Chemistry Laboratory, Oxford University, Oxford, Great Britain

## *Development of Theories of Inhomogeneous Fluids*

**J. S. Rowlinson**

*Oxford University*

*Oxford, Great Britain*

### **I. INTRODUCTION: LAPLACE'S THEORY OF THE SHARP INTERFACE**

From the earliest days of physical science it must have been clear that matter in thin films and at surfaces differed in its properties from the same matter in bulk. The "natural philosophers" of the seventeenth and eighteenth centuries were curious about both the optical and mechanical properties of surface films, as, for example, the interference colors of Newton's rings and the damping of the waves on the sea by a film of oil, a subject that interested Benjamin Franklin, among others. The first of these effects to be tackled quantitatively was that of capillarity—the rise of water (and the depression of mercury) in narrow tubes or, in its more practical aspect, the rise of sap in trees. This apparent defiance of the laws of gravity was correctly perceived to arise from cohesive forces between the ultimate constituents of matter that were not gravitational in origin. Francis Hauksbee, Newton's assistant at the Royal Society, showed this convincingly by observing that the capillary rise of water depended only on the internal diameter of the tube and was independent of the thickness of its walls. The force responsible must therefore be of short range and act essentially only between the layers of liquid and solid that are in contact. As well as this cohesive force it was realized that

there were other, presumably weaker, forces that acted within the body of the liquid since, as James Jurin (1719) and A. C. Clairaut (1743) observed, drops of liquid that are too small for their shape to be influenced by gravity are spherical. J. A. Segner (1751) synthesized these and similar observations into the concept of surface tension.

The nature of the cohesive forces was, of course, unknown and was to remain so until this century, but speculation was not lacking. John Keith (1709) proposed an attractive force that varied as  $r^{-n}$ , where  $n$  exceeded the Newtonian value of 2. More complex schemes were devised by John Rowning (1735) and Rudjer Boskovic, or Roger Boscovich (1758), who suggested alternating zones of attraction and repulsion around each particle, arranged in such a way that the separations at which the force is zero, corresponded to the densities of the material in its solid, liquid, and gaseous forms. Such speculation had outrun the evidence, for there was no theory to link these hypothetical forces with their physical or macroscopic consequences. It was probably because of this lack that the second half of the eighteenth century saw little further advance. At the beginning of the nineteenth century two men independently rescued the subject from its stagnation, Thomas Young [1] in London and Pierre Simon Laplace [2] in Paris. Many of their conclusions were the same, but those of Young are less accessible since in his early papers, he expressed his results in words rather than in symbols and equations, and in his later papers he was still using old methods of handling the calculus which makes his work hard to follow. This short account is, therefore, based substantially on that of Laplace and, indeed, it was his work which, for the same reasons, was more influential later in the century.

Laplace calculated the force between two bodies of liquid with planar parallel walls and separated by vapor of negligible density. He knew that the forces between the molecules must be short-ranged on a human scale but he assumed, nevertheless, that their range was long compared with the mean separation of the molecules. This assumption has now become a formal requirement in some molecular theories of matter and has been given the name of the *mean-field approximation*. It has played an important, and often controversial, role in physics for nearly 200 years.

With this approximation he did not have to worry about the actual distribution of the molecules in the liquid but could assume that it was uniform, that is, that they were distributed at random. His result for the attractive force per unit area between two surfaces in contact,  $K$ , is most easily expressed in modern form in terms of the potential energy,  $\varphi(r)$ , of a pair of molecules at a separation  $r$ . This potential energy is related to the force between the pair,  $f(r)$ , by  $-f(r) = d\varphi(r)/dr$ . If  $\varphi_{\text{att}}(r) < 0$  and  $\varphi_{\text{att}}(\infty) = 0$ , then  $f(r) < 0$ ; that is, the force is attractive. Laplace's

result for the attractive force per unit area of two slabs of liquid in contact can be expressed as

$$K = -2\pi\rho^2 \int_{\sigma}^d \varphi_{\text{att}}(r)r^2 dr \quad (1)$$

where  $\rho$  is the number of molecules per unit volume,  $d$  the range of the intermolecular potential, and  $\sigma$  a cutoff distance for the attractive potential. He showed also that the work done per unit area to separate the two slabs of liquid to a separation  $d$  (or greater) is given by

$$H = -\pi\rho^2 \int_{\sigma}^d \varphi_{\text{att}}(r)r^3 dr \quad (2)$$

Since two surfaces have been created, this quantity is twice the excess energy per unit area of the liquid surface and hence twice the liquid–gas surface tension;  $H = 2\gamma^{lg}$ . The cohesive energy density of the liquid, or energy per unit volume, is  $-2K$ , and the “internal pressure” inside a spherical drop of radius  $R$  is  $K + (H/R)$ , a quantity that is not directly accessible to experiment. The difference of the observed pressure inside and outside the drop is accessible and is given by what we now call *Laplace’s equation*,

$$p^l - p^g = \frac{H}{R} = \frac{2\gamma^{lg}}{R} \quad (3)$$

If a liquid touches a solid, similar arguments can be used to obtain expressions for the two surface tensions,  $\gamma^{sg}$  and  $\gamma^{sl}$ . These are related to the angle  $\theta$  between the liquid–gas and the liquid–solid surface by *Young’s equation*,

$$\gamma^{sg} = \gamma^{sl} + \gamma^{lg} \cos \theta \quad (4)$$

These two equations, of Laplace and Young, suffice to solve all common problems of capillarity, such as the rise (or fall) of liquids in narrow tubes, the shapes of liquid surfaces in contact with solid surfaces, the shapes of systems of bubbles, and so on.

This achievement was an important success in the Laplacian (or Newtonian) program of obtaining the physical properties of matter from the microscopic interparticle forces. The very success of the theory provoked a more detailed examination from which several difficulties emerged. The first was the nature of the repulsive forces that are needed to balance the postulated attractive forces in a system at equilibrium. Laplace, a believer in the caloric theory, at first ascribed the necessary repulsion to heat, a

view that received some support from the observation that most liquids expand on heating. In his later work (1819 onward) he came around to the view that the strength of these caloric-induced repulsions must fall off more rapidly with distance than the attractive forces, as Boskovic and others had deduced earlier. The second mechanical difficulty was the structure of the supposed equilibrium array of stationary particles. It was not difficult to envisage how a crystal might be constructed by packing together in a regular way a large number of molecules of simple shape, but there could be no such geometrical picture of a liquid. This, again, was a problem that could not be tackled within the essentially static model of Laplace, and its solution had to await the development of a kinetic theory of matter later in the century.

A third and more subtle problem concerned the size of the postulated molecules and the range of the forces between them. Young observed that since the integral  $H$  has a factor of  $r^3$  and the integral  $K$ , a factor of  $r^2$ , the ratio  $2H/K$  is a measure of the effective range of the potential,  $\varphi_{\text{att}}(r)$ . We have seen that  $H$  is twice the surface tension, so is easily measured, but that  $K$ , the cohesive energy density, is not directly measurable. Young estimated it for water at 25 kbar (in modern units), probably by an argument based on the compressibility of the liquid. He deduced that the effective range of  $\varphi_{\text{att}}(r)$  is therefore about  $1 \times 10^{-10}$  m, a figure that we now know to be low only by a factor of about 5. He then went on, wrongly, to identify this distance with the mean molecular separation in steam on the point of condensation, since he thought that this was the distance at which the attractive forces must start to act if they were to bring about condensation. Since liquid water is more than 1000 times denser than steam at its normal boiling point, he was able to convince himself that the mean molecular separation in liquid water is many times smaller than the range of the cohesive forces, and so justify the use of the mean-field approximation.

We have seen how the early enthusiasm for Newton's physics in the first half of the eighteenth century led to many attempts to explain the properties of gases and liquids in terms of interparticle forces, and how this enthusiasm faded in the second half of the century when the program failed to produce quantitative results. The work of Laplace and the Arceuil school in France gave the field a renewed vigor that lasted for about 25 years. From about 1830 onward, however, the effort faltered again for the same reason—no significant new results were forthcoming. It was not until the creation of the mechanical theory of heat and of kinetic theory and the development of thermodynamics that the next round in the theory of liquids and their surfaces could be opened.

## II. VAN DER WAALS' THEORY OF THE DIFFUSE INTERFACE

In 1869, Dupré [3] recalculated the internal energy density,  $-K$ , of Laplace's theory. He called this quantity *le travail de désagrégation totale*, a name that reflected the way in which it was calculated—by calculating the force needed to remove the particles in the surface layer of a liquid, one by one. A particle that is within a distance  $d$  of the surface experiences a net inward attraction because of the lack of spherical symmetry in its surroundings. Although his result was correct (within the mean-field approximation), his argument is flawed since a system that contains particles on which there are unbalanced forces cannot be at equilibrium, so the liquid cannot have the sharp surface that he and Laplace had supposed. This flaw was, in fact, pointed out by Poisson [4], a follower of Laplace, in 1831, but he had then gone on to deduce, incorrectly, that if a sharp surface were replaced by a diffuse one, of thickness comparable with the range  $d$ , the surface tension would vanish. His fault lay in an implicit assumption that it is possible to define unambiguously the local values of a thermodynamic function in terms of the local values of other functions, as in a homogeneous system. A systematic application of this argument does, indeed, lead to the vanishing of the surface tension, but the argument itself is correct only if the attractive forces are of zero range, and it is this circumstance that is responsible for the vanishing of the surface tension, as is seen from Eq. (2) in the limit of  $d \rightarrow \sigma$ . A less restrictive view of the local thermodynamics of inhomogeneous systems was needed before an interface of nonzero thickness and forces of nonzero range could be reconciled with a nonzero value of the surface tension.

Three men, apparently independently, found the natural way of generalizing this restricted view to a more general or nonlocal thermodynamics of an inhomogeneous system. They were Karl Fuchs [5] at Pressburg (now Bratislava, in Czechoslovakia), Lord Rayleigh [6], who worked mainly in his laboratory at his home at Terling in Essex in Britain, and J. D. van der Waals [7] in Amsterdam. The theory put forward by Fuchs and by Rayleigh was still in the tradition of Laplace in that it was purely a mechanical treatment of the problem; it ignored the motions of the molecules or, in thermodynamic terms, it used an energy where a free energy was more appropriate. Van der Waals was the first to realize the importance of this distinction.

Fuchs observed that since the attractive force has a nonzero range, molecules in a surface layer will influence, and be influenced by, other molecules that are in a fluid of quite different local density. Hence the



average energy at a given point,  $\mathbf{r}$ , so also the average value of the local pressure, will depend not only on the density  $\rho(\mathbf{r})$  but on its gradient and higher derivatives. If we have a flat surface in the  $xy$ -plane, these derivatives can be written  $\rho'(z)$ ,  $\rho''(z)$ , and so on. For obvious reasons of symmetry, there cannot be a term linear in  $\rho'(z)$ , and Fuchs was the first to show that the excess of the tangential or horizontal component of the pressure over the vertical component at height  $z$  can therefore be expressed as

$$\Delta p(z) = -\frac{1}{60}\{\rho(z)\rho''(z) - [\rho'(z)]^2\}I \quad (5)$$

where

$$I = -\int r^3 f(r) dr \quad (6)$$

and where  $f(r) < 0$  is the force between two molecules at separation  $r$ . He took this result no further, but a simple integration over  $z$  gives for the surface tension,

$$\gamma = \int_{-\infty}^{+\infty} \Delta p(z) dz = \frac{1}{30}I \int_{-\infty}^{+\infty} [\rho'(z)]^2 dz \quad (7)$$

This last step was taken by van der Waals in a short communication to the Academy of Sciences that was published in 1889 and in his definitive paper of 1893 [7], and, in 1892, by Rayleigh [6].

Van der Waals opens his treatment by introducing at once the condition that the free energy is a minimum in a system of fixed mass, volume, and temperature. He makes free use of the hypothetical continuous isotherm that passes smoothly through the two-phase region. The usefulness of this curve had been guessed first by James Thomson in 1871 [8] after the publication of Andrews's classic experiments on the critical point of carbon dioxide, and it had become accepted as a useful construct after its use in van der Waals' thesis in 1873 [9]. The results of van der Waals can be expressed simply by introducing first the Gibbs dividing surface of zero adsorption. This divides the liquid from the gas at an arbitrary height  $z_0$  defined by

$$\int_{-\infty}^{\infty} [\rho(z) - \rho^{l,g}] dz = 0 \quad (8)$$

where  $\rho^{l,g}$  is  $\rho^l$  for  $z < z_0$  and  $\rho^g$  for  $z > z_0$ . A local excess free-energy density  $\Psi(z)$  can then be defined as the sum of two terms,

$$\Psi(z) = \Delta\psi[\rho(z)] + \frac{1}{2}m[\rho'(z)]^2 \quad (9)$$

where  $\Delta\psi$  is the amount by which the free-energy density on the contin-

uous (Thomson–van der Waals) isotherm exceeds that of the two bulk phases at the same overall density, which is

$$\psi^l \frac{\rho(z) - \rho^g}{\rho^l - \rho^g} + \psi^g \frac{\rho^l - \rho(z)}{\rho^l - \rho^g}$$

He showed that the coefficient  $m$  is the fourth moment of the attractive part of the intermolecular potential,

$$m = -\frac{2\pi}{3} \int r^4 \varphi_{\text{att}}(r) dr \quad (10)$$

and so differs only by a numerical factor of 30 from Fuchs's integral  $I$  of Eq. (6). Van der Waals obtained the surface tension from the integral of the excess free-energy density defined with respect to the Gibbs dividing surface of zero adsorption:

$$\gamma = \int_{-\infty}^{\infty} \Psi(z) dz = m \int_{-\infty}^{\infty} [\rho'(z)]^2 dz \quad (11)$$

The two terms in Eq. (9) contribute equally to the surface tension.

This "square-gradient" theory of van der Waals was wholly within the mean-field approximation, all fluctuations are ignored, and it gives rise to a classical critical index:

$$\gamma \sim (T^c - T)^\mu \quad \mu = \frac{3}{2} \quad (12)$$

It was, however, the most satisfactory theory of the surface layer between gas and liquid to be put forward until modern times. Its impact was limited by the general loss of vitality of the field of liquid state physics after 1914 [10], so that its results were rediscovered independently many years later, as will be discussed below.

### III. INTERFACES BETWEEN SOLUTIONS OF ELECTROLYTES

At the end of the nineteenth century the word *solution* usually meant an aqueous solution of an electrolyte, that is, an acid, a base, or a salt. At the same time as Fuchs, Rayleigh, and van der Waals were developing a theory of the liquid–gas interface, Nernst [11] and Planck [12] were taking up the problem of the junction between two aqueous solutions of electrolytes, which could be either solutions of different substances or of the same substance at different compositions. Such an interface differs fundamentally from the liquid–gas interface, for it cannot be at equilibrium; diffusion of the electrolyte must slowly bring about complete mixing and

the junction will disappear. Nevertheless, diffusion in liquids is slow compared with the time needed to establish an almost stationary distribution of ions, so Nernst and Planck were justified in using quasi-thermodynamic arguments. Their work was contemporary with that of Fuchs and of van der Waals' first note, but there is no evidence that either set of workers knew of or was influenced by the other. Nernst and Planck phrased their argument in terms of the force generated by a gradient of osmotic pressure which is balanced by that of the electric field. A modern route to the same result (e.g., that of MacInnes [13]) considers the flow of ions into and out of an infinitesimal layer of the interface. The potential of the liquid junction,  $E_L$ , between two phases,  $\alpha$  and  $\beta$ , is given by

$$E_L = -\frac{RT}{F} \int_{\beta}^{\alpha} \sum_i \frac{t_i}{z_i} d \ln a_i \quad (13)$$

where  $t_i$ ,  $z_i$ , and  $a_i$  are the transport number, number of electronic charges, and activity of the ion of species  $i$ .

This expression is not without its problems. There is the question of the meaning to be attached to single-ion activities since these cannot be measured—a restriction that was not fully appreciated until this century. A characteristically forthright expression of our inability to determine single-ion chemical potentials and electrode potentials was given by Guggenheim in 1929 [14]. The restriction arises from the need to preserve electrical neutrality. If, however, the junction is between two solutions of the same electrolyte, for example a uni-univalent electrolyte in a cell in which the electrodes are reversible to the anion, then, since  $t_+ + t_- = 1$ , we have

$$E_L = \frac{RT}{F} \int_{\alpha}^{\beta} d \ln a_- - 2 \frac{RT}{F} \int_{\alpha}^{\beta} t_+ d \ln a_{\pm} \quad (14)$$

where  $a_{\pm}^2 = a_+ a_-$ , the square of the mean ionic activity, which is measurable. The first term is the contribution to the emf of the cell from the two electrodes, so the last term is the electromotive force (emf) of the whole cell.

Matters are less simple if we have a junction between two different electrolytes. Even if we are willing to make an assumption about single-ion activities (e.g., that  $a_+ = a_- = a_{\pm}$ ), we still cannot integrate Eq. (13) without knowing more about the concentration gradients of the ions in the interface and how  $t_i$  depends on the local concentration. The last problem can be solved by auxiliary experiments, but the problem of the gradients of ionic concentration requires a further ad hoc assumption. Planck took this assumption to be what we now call a boundary zone of

constrained diffusion, which can be envisaged as the zone established by diffusion in the pores of a plug, the two faces of which are washed by the two homogeneous phases sufficiently rapidly for the concentration at each face to be constrained to be that of the appropriate bulk phase. The form of equations to which this gives rise are set out in an appendix in MacInnes's book [13].

A simpler assumption, made later by Henderson [15], seems to agree as well with experiment. He assumed that the composition of each point in the boundary zone was that of a fraction of  $y$  of phase  $\alpha$  and fraction  $(1 - y)$  of phase  $\beta$ . He assumed further that  $y$  is a linear function of distance from either of the faces of the zone, although it was later found that this assumption was redundant. (It is a curiosity that many years later, and in ignorance of Henderson's work, I made exactly the same assumptions about the composition profile of the boundary layer between a binary liquid mixture and its vapor in order to calculate the surface tension [16].)

#### IV. ELECTRICAL DOUBLE LAYER

The surface between an electrode and a solution of an electrolyte is an inhomogeneous system that can be at true equilibrium and so can be treated with more precision than the liquid-liquid junction between two solutions in a common solvent. The treatment of an interface at true equilibrium might, at first sight, be expected to owe something to the earlier work of Laplace or of van der Waals on the liquid-gas surface, but the long range of ionic forces means that the dominant structures are quite different and, at first, the theoretical treatments had nothing in common. It is only in recent times that the theoretical methods have converged, as both have been grounded more thoroughly in modern statistical mechanics.

Helmholtz [17] was the first to realize that a charged metal plate immersed in a solution of an electrolyte would have as its neighbor a zone in which the ions were predominantly of the opposite charge, thus forming a double layer. He defined the moment of this layer as the product of its thickness  $D$  and the density of positive (or negative) electricity within it,  $e$ . He envisaged, however, that  $D$  was of molecular dimensions, so that the electrolytic part of his double layer comprised more an adsorbed layer of ions than a diffuse zone that is thick by comparison with the size of any one ion. Billiter [18] realized that the double layer need not be confined to one layer, or even few layers, but would spread out into the bulk of the liquid phase. He spoke of "a dissociation of the double layer" [19] but did not develop a theory for calculating its thickness and structure.

That task was undertaken independently by Gouy in Lyon in 1910 [20] and by Chapman in Oxford in 1913 [21]. Each treated the problem in the same way and their two papers are remarkable, even by the standards of the day, in that neither of them has a single reference.

The diffuseness of the layer arises from the opposing effects of the electric force from the electrode, which tends to make the layer thin, and the combination of the repulsive forces between the ions and of their own diffusive motion from places of high density to those of low density (then generally called the osmotic force), which tends to make the layer thick. If the layer is sufficiently thick, we can, as a first approximation, assume that the ions are of negligible size.

Their method of tackling the problem is to assume that the concentration profile of the ions satisfies two equations. The first of these is Poisson's equation of electrostatics,

$$\operatorname{div} \operatorname{grad} V(\mathbf{r}) = \frac{\rho(\mathbf{r})}{\epsilon} \quad (15)$$

where  $\rho$  is the density of charge at position  $\mathbf{r}$ ,  $\epsilon$  the permittivity of the solution (taken to be independent of  $\mathbf{r}$ ), and  $V$  the electric potential. The second equation is Boltzmann's distribution for ions in an external potential  $V$ :

$$n_i(\mathbf{r}) = n_i^\infty \exp \left[ \frac{-z_i e V(\mathbf{r})}{kT} \right] \quad (16)$$

where  $n_i(\mathbf{r})$  is the concentration at  $\mathbf{r}$  of ions of species  $i$  which carry a charge of  $z_i e$ , and  $n_i^\infty$  is the concentration at infinite distance from the electrode where  $V$  is zero. Since

$$\rho(\mathbf{r}) = \sum_i n_i(\mathbf{r}) z_i e \quad (17)$$

we have

$$\nabla^2 V(\mathbf{r}) = -\frac{1}{\epsilon} \sum_i n_i^\infty z_i e \exp \left[ \frac{-z_i e V(\mathbf{r})}{kT} \right] \quad (18)$$

which is the Poisson–Boltzmann equation, the most used equation in the theory of inhomogeneous electrolytic solutions. It is not exact because the Boltzmann distribution is correct only for ions of zero size and with no forces between them other than the Coulomb forces. Moreover, the solvent is treated as a continuous dielectric medium, not as a collection of discrete molecules that exert forces on the ions and on each other. Nevertheless, the Poisson–Boltzmann equation embodies much of the essential physics of the problem, at least for dilute solutions.

It is convenient to depart from strict historical order and consider first the linearized equation obtained by assuming that  $V$  is small and hence that the exponential can be expanded to give

$$\nabla^2 V(\mathbf{r}) = -\kappa^2 V(\mathbf{r}) \quad (19)$$

where

$$\kappa = e \left( \sum_i \frac{z_i^2 n_i^\infty}{\epsilon kT} \right)^{1/2} \quad (20)$$

The parameter  $\kappa^{-1}$  has the dimensions of length and is a measure of the thickness of the double layer. This equation was used in 1923 by Debye and Hückel [22] to determine the potential and the concentration of ions around a chosen ion in a dilute solution. The problem is one of spherical symmetry for which the operator has the form

$$\nabla^2 = \frac{d^2}{dr^2} + \frac{(2/r)d}{dr} \quad (21)$$

so  $V(r)$  has the form that is now usually called a Yukawa potential [23]:

$$V(r) = \frac{ze\kappa}{\epsilon} \frac{1}{\kappa r} e^{-\kappa r} \quad (22)$$

where  $z$  is the charge on the central ion and where the constants of integration have been chosen so that  $V(r)$  approaches its Coulomb value as  $r$  becomes infinite.

For a flat surface, as considered by Gouy and Chapman, it is not necessary to linearize the Poisson–Boltzmann equation. The operator  $\nabla^2$  now takes the simple form  $d^2/dx^2$ , where  $x$  is the distance perpendicular to the planar electrode. For a single symmetrical electrolyte,  $z_i = z_+ = z_- = z$ , we have the equation

$$\frac{d^2 V(x)}{dx^2} = \frac{2zen^\infty}{\epsilon} \sinh \frac{zeV(x)}{kT} \quad (23)$$

of which the integral with the appropriate boundary conditions is

$$\tanh \frac{zeV(x)}{4kT} = \tanh \frac{zeV^\circ}{4kT} e^{-\kappa x} \quad (24)$$

where  $V^\circ$  is the potential at the surface of the electrode ( $x = 0$ ). Gouy wrote this as

$$\kappa x = \ln \frac{u_0^{1/2} - 1}{u^{1/2} - 1} - \ln \frac{u_0^{1/2} + 1}{u^{1/2} + 1} \quad (25)$$

where  $u = n_+/n_+^\infty$ , that is, the relative excess of cations, and  $u_0$  is the value at  $x = 0$ . Clearly,  $u_0 < 1$  if the plate carries a positive charge ( $V > 0$ ), and  $u_0 > 1$  if it is negative, and vice versa for the anions since  $n_+ n_- = n_+^\infty n_-^\infty = n^2$ .

The Gouy–Chapman theory and Poisson–Boltzmann equation on which it is based, like many simplest approximations, have virtues that can easily be lost when attempts are made to improve them. Equations (23) to (25) satisfy, for example, the conditions of mechanical equilibrium at all points in the diffuse layer. Nevertheless, the imperfections of the Gouy–Chapman theory and, more particularly, of its linearized version, the Debye–Hückel theory, have been recognized from the earliest days. The best known formal analyses of the Debye–Hückel theory were those of Fowler [24], Onsager [25], and Kirkwood [26].

The first significant attempt to improve the Gouy–Chapman theory was based on the recognition by Stern [27] that the nonzero size of the ions prevented their centers from reaching the actual surface of the electrode, and so prevented the surface concentration of counterions reaching the impossibly high figures that could result from the Gouy–Chapman equation. He assumed that there would be an adsorbed layer of counterions whose density he calculated from arguments similar to those used earlier by Langmuir [28] for calculating the extent of adsorption of molecules at uncharged surfaces. This adsorbed layer of counterions is now usually known as the Stern layer. Much later, Bikerman [29] proposed a correction for the nonzero size of the ions in the diffuse layer by introducing a co-volume,  $b$ , but did not attempt to calculate the consequences of his proposal. Since the two assumptions of a linearized Boltzmann distribution and a co-volume are reminiscent of the two assumptions behind the van der Waals equation of state of homogeneous fluids, it is of interest to see what is the corresponding result for an inhomogeneous electrolyte solution. This point is explored briefly in an appendix to this chapter. Dutta and Bagchi [30] and, independently, Eigen and Wicke [31] proposed similar modifications of the Debye–Hückel equation.

These attempts at improvement are, however, all without formal theoretical foundation. Modern work has developed in two directions. The first is based on the critical work of Kirkwood and others and led in 1951 to the so-called modified Poisson–Boltzmann equation of Loeb [32], which has been developed further by Levine and Outhwaite [33]. The second has been the introduction into these fields of the integral equations used first for homogeneous and uncharged liquids, such as the Yvon–Born–Green and hypernetted chain integral equations. With these developments we reach the modern era, and so subjects of later chapters of this book.

One field of application of the theory of the diffuse layer should, however, not go unnoticed. This is the theory of the forces between colloidal particles, which is based, in part, on the behavior of two interacting double layers. Earlier work on this subject, such as that of Langmuir [34], Derjaguin and Kussakov [35], and Levine [36], was, as has been said, “conflicting on some essential points, even on the important question of whether the double layer interaction produces attraction or repulsion” [37]. The matter was due to have been thrashed out at the Faraday Society Discussion in Cambridge in September 1939, but that meeting was never held, although many of the papers and a little of the discussion by correspondence were published [38]. The classic work on this problem, which resolved many of these difficulties and paved the way for more recent work that is firmly grounded in statistical mechanics, was that carried out in the Netherlands during World War II by Verwey and Overbeek and published by them as a monograph in 1948 entitled *Theory of the Stability of Lyophobic Colloids* [37].

## V. VIRIAL EXPRESSIONS AND FUNCTIONAL EXPANSIONS: THE MODERN ERA

From its earliest development in the 1880s up to World War II the properties of solutions of electrolytes were at the center of what had become known as physical chemistry. The field has developed continuously since the war, although it has never regained the leading position it had in that subject during the 1920s and 1930s. In contrast, the theory of uncharged liquids and solutions, which was a flourishing branch of physics until World War I, became something of a backwater until after World War II [10]. In consequence, the theory of inhomogeneous liquids did not make any significant advance beyond the square-gradient theory of the liquid–gas interface of van der Waals for nearly 60 years. This theory itself was reinvented by Landau and Lifshitz in 1935 [39] to treat the formally similar problem of the interface between two magnetic domains, and by Mitsui and Furuichi in 1953 [40] for that between two ferroelectric domains. In 1958, Cahn and Hilliard [41] independently derived the results again for the liquid–gas surface in a treatment of nucleation, but although they quote, in a different context, results from the relevant papers of Rayleigh and van der Waals, they did not recognize at first that their results were essentially those of van der Waals.

The foundations of the modern treatment of interfaces can be seen in two developments that it is not too farfetched to regard as the completion of the programs of Laplace and van der Waals. The first was the development of an exact virial expression for the surface tension. It had long



been recognized that the tension depended on a difference in the interface between the normal and the tangential components of the pressure tensor. For a plane interface,

$$\gamma = \int_{-\infty}^{\infty} [p_N(z) - p_T(z)] dz \quad (26)$$

The use of this expression requires an exact statistical mechanical expression for the components of the pressure tensor. This was given first in 1949 by Kirkwood and Buff [42] and, in a different form, by Irving and Kirkwood [43]. There is more than one way of tackling this problem, so  $p_T(z)$  is not a unique function, although the integral (26) is invariant to this lack of uniqueness. One of the versions of  $p_T(z)$  is now usually associated with the name of Harasima [44]. The normal component,  $p_N(z)$ , is, by the condition of mechanical equilibrium, a constant at a planar interface and equal to both  $p^l$  and  $p^g$ , the pressures in the liquid and gaseous phases. The result obtained by substituting these statistical mechanical expressions for the pressure tensor into the integral in (26) is the so-called virial expression for the surface tension. It can be regarded as the exact result to which the treatment initiated by Laplace led, even if the path to this result took over 140 years to accomplish.

A natural corollary of this result is the Yvon–Born–Green (YBG) equation, which is obtained by differentiating with respect to the position of particle 1 the statistical mechanical expression for  $\rho(\mathbf{r}_1)$  in an inhomogeneous system:

$$-kT\nabla_1\rho(\mathbf{r}_1) = \rho(\mathbf{r}_1)\nabla_1V(\mathbf{r}_1) + \int \rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)\nabla_1\varphi(\mathbf{r}_{12}) d\mathbf{r}_2 \quad (27)$$

where  $V(\mathbf{r}_1)$  is the external potential at  $\mathbf{r}_1$ , and  $\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$  is the two-body distribution function. In a homogeneous fluid each term vanishes (the integral by symmetry) and the first nontrivial YBG equation is the second member of the hierarchy in which the left-hand side is  $-kT\nabla_1\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)$  and the integral is over the three-body distribution function  $\rho^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)$ . For obvious reasons, early users of these equations paid more attention to this equation than to Eq. (27), the one-body equation.

Yvon [45] was the first, in 1935, to use such equations, although Kirkwood [46] obtained an equivalent two-body equation the same year. There were later independent derivations in 1946 by Born and Green [47] and by Bogoliubov [48]. Because of these many independent works the hierarchy of equations is sometimes known as the YBG and sometimes as the BBGKY hierarchy.

The second foundation of the modern treatment of interfaces has been the method of functional expansions of the distribution functions. It is this approach that was described above as the natural end of the line of development opened by Fuchs, Rayleigh, and van der Waals with the square-gradient approximation. It is a necessary feature of this early work that it postulates the existence of thermodynamic functions of states of the fluid that have no independent equilibrium existence, such as a homogeneous fluid state of a density between that of the orthobaric gas and liquid states. A similar freedom in statistical mechanical theory to suppose the existence of functionals of distribution functions of states not at equilibrium came much later, but has proved to be equally fruitful. Such functionals were introduced in 1960 by Lee and Yang [49] and by Green [50], and were soon applied to the statistical mechanics of inhomogeneous systems by Morita and Hiroike [51], De Dominicis [52], Stillinger and Buff [53], Lebowitz and Percus [54], Mermin [55], and Ebner and Saam [56].

Such functionals are at extrema when their arguments, the distribution functions, take their equilibrium values, and the values of the functionals then correspond to the equilibrium value of a thermodynamic potential such as  $F$  or  $\Omega$ . If  $\hat{\rho}^{(N)}(\mathbf{r}^N)$  denotes an arbitrary  $N$ -body distribution function in the canonical ensemble which is normalized so that

$$\int \hat{\rho}^{(N)}(\mathbf{r}^N) d\mathbf{r}^N = N! \quad (28)$$

thus we can define a functional of  $\hat{\rho}^{(N)}$  that becomes the free energy when  $\hat{\rho}^{(N)}$  becomes  $\rho^{(N)}$ , the equilibrium distribution function; this functional is

$$\mathcal{F}[\hat{\rho}^{(N)}] = \frac{1}{N!} \int \hat{\rho}^{(N)}[\Phi^{(N)} + kT \ln(\Lambda^3 \hat{\rho}^{(N)})] d\mathbf{r}^N \quad (29)$$

The first two functional derivatives of  $\mathcal{F}$  can be obtained by using two equations obtained by Yvon in 1958 [57]. The equations are

$$h^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{-kT}{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)} \frac{\delta\rho(\mathbf{r}_1)}{\delta V(\mathbf{r}_2)} \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{\rho(\mathbf{r}_1)} \quad (30)$$

and its inverse,

$$c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{kT} \frac{\delta V(\mathbf{r}_1)}{\delta\rho(\mathbf{r}_2)} + \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{\rho(\mathbf{r}_1)} \quad (31)$$

where  $h^{(2)}$  and  $c^{(2)}$  are the total and direct correlation functions between

points  $\mathbf{r}_1$  and  $\mathbf{r}_2$ . The functional derivatives of  $\mathcal{F}$  are

$$\frac{\delta \mathcal{F}[\hat{\rho}^{(N)}]}{\delta \hat{\rho}(\mathbf{r}_1)} = \mu - V(\mathbf{r}_1) \quad (32)$$

$$\frac{\delta^2 \mathcal{F}[\hat{\rho}^{(N)}]}{\delta \hat{\rho}(\mathbf{r}_1) \delta \hat{\rho}(\mathbf{r}_2)} = \frac{kT \delta(\mathbf{r}_1 - \mathbf{r}_2)}{\rho(\mathbf{r}_1)} - kT c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \quad (33)$$

where  $\mu$  is the chemical potential. The derivatives are taken in the equilibrium state, so these results can be used to expand  $\mathcal{F}$  about its value for a uniform system in powers of  $\Delta \hat{\rho}(\mathbf{r}) \equiv \hat{\rho}(\mathbf{r}) - \rho_u$ . A first approximation to the excess free energy per unit area of a liquid-gas interface follows from this expansion [58,59] and leads again to the square-gradient approximation to the surface tension of Eq. (11) but with the coefficient  $m$  now given not by Eq. (10) but by

$$m(\rho) = \frac{2\pi}{3} kT \int r^4 c^{(2)}(r; \rho_u) dr \quad (34)$$

where  $c^{(2)}(r; \rho_u)$  is the direct correlation function in a uniform fluid of density  $\rho_u$ . This result is the modern justification for the square-gradient approximation. It differs from the original version in that  $m$  becomes a function of density, and, moreover, one that is not well defined, for two reasons. The first is that  $c^{(2)}(r; \rho)$  is an unknown function if  $\rho$  is a hypothetical uniform density between  $\rho^l$  and  $\rho^g$ , and second, because (34) diverges at the critical point. The two results, old and recent, are, in fact, close in their predictions for the surface tension since a well-known estimate for  $c^{(2)}(r)$ ,

$$-kT c^{(2)}(r) = \varphi_{\text{att}}(r) \quad \text{at large } r \quad (35)$$

is familiar as the mean-spherical approximation [60].

In view of these uncertainties it is fortunate that there are other lines of argument that lead to an exact expression for the surface tension in terms of the direct correlation function of the real inhomogeneous fluid. This expression can be obtained in several ways, such as the change in the grand potential  $\Omega$  that arises from an increase in surface area caused by a fluctuation in density, or from the change of pressure in the liquid needed to transform a planar interface into a spherically curved one. This last method uses Eq. (31), the second of Yvon's two equations. The result is

$$\gamma = \frac{1}{4} kT \int_{-\infty}^{\infty} \rho'(z_1) dz_1 \int (x_2^2 + y_2^2) \rho'(z_2) c^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad (36)$$

This result was obtained first by Yvon in 1948 and reported by him at a

meeting in Brussels that year but was never formally published. It was obtained independently by Triezenburg and Zwanzig in 1972 [61] and again by Lovett et al. in 1973 [62]. Like most exact equations it suffers from the disadvantage that the essential function  $c^{(2)}(\mathbf{r}_1, \mathbf{r}_2)$  is generally not known, and attempts to guess it are apt to lead to a result close to the approximate equation, (11) with (34).

The two expressions for the surface tension, Eq. (26) with the appropriate expression for the pressure tensor, and Eq. (36), are very different. The first is not restricted to a sharp interface, although it is easy to show that for such an interface and with the mean-field approximation for the liquid the virial expression of Kirkwood and Buff reduces to that of Laplace. The second obviously takes into account explicitly the diffuseness of the interface, but its relation to the virial expression is not obvious. Schofield [63] was the first to show the equivalence of the two expressions; Waldor and Wolf [64] have recently rederived the same result by a different method.

It is, perhaps, appropriate to close this chapter by noting that the essential feature of a theory of inhomogeneous fluids is the need to account explicitly for the "nonlocal" character of all properties. By this is meant that the property of the fluid at any point  $\mathbf{r}$  is determined not only by the local density at  $\mathbf{r}$ ,  $\rho(\mathbf{r})$ , and by the local temperature  $T$  and the local chemical potential  $\mu$  (the last two being constant throughout a system at equilibrium) but also by the properties of the fluid near but not at  $\mathbf{r}$ . We can distinguish three levels of accuracy. First the nonlocal character is ignored, so that the free-energy density  $\Psi$  (for example) is held to be a function only of the two independent variables  $T$  and  $\rho(\mathbf{r})$ :

$$\Psi(\mathbf{r}) = \Psi[\rho(\mathbf{r}); T] \quad (37)$$

This was the assumption made by Poisson which led him to conclude that a diffuse interface has a vanishing surface tension. It was made again in modern times by Tolman [65] and by Ono and Kondo [66].

The next level of accuracy is that of Fuchs, Rayleigh, and van der Waals, in which

$$\Psi(\mathbf{r}) = \Psi[\rho(\mathbf{r}), \nabla\rho(\mathbf{r}); T] \quad (38)$$

This leads to the square-gradient approximation and is still a useful approximation for some purposes.

Finally, we have the formally exact results, exemplified by Eq. (36), in which the free-energy density is a function of the properties of the fluid at two points and the correlation between these points:

$$\Psi(\mathbf{r}_1) = \Psi[\rho(\mathbf{r}_1), \rho(\mathbf{r}_2), c^{(2)}(\mathbf{r}_1, \mathbf{r}_2); T] \quad (39)$$

The range over which the nonlocality must be considered is the so-called correlation length in the fluid, which is generally a measure of the range of the intermolecular forces. Near the critical point, however, it grows to macroscopic size, so a classical treatment that does not account accurately for the extent of this growth leads to a significant error in its description of how the surface tension vanishes at that point.

## APPENDIX

Bikerman [29] proposed that Eq. (16) be replaced by

$$\frac{n_i(\mathbf{r})}{1 - bn(\mathbf{r})} = n_i^* \exp[-z_i eV(\mathbf{r})/kT] \quad (\text{A1})$$

where

$$n(\mathbf{r}) = \sum_i n_i(\mathbf{r}) \quad (\text{A2})$$

and  $n_i^*$  is a constant which, for a single symmetrical electrolyte, can be written

$$n_+^* = n_-^* = \frac{1}{2} n^\infty (1 - bn^\infty)^{-1} \quad n_+^\infty = n_-^\infty = \frac{1}{2} n^\infty \quad (\text{A3})$$

The charge density is given by

$$\rho(\mathbf{r}) = ze[n_+(\mathbf{r}) - n_-(\mathbf{r})] \quad (\text{A4})$$

$$= -\frac{zen^\infty \sinh[y(\mathbf{r})]}{1 + 2bn^\infty \sinh^2[y(\mathbf{r})/2]} \quad (\text{A5})$$

where  $y(\mathbf{r})$  (or  $y$ , for simplicity) is  $zeV(\mathbf{r})/kT$ . In the Gouy–Chapman treatment,  $\rho_0$ , the charge density at the plate rises exponentially with  $|V_0|$ , the surface potential, but here it is restricted by the sizes of the ions to maximum value of  $|ze/b|$ . One integration of the Poisson–Boltzmann equation gives

$$\left(\frac{dy}{dx}\right)^2 = \frac{2\kappa^2}{bn^\infty} \ln \left(1 + 2bn^\infty \sinh^2 \frac{y}{2}\right) \quad (\text{A6})$$

The total charge in the diffuse layer is proportional to the potential gradient at the electrode:

$$\begin{aligned} \sigma &= \frac{\epsilon kT}{ze} \left(\frac{dy}{dx}\right)_0 \\ &= \left[\frac{2\epsilon kT}{b} \ln \left(1 + 2bn^\infty \sinh^2 \frac{y}{2}\right)\right]^{1/2} \end{aligned} \quad (\text{A7})$$

Since  $x^{-1} \ln(1 + x) \leq 1$ , this charge is lower than that predicted by the Gouy–Chapman treatment. There seems, however, to be no way of integrating (A6) analytically to obtain  $V(x)$ . On linearization, as in the Debye–Hückel regime, the leading term is independent of  $b$ .

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## *Statistical Mechanical Sum Rules*

**J. R. Henderson**

*University of Leeds  
Leeds, England*

### **I. INTRODUCTION**

The theory of inhomogeneous fluid phenomena has been transformed during the last decade by an explosive input from physicists, into what had previously been a long-established branch of physical chemistry (Derjaguin, 1940). Particularly striking are new conceptual frameworks obtained from rigorously based models (Nakanishi and Fisher, 1982) and a highlighting of the significance of fluctuations to interfacial phenomena (Lipowsky, 1987). For example, in just one subject known as wetting (Sullivan and Telo da Gama, 1986) we now possess a unified theory of all equilibrium behavior associated with adsorption at interfaces. We are likely to see an increasing emphasis on complex fluids (Chapters 11 and 12) and in dynamic phenomena such as interfacial motion (spreading and film growth) and transport at surfaces and in confined media (Chapter 13).

The interest by physicists was driven by the consequences of inhomogeneity rather than a desire to study fluids; in particular, excitement centered on newly understood phase transitions (Cahn, 1977; Ebner and Saam, 1977). In fact, as explained in Section II.B, the physics of interfacial phenomena has opened up a new world inhabited by a myriad of phase transitions, including new classes of critical phenomena. Here the pioneering work has come from phenomenological physics, such as Landau

dau or van der Waals theories (Sullivan, 1981) and interfacial Hamiltonians (Lipowsky, 1984), and also from rigorously based lattice models (Pandit et al., 1982), including some exact results (Abraham, 1980) and Monte Carlo simulations (Binder et al., 1986). However, liquid-state theory based on molecular Hamiltonians has much to offer that complements the foregoing work (van Swol and Henderson, 1984), thanks in particular to the availability of powerful techniques borrowed from functional calculus. In this chapter we are concerned with contributions to the fundamental understanding of equilibrium interfacial phenomena obtainable from liquid-state theory founded on realistic many-body Hamiltonians.

Much of what is discussed below can be traced back to seminal work in the 1950s and 1960s that was focused toward an understanding of liquid-vapor interfaces in simple atomic fluids. In the event, the so-called simple liquid-vapor interface turned out to be an extremely difficult problem from a fundamental point of view, due to the essential role that external fields play in broken symmetry systems (Section II.A). Reviews of this work can be found in Evans (1979), Percus (1982), Rowlinson and Widom (1982), and Henderson (1986c). Here it is convenient to avoid repetition of the painful gestation by presenting a unified discussion of fluids in the presence of external fields. In particular, let us seek to establish a general context appropriate to the many varied problems that have recently been tackled from within this single mathematical framework.

In this chapter the term *statistical mechanical sum rule*, hereafter shortened to *sum rule*, refers to an equilibrium identity between a statistical thermodynamic property and an integral over correlation functions. The former are macroscopic physical quantities such as a free energy, a generalized thermodynamic field, or derivatives of a free energy with respect to thermodynamic fields. To be a sum rule a relationship must be exact (i.e., derivable from a partition function defined by a microscopic Hamiltonian). The significance of sum rules lies in the direct links they create between microscopic correlations and physical properties. Thus sum rules provide a framework for interpreting molecular models of physical phenomena. Of special importance is the fact that all macroscopic phenomena appropriate to a given Hamiltonian must be compatible with any sum rule derived from that Hamiltonian. Hence dramatic collective behavior, such as associated with phase transitions or the appearance of structural order, is often highlighted by deceptively simple sum rules (see Section IV.A). Computer simulation studies benefit from sum rules, both as a framework with which to analyze masses of computer-generated data and as checks on equilibration and incorrect procedures. Density functional theories (Chapter 3), especially those constructed to possess full internal statistical mechanical consistency, are similarly enhanced by a

close attention paid to sum rules (see Section III.D). In contrast, approximate integral equation theories invariably violate key sum rules, pointing the way to future improvements.

It is not our purpose in this chapter to attempt a complete survey of specific applications of sum rule analyses applied to inhomogeneous fluids, but rather, to present a general introduction illustrated by selected examples; the reader might also like to note a recent review by Evans and Parry (1990). In Section II we present an overview of a collection of important concepts known as broken symmetry, as relevant to inhomogeneous fluids. It is important to review these concepts because they form the context in which theoreticians derive and use sum rules applied to interfacial systems. Perhaps the greatest thrill of theoretical science is to be able to see such deep physical understanding emerge miraculously, yet inevitably, from the dry logic of statistical mechanical sum rules. In Section III we present key sum rules of particular importance to the study of inhomogeneous fluids and review their derivation from statistical mechanical theory. In Sections IV and V we discuss examples of sum rule analyses of wall–fluid interfaces and confined fluids, reflecting the tastes of the present author. Such powerful methods are always available for the study of equilibrium properties of inhomogeneous molecular systems, thanks in particular to the utility of functional calculus.

## II. BROKEN SYMMETRY

### A. Importance of External Fields

Equilibrium states of a translationally invariant Hamiltonian must themselves be translationally invariant. This is particularly significant for fluid states because fluid interfaces lack rigidity and thus readily develop fluctuations that lead to instability in the absence of stabilizing boundaries or surface fields. Thus the presence of an external field term in the Hamiltonian is essential to theories of inhomogeneous fluids. A formal proof of this statement is provided by a theorem due to Mermin (1965), reviewed in Chapter 3, which implies that the one-body density profile  $\rho(\mathbf{r})$  is uniquely determined by the one-body external field  $v(\mathbf{r})$ , and vice versa.

An external field can play up to three direct roles in controlling the behavior of inhomogeneous fluids. First, the symmetry of  $v(\mathbf{r})$  will invariably define the interfacial geometry. This includes the important case of confined fluids, where a pore width or radius is defined by a parameter contained in the wall–fluid potential. Second,  $v(\mathbf{r})$  will often be defined by a set of parameters that act as surface fields controlling the microscopic structure of wall–fluid interfaces and in special circumstances the mac-

roscopic behavior as well. The repulsive part of  $v(\mathbf{r})$  will induce oscillatory layering structure in fluids packed against walls by moderate to high pressure. An attractive contribution to  $v(\mathbf{r})$  will always contain at least two important parameters: a well depth and a range parameter, which play key roles in determining adsorption phenomena (wetting). Third, an external field can be used to stabilize an interface against instabilities arising from collective fluctuations. For example, a weak gravitational field is sufficient to stabilize a liquid–vapor interface from the wandering induced by capillary-wave fluctuations (see Section II.E).

An important class of indirect external field effects arises because boundary conditions cannot be ignored when considering phase transitions and when comparing results from different choices of ensemble. Often these macroscopic phenomena run counter to intuition obtained from work based on the strict thermodynamic limit. For example, consider the consequences of planar interfacial symmetry on wetting transitions at wall–vapor interfaces. Namely, if one induces a wetting transition (first order or continuous) by varying temperature or a surface field, the final outcome is a system with an infinitely thick film of liquid separating the wall from bulk vapor (which constitutes the far boundary condition). Clearly, this interfacial phase transition cannot be reversed; instead, to dry the wall one would now have to induce a drying transition, thereby creating an infinitely thick layer of vapor between the wall and the infinitely thick liquid film. Similar comments apply to finite systems as used in computer simulation studies. Related to these effects is the significance of boundary conditions to collective dynamics. Thus a planar liquid film does not have the same collective modes available to it as does a curved meniscus, which can spread out along a boundary wall. One should therefore bear in mind that a particular choice of geometry may induce extremely high metastable barriers preventing passage to true equilibrium states. Interesting examples of boundary effects have also been highlighted in studies of confined fluids. For example, models of capillary condensation based on pores of infinite length possess metastable barriers to pore filling (a drop must nucleate inside the pore) and to pore emptying (a bubble must nucleate inside the pore), whereas a finite open pore can empty from the pore ends without encountering significant metastability (provided that the system is not immersed in a bath of liquid) (Saam and Cole, 1975; Marini Bettolo Marconi and van Swol, 1989). Similarly, very strongly confined fluids exhibit extreme sensitivity to the choice of ensemble; for example, modeling a planar slit of width  $L$  in the canonical ensemble (fixed  $N$ , closed pore) will yield a true two-dimensional system as  $L$  tends to zero, whereas in this limit an open pore at finite chemical potential (grand canonical ensemble) can only approach a two-dimen-

sional weak gas, due to fluid being squeezed out from the pore ends (Henderson, 1986b).

## B. Phase Diagrams and Surface Phase Transitions

Experimental science tends to restrict physical understanding to that available from the use of variables that are readily to hand in the laboratory. This leads to a limited view of phenomena that are better understood as part of a larger reality—like the ant confined to a two-dimensional table top. The most important collection of physical knowledge is summarized in phase diagrams, which plot the points, lines, and surfaces that separate distinct phases of matter distinguishable via their macroscopic properties. Passage across such a boundary in phase space is known as a *phase transition*. Describing and understanding phase transitions, a favorite pastime of physicists, is of special significance because here one controls large changes in physical behavior through small changes in thermodynamic variables.

A proper understanding of phase behavior is based on the identification of thermodynamic fields (Griffiths and Wheeler, 1970). Fields are those thermodynamic variables that always yield identical values in two or more phases that lie in thermodynamic equilibrium. Thus all-field phase diagrams are the most succinct way to represent phase behavior. Furthermore, each thermodynamic field acts as a degree of freedom relevant to the Gibbs phase rule. In general, thermodynamics proceeds by constructing a thermodynamic potential to be a concave function of all relevant fields (and thus the potential itself can be regarded as a field). Taking partial derivatives of the potential with respect to each field generates a set of conjugate densities (defined to be intensive variables by appropriate division with respect to volume or area, as necessary). One then chooses spaces from within this collection of fields and densities in which to describe physical phenomena under study. The topology of such a phase space is controlled by the number of densities used. In the following section an explicit version of such a theory is given for inhomogeneous fluids, and Section II.D introduces the development of statistical mechanical models that are mathematically exact realizations of this structure.

From the above it follows that a failure to identify thermodynamic fields relevant to a class of phenomena will severely cripple attempts at a rigorous understanding, particularly with regard to conceptual meaning. This lesson has been highlighted more than once during the recent expansion of theories of inhomogeneous fluids. Here, the problem can be broken

down into two questions. First, what bulk thermodynamic fields remain applicable in inhomogeneous systems? In general, the answer is temperature ( $T$ ) and chemical potential ( $\mu$ ) but not pressure, because interfacial stress must be described by pressure tensor component profiles (Section II.D). Both  $T$  and  $\mu$  can be defined at any point within an inhomogeneous system such that each take on a constant value everywhere throughout an equilibrium state;  $T$  is given by the average molecular kinetic energy (in classical systems) and  $\mu$  by a statistical mechanical sum rule known as potential distribution theory (Section II.D). Second, do interfacial systems possess additional thermodynamic fields arising from the presence of surfaces? It was the latter question that remained largely unrecognized until the 1980s.

For example, consider wetting phenomena in the context of fluid adsorbed at a wall. Can a wall–fluid interface exhibit two or more states of adsorption at the same grand potential? If so, varying the temperature will be one route to induce interfacial phase transitions, but are there field variables present with more direct impact? In particular, note that a mathematical description of the wall–fluid interaction will introduce at least two new parameters; a well depth ( $\epsilon_w$ ) and a range ( $a_w$ ) of the wall–fluid attractive potential energy. Since we are asking whether two equilibrium states of adsorption correspond to the same values of  $(T, \mu, \epsilon_w, a_w)$ , it follows that  $\epsilon_w$  and  $a_w$  act as generalized thermodynamic fields. One realizes immediately that if the fluid is held at bulk liquid–vapor coexistence at a given temperature, a sufficiently high value of  $\epsilon_w$  will induce complete wetting of a wall–vapor interface (liquid prefers to lie next to the wall). At the other extreme, too little attraction will ensure that a wall–liquid interface can lower its free energy by interposing an infinite film of vapor between the wall and bulk liquid (a drying transition). Thus the key phase diagram for understanding wetting phenomena lies in the space  $(T, \mu, \epsilon_w)$ ; usually, one subtracts from  $\mu$  its value at bulk liquid–vapor coexistence,  $\mu_{\text{sat}}(T)$ , so that wetting transitions are confined to the plane  $\mu - \mu_{\text{sat}}(T) = 0$ . In general, Nakanishi and Fisher (1982) argue that for wall–fluid systems one expects to find a tricritical point on the wetting transition line separating first-order transitions at lower  $T$  from second-order behavior (called *critical wetting*). Adding the field  $a_w$  will turn such a tricritical point into a tricritical line; thus the key phase diagram for recording the separatrix between first-order and critical wetting lies in the field space  $(\epsilon_w, a_w)$ . It is perhaps worth noting that  $\epsilon_w$  has a direct magnetic analog: namely,  $\epsilon_w$  translates to a surface magnetic field strength and its conjugate density to the surface magnetization [see (56)]. Experimental progress in studying wall–fluid wetting phenomena has been severely hampered by a lack of control over the fields  $(\epsilon_w, a_w)$ , in

complete contrast to statistical mechanical theory and computer simulation studies, although pioneering work by Durian and Franck (1987) has shown the way to the development of early approaches toward laboratory control. The future will surely see such work gaining enormous technological significance.

Another example of the significance of statistical physics to inhomogeneous fluid phenomena concerns the subject of fluids absorbed in porous media (confined fluids). The basic parameter of a pore is its width ( $L$ ) or radius ( $R$ ) (i.e., the extent along the confining direction). Two-phase coexistence of fluid within an open pore (equilibrated with an outside reservoir via exchange of particles through the ends of the pore) is known as capillary condensation or evaporation and has long been observed as a shift in the bulk liquid–vapor coexistence curve.\* A full conceptual understanding of this phenomena requires the realization that  $L$  (or  $R$ ) plays the role of yet another thermodynamic field. Thus capillary condensation takes place in the space  $(T, \mu, L)$ . The density conjugate to  $L$  is known as the *solvation force* (or *disjoining pressure*) (Evans and Marini Bettolo Marconi, 1987). The field  $\epsilon_w$  is also important, since capillary condensation will interact strongly with any nearby instability toward wetting at a pore wall. Also, it is thermodynamically possible for layering transitions at the pore wall(s) to precede capillary condensation.

The foregoing considerations constitute a qualitative explanation of the striking richness of the phase behavior of inhomogeneous fluids. Each new relevant field increases phase space by an extra dimension and introduces additional potential phase transitions, following the Gibbs phase rule. Recent work on theories of single-component atomic fluids adsorbed at walls and in pores has identified examples of layering transition sequences, prewetting transitions between thin and thick films, various classes of wetting transitions, and capillary condensation transitions. Generalizations to molecular fluids or fluid mixtures would greatly enhance this complexity (Section II.C). Furthermore, the full mathematical technology of thermodynamics is immediately applicable to these extended phase spaces (i.e., Maxwell relations, Clapeyron equations,  $C_p - C_v$  relations, etc.). This includes standard approaches to phase transitions, such as mean-field van der Waals loops and renormalization group critical phenomena but now involving the newly identified thermodynamic variables. Surface critical phenomena have excited particular theoretical interest

\*Strictly speaking, one should limit this use of the phrase two-phase coexistence to systems in which the fluid remains unconfined in at least two dimensions (slit pores). However, the effects of finite-size rounding of phase transitions are usually exponentially small and thus will rarely be seen (Evans, 1990).



because of the association with exponent relations, scaling theories, and dramatic collective fluctuations (soft modes). In some cases these modes are familiar from bulk statistical mechanics, but here they possess the character of a lower dimensionality (the dimensionality of the interface), while other surface critical phenomena concern interfacial modes such as capillary waves.

Explicit examples of the foregoing conclusions are discussed below; here, let us end by noting that phase diagrams of inhomogeneous fluid phenomena are not always restricted to spaces belonging to the set of fields and densities discussed above, where one can be assured of the usual rules. Instead, some workers have found it useful to introduce hybrid surface–bulk diagrams, in which surface thermodynamic variables are mixed with purely bulk variables. For example, in discussing wetting transitions it has been common to plot, at fixed  $(\epsilon_w, a_w)$ , the transition point and any associated prewetting transition line, superimposed on the bulk liquid–vapor coexistence curve drawn in  $(T, \rho)$  space.  $T$  is a valid surface field, but  $\rho$  is merely the bulk fluid density in equilibrium with the interface. Given the bulk equation of state,  $(T, \rho)$  can be transformed into  $(T, \mu)$ , which are both true surface fields. Similar comments can be made about adsorption isotherms for confined fluids plotted versus a bulk pressure  $p$  belonging to a reservoir with which the pore fluid is defined to be in thermodynamic equilibrium; in particular,  $p$  is not related to any pressure tensor component describing the inhomogeneous fluid.

### C. Statistical Thermodynamics of Broken Symmetry

Gibbs (1906) has shown how to construct thermodynamic theories of interfacial properties that remain consistent with rigorous models without the need for explicit statistical mechanical solutions of inhomogeneous systems. The trick is to introduce mathematically defined dividing surfaces, equivalent to factoring the partition function into a bulk term (hereafter assumed to be known or defined) and surface terms; the latter are simply the parts left over. For model wall–fluid interfaces the natural choice of dividing surface lies on the equipotential of infinite wall–fluid repulsion. This choice has the benefit that at fixed geometry the dividing surface is independent of all relevant thermodynamic fields. The statistical thermodynamics of inhomogeneous fluids is invariably most conveniently based on  $\Omega$ , the *grand-canonical potential* (often shortened to *grand potential*). This is because most fluid interfaces exchange molecules with neighboring bulk fluids; consider, for example, a wall–liquid interface

modeled in semi-infinite geometry, or liquid confined to an open pore immersed in a reservoir of gas.

Thus, following Gibbs, let us define the surface excess grand potential with respect to a choice of dividing surface as

$$\Omega^{\text{ex}} = \Omega - \Omega_b \quad (1)$$

where subscript  $b$  denotes the usual bulk term. Then the second law of thermodynamics applied to a planar wall–fluid interface of area  $A$ , such as discussed in Section II.B, will read

$$d\Omega^{\text{ex}} = -S^{\text{ex}} dT - A\Gamma d\mu + \left(\frac{\Omega^{\text{ex}}}{A}\right)dA - A\Theta d\epsilon_w - A\Psi da_w \quad (2a)$$

where  $S^{\text{ex}}$  is the surface excess entropy defined analogous to (1), and  $\Gamma$  denotes adsorption (i.e.,  $N^{\text{ex}} \equiv A\Gamma$ , where  $N$  is the total number of fluid molecules). If the system was bounded by two planar walls of separation  $L$  (a slit pore), then, in addition to doubling the single wall terms appearing on the right side of (2a), one would need to add the term

$$-Af dL \quad (2b)$$

where  $f$  is known as the *solvation force*.

Underlying (2) is the fact that the thermodynamic potential can be expressed as a function of all relevant field variables [i.e.,  $\Omega^{\text{ex}}(T, \mu, A, \epsilon_w, a_w, L)$ ]. The coefficients of each term on the right side of Eq. (2) are the thermodynamic densities conjugate to each field:

$$\frac{\partial(\Omega^{\text{ex}}/A)}{\partial T} = \frac{-S^{\text{ex}}}{A} \quad (3a)$$

$$\frac{\partial(\Omega^{\text{ex}}/A)}{\partial \mu} = -\Gamma \quad (3b)$$

$$\frac{\partial\Omega^{\text{ex}}}{\partial A} = \frac{\Omega^{\text{ex}}}{A} \quad (3c)$$

$$\frac{1}{A} \frac{\partial\Omega}{\partial \epsilon_w} = -\Theta \quad (3d)$$

$$\frac{1}{A} \frac{\partial\Omega}{\partial a_w} = -\Psi \quad (3e)$$

$$\frac{\partial(\Omega^{\text{ex}}/A)}{\partial L} = -f \quad (3f)$$

where  $\Omega$  has appeared in (3d) and (3e) to highlight the fact that  $\epsilon_w$  and

$a_w$  are strictly surface fields. In Section II.D we explain how statistical mechanics leads to sum rule expressions for the densities above; in particular,  $\Gamma$ ,  $\Theta$ ,  $\Psi$ , and  $f$  are all defined by simple integrals over the one-body density profile and thus act as order parameters for interfacial structure. It follows that further differentiation of these densities with respect to the fields  $(\mu, \epsilon_w, a_w, L)$  generates surface compressibilities.

Equations (2) and (3) admit many generalizations. One example would be the addition of external electric field terms; see Chapters 5 and 6 for explicit results concerning inhomogeneous plasmas and electrolytes. Generalizations to molecular fluids and fluid mixtures are straightforward and will be touched on briefly later in this chapter. Here, let us confine our remarks to noting the rapid increase in complexity that such generalizations must bring (i.e., the large growth in the number of relevant field variables). For example, a molecular fluid interacts with a wall not just through center of mass fields  $(\epsilon_w, a_w)$  but also through fields that act on orientational degrees of freedom. Thus molecular fluids exist within an extended space that allows for such phenomena as orientational wetting. The situation with mixtures is particularly complex in general, since each additional fluid component will involve not just one extra chemical potential field but will also add a new member to every class of surface field; the latter fields directly control phenomena such as selective adsorption. In this way, (2) enables us to truly appreciate the scale of the complexity of phase behavior belonging to the natural world.

An important paper by Evans and Marini Bettolo Marconi (1987) has emphasized that the standard mathematical procedures of bulk thermodynamics are equally applicable to inhomogeneous fluid problems, such as defined by (2). For example, a plethora of surface Maxwell relations follow directly from (2) and (3), such as

$$\frac{\partial \Gamma}{\partial \epsilon_w} = \frac{\partial \Theta}{\partial \mu} \quad (4a)$$

$$\frac{\partial \Gamma}{\partial L} = \frac{\partial f}{\partial \mu} \quad (4b)$$

and defining additional functions (e.g.,  $Z \equiv \Omega^{\text{ex}} + N^{\text{ex}}\mu$ ) yields many more of these relations:

$$\left( \frac{\partial \mu}{\partial \epsilon_w} \right)_{\Gamma} = - \left( \frac{\partial \Theta}{\partial \Gamma} \right)_{\epsilon_w} \quad (4c)$$

$$\left( \frac{\partial \mu}{\partial L} \right)_{\Gamma} = - \left( \frac{\partial f}{\partial \Gamma} \right)_{L} \quad (4d)$$

Further standard manipulations lead to results mathematically equivalent to the well-known  $C_p-C_v$  relation; for example, at fixed  $\{T, A, a_w\}$  we obtain from  $\Theta(\mu, \epsilon_w)$  and  $\Theta(\Gamma, \epsilon_w)$  a result of particular significance to critical wetting transitions (Evans and Parry, 1989):

$$\left(\frac{\partial\Theta}{\partial\epsilon_w}\right)_\Gamma - \left(\frac{\partial\Theta}{\partial\epsilon_w}\right)_\mu = \left(\frac{\partial\Theta}{\partial\mu}\right)_{\epsilon_w} \left(\frac{\partial\mu}{\partial\epsilon_w}\right)_\Gamma \quad (5a)$$

$$= -\left(\frac{\partial\Gamma}{\partial\epsilon_w}\right)_\mu^2 \left(\frac{\partial\Gamma}{\partial\mu}\right)_{\epsilon_w}^{-1} \quad (5b)$$

where the second version follows from (4a) and  $\Gamma(\mu, \epsilon_w)$ .

Phase coexistence in inhomogeneous fluids can be analyzed similarly. In particular, consider all the Clapeyron equations that follow from inserting (2) into

$$d\Omega_\alpha^{\text{ex}} = d\Omega_\beta^{\text{ex}}$$

Thus the slope of phase coexistence at fixed  $(A, \epsilon_w, a_w, L)$  is determined by

$$\left(\frac{d\mu}{dT}\right)_{\text{cc}} = -\frac{(S_\alpha^{\text{ex}} - S_\beta^{\text{ex}})/A}{\Gamma_\alpha - \Gamma_\beta} \quad (6a)$$

where cc denotes coexistence curve. Similarly, at fixed  $(T, A, \epsilon_w, a_w)$ ,

$$\left(\frac{d\mu}{dL}\right)_{\text{cc}} = -\frac{f_\alpha - f_\beta}{\Gamma_\alpha - \Gamma_\beta} \quad (6b)$$

and so on. Evans and Marini Bettolo Marconi (1987) point out that mean-field theories of first-order transitions will yield van der Waals loops in isotherms of order parameters such as  $\Gamma$ ,  $\Theta$ ,  $\Psi$ , and  $f$  when plotted versus their conjugate fields. Furthermore, it follows from (3b) and (3d) to (3f), respectively, that the coexisting values of these order parameters are determined by applying equal-area constructions to the loops. The vanishing of such loops yields standard criteria for criticality, but now in unfamiliar variables.

## D. Grand-Canonical Ensemble

Explicit statistical mechanical realizations of the thermodynamic structure discussed in Section II.C follow from introduction of the grand partition function  $\Xi$ :

$$\Omega \equiv -kT \ln \Xi \quad (7a)$$

$$\Xi = \sum_{N=0}^{\infty} \frac{\Lambda^{-3N}}{N!} \int \prod_{i=1}^N di \exp\left(\frac{-H_N + \mu N}{kT}\right) \quad (7b)$$

where  $\Lambda \equiv (h^2/2m\pi kT)^{1/2}$  is the translational de Broglie wavelength (i.e., let us assume classical dynamics) and  $H_N$  denotes an  $N$ -body potential. For models of inhomogeneous fluids we write

$$H_N \equiv \Phi(1 \cdots N) + \sum_{i=1}^N v(i) \quad (7c)$$

where  $\Phi$  is a fluid–fluid many-body potential and  $v$  is the external field. Note that  $H_N$  does not depend on the fields  $T$  and  $\mu$ , while all the remaining fields appearing on the right side of (2) can be introduced exclusively in terms of the one-body potential. For example, at fixed  $a_w$  a basic model of a planar wall–fluid interface is

$$v(z, \epsilon_w) = \epsilon_w v_{\epsilon_w}(z) \quad (8)$$

and a simple model of confined fluids is given by a symmetric planar slit of width  $L$ , at fixed  $(\epsilon_w, a_w)$ :

$$v(z, L) = v^\infty(z) + v^\infty(L - z) \quad [v^\infty(z) \equiv \infty, \quad z < 0] \quad (9)$$

where the superscript  $\infty$  denotes the potential of a single planar wall situated at  $z = 0$ . It follows that it is not necessary to specify the intermolecular potential  $\Phi$  in order to take derivatives of the grand potential with respect to field variables. In fact, at fixed temperature the effects of  $\Phi$  can be entirely subsumed within the distribution functions. Thus isothermal statistical mechanics generates theories of inhomogeneous fluids that are completely general with respect to fluid–fluid intermolecular forces.

A formal statement of this statistical mechanical approach is given by the following hierarchy of functional derivatives, which follow immediately from (7):

$$\left( \frac{\delta \Omega}{\delta [\mu - v(1)]} \right)_T = -\rho(1) \quad (10a)$$

$$\left( \frac{\delta^2 \Omega}{\delta [\mu - v(1)] \delta [\mu - v(2)]} \right)_T = -\frac{1}{kT} [\rho^{(2)}(12) - \rho(1)\rho(2) + \rho(1)\delta(12)] \quad (10b)$$

and so on; that is, the  $s$ th functional derivative generates the  $s$ -body distribution function  $\rho^{(s)}(1 \cdots S)$ . Note that (10a) constitutes a general sum rule expression for all of the field derivatives listed in (3), apart from (3a) and (3c) (van Swol and Henderson, 1986):

$$\left( \frac{\partial \Omega}{\partial \lambda_i} \right)_{T, \{\lambda_j \neq i\}} = - \int d1 \rho(1) \frac{\partial}{\partial \lambda_i} [\mu - v(1)] \quad \lambda_i \in \{\mu, \epsilon_w, a_w, L\} \quad (11)$$

Further differentiation and (10b) yields sum rules for a set of compressibilities:

$$\begin{aligned} \left( \frac{\partial^2 \Omega}{\partial \lambda_i \partial \lambda_j} \right)_{T, \{\lambda_k \neq i, j\}} &= -\frac{1}{kT} \int d1 \rho(1) \frac{\partial}{\partial \lambda_i} [\mu - v(1)] \int d2 \rho(2) \frac{\partial}{\partial \lambda_j} [\mu - v(2)] \\ &\times \left[ h(12) + \frac{\delta(12)}{\rho(1)} \right] - \int d1 \rho(1) \frac{\partial^2}{\partial \lambda_i \partial \lambda_j} [\mu - v(1)] \lambda_i, \lambda_j \in \{\mu, \epsilon_w, a_w, L\} \end{aligned} \quad (12)$$

where we have introduced the total correlation function  $h(12) \equiv [\rho^{(2)}(12) - \rho(1)\rho(2)]/\rho(1)\rho(2)$ . In recognition of the importance of (12), the statistical mechanical theory above is referred to as the *compressibility route*. The compressibility route to the statistical mechanics of inhomogeneous fluids is of special significance because it focuses directly on the thermodynamic fields and densities of relevance, apart from the temperature and entropy. Thus (11) generates single integral sum rules for the densities  $\Gamma$ ,  $\Theta$ ,  $\Psi$ , and  $f$ , and (12) highlights the microscopic nature of collective modes responsible for interfacial critical phenomena. The surface excess grand potential itself is a special case that is treated separately in Section III.C.

Other important results also follow from the hierarchy (10). In particular, consider the consequences of translational symmetry (i.e., applied to the entire system, including boundaries):

$$\begin{aligned} \delta \rho(\mathbf{r}) &\equiv [\rho(\mathbf{r} + \mathbf{\Delta}) - \rho(\mathbf{r})] \rightarrow \mathbf{\Delta} \cdot \nabla \rho(\mathbf{r}) + \mathcal{O}(\Delta^2) \\ \delta v(\mathbf{r}) &\equiv [v(\mathbf{r} + \mathbf{\Delta}) - v(\mathbf{r})] \rightarrow \mathbf{\Delta} \cdot \nabla v(\mathbf{r}) + \mathcal{O}(\Delta^2) \end{aligned} \quad (13)$$

Combining (13) with (10a) just confirms that finite pressure and finite volume go together [see (23b)]. However, (13) and (10b) yield a key integrodifferential equation for the density profile (Lovett et al., 1976; Wertheim, 1976):

$$\nabla^\alpha \rho(1) = -\frac{1}{kT} \left[ \rho(1) \nabla^\alpha v(1) + \rho(1) \int d2 \rho(2) h(12) \nabla^\alpha v(2) \right] \quad (14)$$

Note that integrating equations such as (14) across an interface generates potentially useful sum rules. Even in cases where  $v(\mathbf{r})$  contains discontinuities it is straightforward to make use of the integral equations and sum rules above; one simply introduces the one-body  $y$ -function  $n(\mathbf{r})$ , defined by

$$\rho(\mathbf{r}) \equiv n(\mathbf{r}) \exp \left[ \frac{-v(\mathbf{r})}{kT} \right] \quad (15)$$

and uses the fact that graphical analysis will always prove that  $n(\mathbf{r})$  is a continuous function, even across a hard wall boundary [see also (17) and (29)].

The statistical mechanical hierarchy (10) treats the grand potential as a functional of the one-body field,  $\Omega[\mu - v]$ . It is equally permissible to regard  $\Omega$  as a functional of the one-body density,  $\Omega[\rho]$ , because at fixed  $(T, \mu)$  we know that  $\rho(\mathbf{r})$  is uniquely defined by  $v(\mathbf{r})$  and vice versa (Mermin, 1965). This inversion of (10) generates a complementary hierarchy of correlation functions, called direct correlation functions. Since this approach forms the basis of density functional theory (Chapter 3), let me restrict the discussion here to listing a few key results:

$$\Omega[\rho] \equiv \mathcal{F}[\rho] - \int d1 \rho(1)[\mu - v(1)] \quad (16a)$$

$$\mathcal{F}[\rho] \equiv \mathcal{F}_{\text{ex}}[\rho] + kT \int d1 \rho(1) \{\ln[\Lambda^3 \rho(1)] - 1\} \quad (16b)$$

$$\frac{\delta^s \mathcal{F}_{\text{ex}}[\rho]}{\delta \rho(1) \cdots \delta \rho(S)} \equiv -kT c^{(s)}(1 \cdots S) \quad (16c)$$

The first two of these results decompose the grand potential into one-body terms plus the many-body free energy,  $\mathcal{F}_{\text{ex}}$ ; here, the subscript refers to the excess over ideal free energy. The hierarchy (16c) is the analog of (10), with  $c^{(s)}(1 \cdots S)$  denoting the  $s$ -body direct correlation function. At equilibrium, the first member of this hierarchy can be rewritten as

$$\ln [\Lambda^3 \rho(1)] = c^{(1)}(1) + \frac{\mu - v(1)}{kT} \quad (17)$$

that is,  $-kT c^{(1)}(1)$  is the excess (over ideal) chemical potential. Applying (13) to the second member of (16c) and inserting this into the gradient of (17) yields the inverse of (14):

$$\nabla^\alpha \rho(1) = -\frac{1}{kT} \rho(1) \nabla^\alpha v(1) + \rho(1) \int d2 c^{(2)}(12) \nabla^\alpha \rho(2) \quad (18)$$

The general statement of this functional inversion between density and external field, known as the Ornstein–Zernike equation, can be written compactly as

$$\int d3 G(13) G^{-1}(32) = \delta(12) \quad (19a)$$

where I have used (10b) and (16c) and (17) to define

$$G(12) \equiv kT \frac{\delta \rho(1)}{\delta [\mu - v(2)]} = \rho^{(2)}(12) - \rho(1)\rho(2) + \rho(1)\delta(12) \quad (19b)$$

$$G^{-1}(12) \equiv \frac{1}{kT} \frac{\delta [\mu - v(1)]}{\delta \rho(2)} = \frac{\delta(12)}{\rho(1)} - c^{(2)}(12) \quad (19c)$$

Macroscopic symmetry will considerably simplify (19a); for example, in planar symmetry we have

$$\int_{-\infty}^{\infty} dz_3 G(z_1, z_3; Q) G^{-1}(z_3, z_2; Q) = \delta(z_{12}) \quad (20a)$$

where I have introduced the transverse Fourier transform

$$G(z_1, z_2; Q) \equiv \int d^{d-1} \mathbf{R}_{12} e^{i\mathbf{Q} \cdot \mathbf{R}_{12}} G(z_1, z_2, R_{12}) \quad (20b)$$

and similarly for its inverse;  $\mathbf{R}_{12}$  lies in the plane of the surface and  $d$  denotes the overall dimensionality (e.g., in  $d = 3$ ,  $R_{12}^2 = x_{12}^2 + y_{12}^2$ ). Provided that  $G$  and  $G^{-1}$  can be expanded up to order  $Q^2$ ,

$$G(z_1, z_2; Q) = G_0(z_1, z_2) + Q^2 G_2(z_1, z_2) + \dots \quad (20c)$$

one can equate terms up to order  $Q^2$  in (20a) to derive

$$G_2(z_1, z_2) = - \int_{-\infty}^{\infty} dz_3 \int_{-\infty}^{\infty} dz_4 G_0(z_1, z_4) G_2^{-1}(z_4, z_3) G_0(z_3, z_2) \quad (20d)$$

This result is important for an understanding of surface critical phenomena because it enables singular contributions to  $G_2(z_1, z_2)$  to be deduced from divergences in  $G_0$ , given that  $G_2^{-1}$  is sufficiently well behaved (Evans and Parry, 1989). Of course, the above relies on the assumption that the decay of  $G(z_1, z_2, R_{12})$  along the interface is not such as to render the integral

$$G_2(z_1, z_2) = - \frac{1}{2(d-1)} \int d^{d-1} \mathbf{R}_{12} R_{12}^2 G(z_1, z_2, R_{12}) \quad (20e)$$

ill defined. In Section III.C we shall see that  $G_2(z_1, z_2)$  determines the interfacial tension; thus planar surface critical phenomena at which the interface remains intact (neither zero nor infinite surface tension) should always be described by (20) up to and including order  $Q^2$ . This is in contrast to Ornstein–Zernike theory of bulk critical phenomena, which breaks down in  $d \leq 4$ ; that is, below some upper-critical dimension the disappearance of interfacial structure is associated with a nonzero value of the exponent  $\eta$ .

Compressibility route analyses of interfacial fluid phenomena are carried out without explicit reference to fluid–fluid intermolecular forces; instead, one proceeds via increasing familiarity with the behavior of the distribution functions  $\rho(1)$  and  $\rho^{(2)}(12)$ . Alternatively, one can introduce specific molecular models of fluids

$$\Phi(1 \cdots N) = \sum_{i < j} \varphi^{(2)}(ij) + \sum_{i < j < k} \varphi^{(3)}(ijk) + \dots \quad (21)$$



and generate the distribution function hierarchy by taking functional derivatives with respect to  $\varphi^{(s)}$ . This is the formal basis of the virial route to statistical mechanics; in particular, introducing a displacement field  $\mathbf{e}(\mathbf{r})$ , it follows that the leading-order change in free energy is given by

$$(\delta\Omega)_{T,\mu} = \langle -kT \sum_i \nabla \cdot \mathbf{e}_i + \sum_i \mathbf{e}_i \cdot \nabla v_i + \sum_i \mathbf{e}_i \cdot \nabla_i \Phi \rangle \quad (22)$$

which is the general expression for a virial equation of state; hereinafter  $\langle \rangle$  denotes a statistical mechanical average defined by a partition function. It is convenient to introduce a pressure tensor  $p^{\alpha\beta}$ :

$$\nabla^\beta p^{\alpha\beta}(\mathbf{r}) \equiv kT \nabla^\alpha \rho(\mathbf{r}) + \langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i^\alpha \Phi \rangle \quad (23a)$$

$$= -\rho(\mathbf{r}) \nabla^\alpha v(\mathbf{r}) \quad (23b)$$

(where the usual summation convention over Greek indices applies) so that (22) reduces to the usual stress-strain form [e.g., Henderson, 1986c]:

$$(\delta\Omega)_{T,\mu} = - \int p^{\alpha\beta} \nabla^\beta e^\alpha + \int \rho e^\alpha \nabla^\alpha v \quad (24)$$

The step from the right side of (23a) to (23b) follows directly from the statistical mechanical definition of  $\rho(\mathbf{r})$  [eq. (26c)]. The hierarchy of equations obtained from direct differentiation of the distribution functions is usually referred to as the YBG hierarchy (Yvon, 1935). Equation (23b) shows that formally the two terms on the right side of (24) cancel (i.e., the force exerted on the walls by the fluid balances the force exerted on the fluid by the walls). Thus (23b) expresses mechanical equilibrium. When applying the virial theorem to inhomogeneous fluids, one notes that it is the first term on the right side of (24) that concerns the work done on the fluid. For example, in planar symmetry it follows that [e.g., Henderson and van Swol (1984)]

$$\frac{\Omega}{A} = - \int_{-z}^{\infty} dz p_T(z) \quad (25a)$$

where  $p_T$  denotes the transverse component of the pressure tensor:

$$p^{\alpha\beta}(z) = \begin{pmatrix} p_T(z) & 0 & 0 \\ 0 & p_T(z) & 0 \\ 0 & 0 & p_N(z) \end{pmatrix} \quad (25b)$$

However, only the normal component is determined by (23) in planar symmetry:

$$p'_N(z) = -\rho(z)v'(z) \quad (25c)$$

More generally, (23) follows from consideration of the rate of change of momentum density:

$$j^\alpha(\mathbf{r}, t) = -\nabla_r^\beta \left[ \sum_i \frac{p_i^\alpha p_i^\beta}{m_i} \delta(\mathbf{r} - \mathbf{r}_i) \right] - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) (\nabla_i^\alpha \Phi + \nabla_i^\alpha v) \quad (26a)$$

$$\equiv \nabla^\beta \sigma^{\alpha\beta}(\mathbf{r}, t) - \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i^\alpha v(\mathbf{r}) \quad (26b)$$

and the conservation of linear momentum (i.e.,  $\langle \dot{J}_\alpha \rangle = 0$ ) implies (23), with

$$p^{\alpha\beta} \equiv -\langle \sigma^{\alpha\beta} \rangle \quad \rho(\mathbf{r}) \equiv \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle \quad (26c)$$

Equation (26) does not uniquely define the many-body contribution to the pressure tensor:

$$\nabla^\beta p_c^{\alpha\beta}(\mathbf{r}) \equiv \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i^\alpha \Phi \right\rangle \quad (27)$$

In particular, for pair potential fluids, Schofield and Henderson (1982) have shown that (27) is consistent with an infinite class of pressure tensors, with the nonuniqueness expressed in terms of an arbitrary path integral representing lines of intermolecular stress. The result (25a) is invariant with respect to such a choice of pressure tensor, but not higher-order moments of  $p_T(z)$ . For computer simulation studies of pair potential models of inhomogeneous fluids a convenient choice is to adopt the pressure tensor of Irving and Kirkwood (1950):

$$p_{\text{IK}}^{\alpha\beta}(\mathbf{r}) = kT\rho(\mathbf{r})\delta^{\alpha\beta} - \frac{1}{2} \int d\mathbf{r}_{12} r_{12}^\alpha r_{12}^\beta \frac{\varphi'(r_{12})}{r_{12}} \int_0^1 dl \times \rho^{(2)}[\mathbf{r} - l\mathbf{r}_{12}, \mathbf{r} + (1-l)\mathbf{r}_{12}] \quad (28)$$

but one must beware of using this result to calculate expressions which, in contrast to (25a), are ill defined by (27).

In general, it is notoriously difficult to transform explicitly between complementary integral equations and sum rules generated by the compressibility route and the virial route, respectively [see, e.g., eqs. (14), (18), and (23)]. Thus it is of some interest to note that a specific correspondence between the two routes can be made (Henderson, 1983). The link is via a sum rule for the configurational chemical potential (i.e., the one-body direct correlation function), known as potential distribution theory (Widom, 1963):

$$c^{(1)}(\mathbf{r}) = \ln \left\langle \exp \left[ -\frac{\Phi(\mathbf{r})}{kT} \right] \right\rangle \quad (29a)$$

where  $\Phi'(\mathbf{r})$  denotes the potential field due to a hypothetical test molecule fixed at position  $\mathbf{r}$ :

$$\Phi_{N'}(\mathbf{r}) = \Phi(1 \cdots N + 1)_{\mathbf{r}_{N+1} = \mathbf{r}} - \Phi(1 \cdots N) \quad (29b)$$

The proof of (29) follows immediately from consideration of the partition function  $\Xi'(\mathbf{r})$  defined by a molecular system (7c) in the presence of the many-body external field defined by (29b):

$$\Xi'(\mathbf{r}) = \exp\left[-\frac{\mu - v(\mathbf{r})}{kT}\right] \Lambda^3 \rho(\mathbf{r}) \Xi \quad (30a)$$

That is, the configurational chemical potential at position  $\mathbf{r}$  is given by the work done, at constant  $(T, \mu)$ , to insert a test molecule at that position [see (17)]:

$$\begin{aligned} \Omega'(\mathbf{r}, T, \mu) - \Omega(T, \mu) &\equiv -kT \ln \frac{\Xi'(\mathbf{r})}{\Xi} \\ &= -kT c^{(1)}(\mathbf{r}) \end{aligned} \quad (30b)$$

Direct differentiation of (29a) yields (Henderson, 1983)

$$\nabla^{\alpha} c^{(1)}(\mathbf{r}) = -\frac{\left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i^{\alpha} \Phi \right\rangle}{kT \rho(\mathbf{r})} \quad (31a)$$

or, using (17) together with  $\nabla^{\alpha} \mu = 0$ ,

$$\nabla^{\alpha} \rho(\mathbf{r}) = -\frac{1}{kT} [\rho(\mathbf{r}) \nabla^{\alpha} v(\mathbf{r}) + \left\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i^{\alpha} \Phi \right\rangle] \quad (31b)$$

Thus, for a pure field, Eqs. (14), (18), and (23) are all equivalent expressions of mechanical equilibrium (hydrostatic stability). One can also use potential distribution theory to derive various statistical mechanical hierarchies based on alternative formulations of configurational chemical potential, such as Kirkwood–Hill scaling (Hill, 1959) and scaled particle theory (Reiss et al., 1960). Namely, if  $\lambda$  is any parameter that one chooses to introduce into the test particle field  $\Phi'$ , then  $\partial c^{(1)}/\partial \lambda$  follows immediately from (29a), or alternatively, from the functional derivative  $\delta \Omega'/\delta \Phi'$  (Henderson, 1983). Note that for pair potential fluids  $\Phi'$  is a one-body field and  $\rho'(\mathbf{r}')$ , in the presence of a test molecule at  $\mathbf{r}$ , is just  $\rho^{(2)}(\mathbf{r}, \mathbf{r}')/\rho(\mathbf{r})$  in the real system (defined by unfreezing the test molecule); in this case by transforming to a frozen test-molecule system one can immediately make use of the compressibility route hierarchy (10). Thus, for pair potential fluids Kirkwood–Hill scaling and scaled particle theory are just specific versions of the general sum rule (11).

The test-molecule approach is easily generalized to encompass the entire distribution function hierarchy; in particular, (30a) generalizes to

$$\Xi^{t_1 \cdots t_s}(\mathbf{r}_1 \cdots \mathbf{r}_s) = (\Lambda^3 e^{-\mu/kT})^s \exp \left[ \sum_{i=1}^s \frac{v(\mathbf{r}_i)}{kT} \right] \rho^{(s)}(\mathbf{r}_1 \cdots \mathbf{r}_s) \Xi \quad (32a)$$

and (30b) generalizes to

$$\begin{aligned} \Omega^{t_1 \cdots t_s}(\mathbf{r}_1 \cdots \mathbf{r}_s, T, \mu) - \Omega(T, \mu) &= \sum_{i=1}^s [\Omega^t(\mathbf{r}_i, T, \mu) - \Omega(T, \mu)] \\ &= -kT \ln [g^{(s)}(\mathbf{r}_1 \cdots \mathbf{r}_s)] \end{aligned} \quad (32b)$$

where  $g^{(s)}$  denotes the  $s$ -body correlation function  $\rho^{(s)}(\mathbf{r}_1 \cdots \mathbf{r}_s) / \rho(\mathbf{r}_1) \cdots \rho(\mathbf{r}_s)$ . The right side of (32b) is referred to as a potential of mean force, that is, the work done to insert  $s$  test molecules at positions  $\mathbf{r}_1 \cdots \mathbf{r}_s$ , minus the work required to insert them singly at these same positions. In homogeneous fluids a potential of mean force is just the work required to bring test molecules together from infinity. Note that the partition function (32a) includes direct interactions between the test molecules; alternatively, one can leave this contribution out and then (32b) would yield the  $s$ -body  $y$ -function. Note also that the left sides of (30b) and (32b) are surface excess grand potentials, belonging to test-molecule systems. For homogeneous pair potential fluids (32) implies that

$$-kT \frac{\partial}{\partial r_{12}} \ln [g(r_{12})] = \frac{\partial}{\partial r_{12}} \Omega^{t_1 t_2}(r_{12}) \quad (33)$$

Here the potential of mean force is a type of solvation force similar to (3f).

To conclude this survey of the grand ensemble applied to inhomogeneous fluids, let me indicate the nature of generalizations to mixtures and to molecular fluids. If the fluid has  $\nu$  components, the partition function (7b) is extended to include a sum over  $\mu_\nu$  and in general,  $v_\nu(\mathbf{r})$  (i.e., each type of molecule is associated with a particular one-body field). Functional derivatives of  $\Omega$  with respect to these one-body fields generates  $\rho_\nu(1)$  and  $\rho_{\nu\nu}^{(2)}(12)$ , directly analogous to (10). Thus (11) to (15) are straightforwardly generalized to the case of mixtures. Similar remarks apply to the density functional formalism [Eqs. (16) to (20)] (i.e., one considers functional derivatives with respect to  $\delta\rho_\nu$ ) (Lebowitz, 1964). The only point that requires some care is to note that whereas the correlation functions are defined by partial functional derivatives (all remaining variations set to zero), results such as the generalizations of (14), (18), and (19a) concern full variations and thus contain a sum over  $\nu$  (i.e., each  $\rho_\nu$  is a functional of all the external fields and each  $v_\nu$  is a functional of all the

density profiles). The virial route is generalized to mixtures by extending (21) to include all the various classes of intermolecular potentials. The pressure tensor gradient, defined as (26), now involves a sum over components  $\nu$ ; however, the YBG hierarchy splits into separate equations (one for each component):

$$\nabla^\alpha \rho_\nu(\mathbf{r}) = -\frac{1}{kT} [\rho_\nu(\mathbf{r}) \nabla^\alpha v_\nu(\mathbf{r}) + \langle \sum_{i_\nu} \delta(\mathbf{r} - \mathbf{r}_{i_\nu}) \nabla_{i_\nu}^\alpha \Phi \rangle] \quad (34)$$

From the obvious generalization of potential distribution theory [i.e., (29a) with  $\Phi_\nu'(\mathbf{r})$ ] it follows that for any given  $\nu$ , (34) is equivalent to  $\nabla_{\mu_\nu} = 0$  (Henderson, 1983). Thus in mixtures the condition for diffusive equilibrium applies to each component separately, but not mechanical equilibrium [i.e., the latter requires all members of the set (34) to hold].

A conceptually straightforward generalization to molecular fluids follows from decomposing all the forces into center-of-mass interactions (involving  $\mathbf{r}$ ) and angular interactions (involving a set of angles  $\boldsymbol{\omega}$ ). Thus the external field is now  $v(\mathbf{r}, \boldsymbol{\omega})$ . Note that this form applies even in simple cases such as planar boundary, since the center of mass of, say, a rod-shaped molecule can approach more closely to the wall when the molecule is oriented along the wall than when it points perpendicular to the wall. In this formalism all of the statistical mechanics above is immediately applicable, with positions and gradients referring to center-of-mass coordinates and integrations over angular variables included to remove dependences on  $\boldsymbol{\omega}$ . For example, since linear momentum is concerned with center-of-mass motion, (26) carries over essentially as before, apart from the addition of a simple integral over angles; for example, (23b) now reads

$$\begin{aligned} \nabla^\beta \mathbf{P}^{\alpha\beta}(\mathbf{r}) &\equiv -\langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \nabla_{\mathbf{r}_i}^\alpha v(\mathbf{r}_i, \boldsymbol{\omega}_i) \rangle \\ &= -\int d\boldsymbol{\omega} \langle \sum_i \delta(\mathbf{r} - \mathbf{r}_i) \delta(\boldsymbol{\omega} - \boldsymbol{\omega}_i) \nabla_{\mathbf{r}_i}^\alpha v(\mathbf{r}_i, \boldsymbol{\omega}_i) \rangle \quad (35) \\ &= -\int d\boldsymbol{\omega} \rho(\mathbf{r}, \boldsymbol{\omega}) \nabla_{\mathbf{r}}^\alpha v(\mathbf{r}, \boldsymbol{\omega}) \end{aligned}$$

Integral equations such as (14) and (18), sum rules for free-energy derivatives carried over from the atomic fluid case, sum rules for surface tension (Section III.C), and explicit formulas for pressure tensors such as (28) are similarly modified only by the inclusion of trivial integrals over angular degrees of freedom [see, e.g., Walton and Gubbins (1985)]. This is because up to now only center-of-mass coordinates have been directly involved (i.e., no new physics associated with the extension to molecular systems has so far been discussed). However, this situation changes as

soon as one focuses on the angular degrees of freedom. In particular, the hierarchy (10) is equally applicable to differentiation with respect to angular field variables. It follows that (11) and (12) generate a set of sum rules determining order parameters and interfacial compressibilities that are directly concerned with orientational order, in addition to sum rules concerned with positional order. Similarly, the presence of angular coordinates means that applying rotational invariance to the hierarchies (10) and (16c), analogous to the derivation of (14) and (18), will lead to new physics: namely, integral equations for  $(\mathbf{r} \times \nabla_{\mathbf{r}} + \nabla_{\omega})\rho(\mathbf{r}, \omega)$ . For explicit derivations, see Percus (1980) and Tarazona and Evans (1983). In addition, one has a hierarchy of orientational YBG equations, involving angular derivatives of the many-body potential: generated by direct differentiation of the distribution functions and presumably also by potential distribution theory analogous to the derivation of (31). To date, little application has been made of this powerful statistical mechanical approach to orientational phenomena at fluid interfaces.

## E. Fluctuations and Instabilities of Fluid Interfaces

Light-scattering experiments demonstrate that fluid–fluid interfaces are constantly in motion, due to the thermal excitation of long-wavelength capillary-wave (cw) modes [see, e.g., Katyl and Ingard (1967, 1968)]. In addition, computer simulation studies have confirmed that this picture remains down to microscopic wavelengths (Kalos et al., 1977). The longer the wavelength of a collective mode, the longer is its oscillatory period. Thus in the long-wavelength limit it should be correct to treat the capillary-wave modes of a fluid interface as hydrodynamic fluctuations (e.g., considering distortions from planar symmetry) (Buff et al., 1965):

$$\hat{l}(\mathbf{R}, t) = l + \sum_{\mathbf{Q}} \zeta_{\mathbf{Q}}(t) e^{i\mathbf{Q} \cdot \mathbf{R}} \quad l \equiv \langle \hat{l} \rangle \quad (36a)$$

$$H_{\text{cw}} = \frac{1}{2} \sum_{\mathbf{Q}} m_{\mathbf{Q}} (|\dot{\zeta}_{\mathbf{Q}}|^2 + \omega_{\mathbf{Q}}^2 |\zeta_{\mathbf{Q}}|^2) \quad Q \rightarrow 0 \quad (36b)$$

where  $\hat{l}$  denotes the position of the midpoint of the fluctuating interface. The probability  $P(\hat{l})$  that any point in the interface lies at height  $\hat{l}$  is determined by the free-energy contribution to (36b):

$$P(\hat{l}) = \mathcal{N} \exp\left(\frac{-F_{\text{cw}}}{kT}\right) \quad F_{\text{cw}} \equiv \frac{1}{2} \sum_{\mathbf{Q}} m_{\mathbf{Q}} \omega_{\mathbf{Q}}^2 |\zeta_{\mathbf{Q}}|^2 \quad (36c)$$

where  $\mathcal{N}$  is a normalization factor.  $F_{\text{cw}}$  is often referred to as an interface

Hamiltonian. In general, the interface Hamiltonian takes the form

$$F_{\text{cw}} \equiv \gamma \Delta A + \delta V(l) \quad (37a)$$

where  $\gamma$  is the interfacial tension and  $\delta V(l)$  denotes the modification of the capillary-wave contribution due to damping from external fields. It is straightforward to show that up to order  $Q^2$  the change in interfacial area due to the distortions (36a) is

$$\Delta A = \frac{1}{2} A \sum_{\mathbf{Q}} Q^2 |\zeta_{\mathbf{Q}}|^2 \quad (37b)$$

where  $A$  denotes the planar interfacial area. The leading-order contribution from the damping term is

$$\delta V(l) = \frac{1}{2} (\delta l)^2 \left[ \frac{\partial^2 V(l)}{\partial l^2} \right]_{l=l_{\text{eq}}} \quad (37c)$$

$$(\delta l)^2 \equiv A^{-1} \int d^{d-1} \mathbf{R} (\hat{l} - l)^2 = \sum_{\mathbf{Q}} |\zeta_{\mathbf{Q}}|^2 \quad (37d)$$

where  $l_{\text{eq}}$  denotes the equilibrium position of the interface. Thus (37) is of the form (36), with

$$m_Q \omega_Q^2 = AkT \left( W + \frac{Q^2 \gamma}{kT} \right) \quad (38a)$$

and

$$W \equiv (AkT)^{-1} \left[ \frac{\partial^2 V(l)}{\partial l^2} \right]_{l=l_{\text{eq}}} \quad (38b)$$

Since we have ignored any contribution from the damping at order  $Q^2$  it follows that (38) is relevant to the weak damping regime. For a specific example, consider a liquid-vapor interface in the presence of the earth's gravitational field:

$$V(l) = \frac{1}{2} mg \Delta \rho A l^2 + c \quad (39a)$$

$$W = \frac{mg \Delta \rho}{kT} \quad (39b)$$

where  $\Delta \rho$  is the number density difference between liquid and vapor. Applying equipartition to (36) and (38),

$$kT = m_Q \omega_Q^2 \langle |\zeta_{\mathbf{Q}}|^2 \rangle = AkT \left( W + \frac{Q^2 \gamma}{kT} \right) \langle |\zeta_{\mathbf{Q}}|^2 \rangle \quad (40a)$$

it follows that the capillary-wave correlation length for correlations perpendicular to the interface diverges as  $W$  tends to zero in dimensions  $d$

$\leq 3$  [see, e.g., Bedeaux and Weeks (1985)]:

$$\xi_{\perp}^2 \equiv \sum_{\mathbf{Q}} \langle |\zeta_{\mathbf{Q}}|^2 \rangle = \frac{1}{A} \sum_{\mathbf{Q}} \left( W + \frac{Q^2 \gamma}{kT} \right)^{-1} \quad (40b)$$

$$\sim \begin{cases} W^{(d-3)/2} & d < 3 \\ \ln(W^{-1}) & d = 3 \\ \text{finite} & d > 3 \end{cases}$$

So in  $d \leq 3$  capillary-wave wandering of a fluid interface will increase progressively as the external damping is reduced. Note also that the three-dimensional world is the borderline dimension for this singular, or critical, capillary-wave phenomena.

Capillary-wave correlations will be strongest in the plane of the interface:  $\xi_{\parallel}$ . For the interface Hamiltonian (36) we can define

$$G(z_1, z_2, R_{12})_{\text{cw}} = \langle \delta \hat{\rho}(1) \delta \hat{\rho}(2) \rangle$$

$$\delta \hat{\rho}(\mathbf{r}, t) \equiv -\rho'(z) [\hat{l}(\mathbf{r}, t) - l] \quad Q \rightarrow 0 \quad (41a)$$

where the subscript cw reminds us that only capillary-wave correlations are present in a system defined by an interface Hamiltonian. It therefore follows that

$$G(z_1, z_2; Q)_{\text{cw}} = A \langle |\zeta_{\mathbf{Q}}|^2 \rangle \rho'(z_1) \rho'(z_2)$$

$$= \frac{\rho'(z_1) \rho'(z_2)}{W(1 + Q^2 \xi_{\parallel}^2)} \quad Q \rightarrow 0 \quad (41b)$$

where we have defined

$$\xi_{\parallel}^2 \equiv -\frac{G_2(z_1, z_2)_{\text{cw}}}{G_0(z_1, z_2)_{\text{cw}}} = \frac{\gamma}{kTW} \quad (41c)$$

Thus long-wavelength correlations in the plane of the interface are universally divergent in the zero damping limit. Furthermore, we see that interface Hamiltonians lead to Ornstein–Zernike behavior [i.e., Eq. (41b)]. This is a consequence of the fact that  $\gamma$  is defined in (37a) to be a constant and thus cannot introduce additional singular behavior. Combining (37) to (41), we can identify the form of the singular part of the free energy as

$$F^{\text{sing}} \sim \left( \frac{\xi_{\perp}}{\xi_{\parallel}} \right)^2 \quad (42a)$$

Substituting (40b), it follows that below the upper critical dimension capillary-wave phenomena obey a universal hyperscaling relation:

$$F^{\text{sing}} \xi_{\parallel}^{d-1} = \text{constant} \quad d < 3 \quad (42b)$$



Mathematically rigorous versions of interface Hamiltonian theory may be based on column models, as introduced by Weeks (1977). Here, one divides the planar interface into columns and treats capillary-wave modes as inducing correlations between different columns. The probability that the instantaneous position of the interface lies at height  $\hat{l}$  within any column is  $P(\hat{l})$  defined by (36c). Evaluating the Fourier transform of (36c) [i.e.,  $\langle \exp(iQ\hat{l}) \rangle$ ] implies that  $P(\hat{l})$  is a Gaussian [see, e.g., Evans (1979)]:

$$P(\hat{l}) = (2\pi\xi_{\perp}^2)^{-1/2} \exp\left(\frac{-\hat{l}^2}{2\xi_{\perp}^2}\right) \quad (43a)$$

where  $\xi_{\perp}$  is defined by (40b). Similarly, the joint fluctuation probability  $P(\hat{l}(1), \hat{l}(2))$ , defining intercolumn correlations, follows from evaluating the quantity  $\langle \exp[iQ\hat{l}(1) + iQ\hat{l}(2)] \rangle$  given the normal mode probability (36c) [see, e.g., Rao et al. (1979)]. The long-wavelength expansion of this "transform" is consistent with the following "inversion" to order  $|\zeta_Q|^2$  (Rao et al., 1979; Percus, 1981):

$$P(\hat{l}(1), \hat{l}(2)) = P(\hat{l}(1))P(\hat{l}(2)) + P'(\hat{l}(1))P'(\hat{l}(2)) \sum_{\mathbf{Q}} \langle |\zeta_{\mathbf{Q}}|^2 \rangle e^{i\mathbf{Q}\cdot\mathbf{R}^{12}} \quad \mathbf{Q} \rightarrow 0 \quad (43b)$$

From (43) we identify the long-wavelength contribution to the surface structure factor as shown in (41b).

Let us now consider the relationship of the capillary-wave theory above to molecular models of inhomogeneous fluids. Following Weeks (1977), it is natural to inquire if one may treat the fluctuating interface (the so-called *bare profile*) as being qualitatively defined by including all correlations up to a length of order of the bulk correlation length,  $\xi_b$  (and hence  $\xi_b$  defines the column width). If so, the full profile is obtained by including capillary waves of wavelengths larger than  $\xi_b$ ; in particular, from (43a) we have

$$\rho'(z) = (2\pi\xi_{\perp}^2)^{-1/2} \int_{-\infty}^{\infty} d\hat{l} \rho_0'(z - \hat{l}) \exp\left(\frac{-\hat{l}^2}{2\xi_{\perp}^2}\right) \quad (44)$$

where subscript 0 denotes the bare profile. The central portion of the full interfacial profile gradient receives contributions from both the bare profile gradient and the capillary-wave term, each of which is a strongly peaked factor. However, in the tails (or asymptotic wings) of the density profile the right side of (44) is dominated by only one of the factors appearing in the integrand, depending on the behavior of  $\xi_{\perp}$  [i.e., (40b) implies a crossover in the nature of the profile tails, at the upper critical dimension ( $d_{>}$ ) for interfacial fluctuations]. For  $d > d_{>}$  the capillary-wave

fluctuations do not broaden the tails of the profile because in comparison with the rest of the integrand, the Gaussian factor on the right side of (44) acts as a delta function:

$$\rho'(z) \rightarrow \rho'_0(z) \quad |z| \rightarrow \infty, \quad d > d_c \quad (45)$$

This is precisely what is found in mean-field theories (i.e., from van der Waals-like approximations to integral equation theories or density functional theories, in any dimension), where  $\xi_\perp$  is always a finite microscopic length and the mean-field profile gradient decays no faster than an exponential. It follows that for the purpose of evaluating the asymptotic behavior of the full profile it is appropriate to calculate the bare profile from mean-field theory. For example, consider the case of strictly finite-range interactions, or exponentially decaying interactions, for which the mean-field liquid-vapor profile is readily shown to have the following asymptotic behavior [see, e.g., Henderson (1987b)]:

$$\rho'_{MF}(z) \rightarrow ae^{-\lambda|z|} + be^{-2\lambda|z|} + \dots \quad \lambda|z| \gg 1 \quad (46)$$

where in general the liquid and vapor tails will have different values of the temperature-dependent parameters  $\lambda$ ,  $a$ , and  $b$ . Close to the mean-field critical point, (46) becomes symmetric and  $1/\lambda$  reduces to the bulk correlation length (Fisk and Widom, 1969). Identifying (46) with  $\rho'_0(z)$ , as discussed above, we see that in  $d > 3$  we obtain (45) because a Gaussian decays faster than an exponential. However, for  $d \leq 3$ , one must take into account the divergent behavior of  $\xi_\perp$ . In particular, substituting (46) into (44), as  $\rho'_0(z)$ , we see that the behavior of the tails of  $\rho(z)$  is determined by the integral

$$\begin{aligned} I(\lambda, |z|) &= (2\pi\xi_\perp^2)^{-1/2} \int_z^\infty d\hat{l} e^{\lambda(z-\hat{l})} e^{-\hat{l}^2/2\xi_\perp^2} \quad z \rightarrow -\infty \quad (47a) \\ &= (2\pi\xi_\perp^2)^{-1/2} \int_0^\infty dx e^{-\lambda x} e^{-(x-|z|)^2/2\xi_\perp^2} \end{aligned}$$

This integral is readily evaluated in terms of a standard error function, giving the following asymptotic behavior:

$$I(\lambda, |z|) \rightarrow \begin{cases} \exp\left(-\lambda|z| + \frac{\lambda^2\xi_\perp^2}{2}\right) & |z| \gg \lambda\xi_\perp^2, \text{ large } |z| \\ \left[ (2\pi)^{1/2} \left( \lambda\xi_\perp - \frac{|z|}{\xi_\perp} \right) \right]^{-1} \exp\left(\frac{-z^2}{2\xi_\perp^2}\right) & |z| \ll \lambda\xi_\perp^2, \text{ large } \xi_\perp \end{cases} \quad (47b)$$

For large enough  $|z|$  and at nonzero damping, the value of (47) is dominated by the  $\hat{l} \approx 0$  contribution (i.e., the profile eventually decays ex-

ponentially). However at  $|z| < \lambda \xi_{\perp}^2$  the leading-order part of (47) arises from the region  $\hat{l} \approx z$ . In the latter case, we must include the contribution to (44) arising from  $\hat{l} < z$  [i.e., now it is the  $\rho'_0(z - \hat{l})$  factor in the integrand of (44) that acts as a delta function]:

$$\rho'(z) \rightarrow \pm \Delta \rho (2\pi \xi_{\perp}^2)^{-1/2} \exp\left(\frac{-z^2}{2\xi_{\perp}^2}\right) \quad 1 \ll \lambda |z| \leq \lambda^2 \xi_{\perp}^2 \quad (48)$$

The physical interpretation of the origin of (48) is that it arises from capillary-wave fluctuations that move the central portion of the bare profile across the height  $z$ . Below the upper critical dimension, which for short-range forces is clearly  $d = 3$ , such fluctuations will always arise in the limit of infinitesimal damping ( $W \rightarrow 0_+$ ), regardless of the value of  $z$  [i.e., (48) dominates the asymptotic decay of  $\rho(z)$  as  $\xi_{\perp} \rightarrow \infty$ ]. For this reason,  $d \leq d_>$  is known as the fluctuation regime. In the borderline case for short-range interactions,  $d = 3$ , one should add a warning concerning the extremely slow divergence of  $\xi_{\perp}$ ; namely, note the logarithmic behavior of (40b) in  $d = 3$  and the fact that (40b) arises only if one is permitted to include arbitrarily small values of  $Q$  [this involves the requirement that one must be able to perform statistical averages over arbitrarily large times (Henderson, 1987b)].

With regard to capillary-wave correlations in the plane of the interface, the link between interface Hamiltonians and molecular-based theories is described in a seminal paper by Wertheim (1976). In particular, Wertheim (1976) noted that in the weak damping limit the single eigenfunction result (41) for  $G_0(z_1, z_2)$  is more or less implied by the integral equation (14), giving (Rao et al., 1979):

$$W = -\frac{1}{kT} \int dz \rho'(z)v'(z) \quad W \rightarrow 0 \quad (49)$$

and note, for example, that (49) rederives (39b) in the case  $v(z) = mgz$ . Furthermore, substituting  $G_0(z_1, z_2)_{\text{cw}} = \rho'(z_1)\rho'(z_2)/W$  into (20d) and using sum rule (77b) implies that

$$G_2(z_1, z_2) = -\frac{\gamma}{kTW^2} \rho'(z_1)\rho'(z_2) \quad W \rightarrow 0 \quad (50)$$

This result explains the mysterious surface tension sum rule (77a), given (49). Thus in a few short lines the statistical mechanical theory of inhomogeneous fluids is able to confirm the general significance of the Ornstein-Zernike behavior of interfacial fluctuations in the weak damping regime [Eq. (41b)]. Some workers have attempted to cast doubt on this conclusion in the special but physically relevant case of  $d = 3$ . In par-

ticular, Robert (1985), Ciach (1987), and Requardt and Wagner (1989) have suggested that capillary-wave correlations might be so divergent as to make the right sides of sum rules (77a) and (77b) ill defined, thus invalidating (50); room for such doubt is provided by the nonscaling nature of capillary-wave correlations in the borderline dimension  $d = 3$ . However, all such arguments to date have relied on explicit results concerning the strict  $W = 0$  limit (i.e., the thermodynamic limit). Here, one does not have a well-defined interface ( $\gamma = 0$ ), so one should not anticipate any link with the  $W \rightarrow 0_+$  limit of a nondiffuse interface [see the remark following (20e)]. Weeks et al. (1989) have provided the strongest rebuff to date of doubts concerning the validity of Ornstein–Zernike interfacial behavior in  $d = 3$ ; if such arguments are ultimately proved to be incorrect, interface Hamiltonians of the class (36) would not be applicable to  $d = 3$  and none of the critical wetting phenomena that have been derived from such theories would be relevant to molecular Hamiltonians (Section IV).

To conclude this section, let me highlight the significance of soft interfacial modes to fluid interfacial phenomena such as wetting. As discussed above, all fluid interfaces are inherently unstable to capillary-wave contributions to  $\xi_{\parallel}$ , and in  $d \leq 3$  this further involves a divergent  $\xi_{\perp}$ . For example, consider the growth of a liquid film at a substrate–vapor interface. At finite film thickness the capillary-wave modes are damped by the wall–fluid potential (e.g., capillary waves cannot penetrate the substrate). However, the thicker the film, the smaller the damping, and thus we see that the continuous growth of a liquid film is an example of the  $W \rightarrow 0_+$  limit discussed above. Similar remarks apply to continuous melting of a solid–gas interface (i.e., surface melting) (Lipowsky, 1986). Soft modes also play significant roles in first-order interfacial transitions. For example, consider the growth of liquid films at the walls of a planar slit pore of width  $L$ . As soon as the film thicknesses are large enough to support capillary-wave modes, the size of  $\xi_{\perp}$  will determine the likelihood of collisions between interfacial fluctuations spanning the gap  $L$ , thereby nucleating capillary condensation.

## F. Intermolecular Forces and Nonuniversality in Interfacial Systems

The conclusions of the preceding section imply that below the upper critical dimension for interfacial fluctuations ( $d < d_>$ ) the details of intermolecular forces are irrelevant to the qualitative nature of fluid interfacial phenomena in the weak damping regime. That is, in this situation capillary-wave fluctuations will dominate the properties of fluid interfaces and interfacial critical phenomena will belong to universal scaling regimes

described by (40b), (41c), and (42b). However, this universality cannot be expected to be generally applicable to the physical world because  $d_{\geq} \leq 3$ . Thus it is necessary to inquire whether or not the details of intermolecular forces play a qualitative role in interfacial critical phenomena. In particular, the ubiquitous presence of dispersion forces in molecular systems means that the asymptotic decay of intermolecular interactions is invariably a power law:

$$\varphi^{(2)}(r) \sim r^{-(3+m)} \quad (51a)$$

where  $m = 3$  at intermediate range (i.e., until retardation effects take over and enforce the macroscopic limit  $m = 4$ ). Thus in planar symmetry the wall–fluid potential arising from a semi-infinite solid will decay as

$$v_{\epsilon_w}(z) \sim z^{-(m-3-d)} + \mathcal{O}(z^{-(m-4-d)}) \quad z \rightarrow \infty \quad (51b)$$

where (as usual)  $d$  denotes the overall dimensionality.

For an example of the significance of (51), consider a wall–gas interface with  $v(z)$  defined by (51b). From (15) and (17) it follows that in the low-density limit of the bulk gas, the density profile falls off as

$$\rho(z) \rightarrow \rho_b \left( 1 - \frac{v(z)}{kT} \right) \quad \rho_b \rightarrow 0, \quad z \rightarrow \infty \quad (52)$$

That is, a power-law decay of  $v(z)$  induces a power-law decay of  $\rho(z)$  and so in molecular systems one cannot treat a wall–fluid interface as being of finite range. The crucial significance of this fact to fluid adsorption and wetting phenomena has long been apparent to the Soviet school [see, e.g., Derjaguin (1940)] but has only been generally appreciated in the West since the early 1980s (de Gennes, 1981).

The asymptotic wings of a liquid–vapor or a fluid–fluid profile are similarly affected by the presence of power-law interactions. Naively, one can construct an analogy with (52) by treating the liquid phase as the wall, and then on the liquid side of the interface it follows that the same effect must arise from the absence of intermolecular interactions; for an explicit theory, see Barker and Henderson (1982). Thus, in molecular systems we should replace (46) with

$$\rho'_{MF}(z) \rightarrow a | \lambda z |^{-(m+4-d)} + b | \lambda z |^{-(m+5-d)} + \dots \quad (53)$$

Here, the relevant integral replacing (47) is

$$(2\pi\xi_{\perp}^2)^{-1/2} \int_{\sigma}^{\infty} dx x^{-(m+4-d)} e^{-(x-|z|)^2/2\xi_{\perp}^2} \quad (54)$$

where  $\sigma$  is a microscopic length of order  $1/\lambda$  or perhaps  $10/\lambda$ . The mean-field region of the profile is now given by the condition  $|z| \ll [\ln(|z|/\sigma)]^{-1/2}$

$\gg \xi_{\perp}$ , and comparing with (47b) we see that at a fixed value of the capillary-wave damping, power-law interactions are much more dominant over the fluctuation contribution than are short-range interactions. For the case of a liquid–vapor interface in a gravitational field, these remarks are of little significance, except to experiments that specially probe the asymptotic region, because the amplitude of these profile tails is so insignificant in comparison with  $\Delta\rho$  (Barker and Henderson, 1982). In contrast, the study of continuous wetting phenomena is concerned directly with the behavior of the profile wings, which are the means by which a liquid–vapor surface interacts with the short-range field of a distant substrate. In particular, Lipowsky (1984) noted that power-law interactions imply a lowering of the upper-critical dimension for interfacial critical phenomena;  $2 < d_{\>} < 3$ . So in the absence of bulk critical phenomena, mean-field theory is qualitatively correct in  $d = 3$  (but not  $d = 2$ ), except for models restricted to finite-range or exponentially decaying interactions.

It follows from the above that interfacial critical phenomena is non-universal in  $d = 3$ , with free-energy scaling functions and associated exponents that depend explicitly on the power-law interaction parameter  $m$  (Dietrich and Schick, 1985; Ebner et al., 1985). In fact, even exponential forces cannot always be treated as short ranged, since an exponential wall field can compete with the exponential decay of a mean-field profile determined by strictly finite-ranged fluid–fluid interactions or by exponential interactions [i.e., Eq. (46)]. Furthermore, because  $d = 3$  is the upper-critical dimension for capillary-wave fluctuations in the absence of power-law forces, these competing exponential effects can in turn compete with capillary-wave broadening (Hauge and Olaussen, 1985). It follows that models of inhomogeneous fluids without power-law forces possess particularly complex nonuniversal behavior in the special case of  $d = 3$ . Physically, one must get used to the fact that distant surfaces will always interact via the tails of their density profiles, even if the only effect present is exponential decay; for example, exponential decay is associated with logarithmic film growth. For inhomogeneous fluids the qualitative details of molecular models have qualitative consequences and one cannot get away with pretending that intermolecular forces are strictly short ranged.

### III. SUM RULES

#### A. Compressibility Route

For the sake of definitiveness I restrict this discussion of explicit examples to the models defined by external fields (8) and (9). These two models