SURFACE EFFECTS IN SIMPLE MOLECULAR SYSTEMS

Thesis by

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ABSTRACT

This thesis examines two problems concerned with surface effects in simple molecular systems. The first is the problem associated with the interaction of a fluid with a solid boundary, and the second originates from the interaction of a liquid with its own vapor.

For a fluid in contact with a solid wall, two sets of integro-differential equations, involving the molecular distribution functions of the system, are derived. One of these is a particular form of the well-known Bogolyubov-Born-Green-Kirkwood-Yvon equations. For the second set, the derivation, in contrast with the formulation of the B.B.G.K.Y. hierarchy, is independent of the pair-potential assumption. The density of the fluid, expressed as a power series in the uniform fluid density, is obtained by solving these equations under the requirement that the wall be ideal.

The liquid-vapor interface is analyzed with the aid of equations that describe the density and pair-correlation function. These equations are simplified and then solved by employing the superposition and the low vapor density approximations. The solutions are substituted into formulas for the surface energy and surface tension, and numerical results are obtained for selected systems. Finally, the liquid-vapor system near the critical point is examined by means of the lowest order B.B.G.K.Y. equation.

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I. GENERAL INTRODUCTION

Whenever macroscopically dissimilar materials are in contact, the molecules or atoms of one material near the contact surface interact with their counterparts across the surface. These interactions may give rise to important macroscopic effects. Examples of phenomena where surface effects play an important role include phase transition, nucleation, gas adsorption, behavior of solid state components, fluid-gas interactions and various chemical reactions.

In this thesis we use the equilibrium statistical mechanical theory of classical fluids to investigate liquid-solid interactions (adsorption) and the surface characteristics of liquid-vapor phase transitions. Because of the technological and scientific importance of fluid-solid interactions and phase transitions, a study of these phenomena is certainly justified. A rigorous statistical mechanical approach is employed so that the basic goal of predicting observables solely from a knowledge of intermolecular forces can be achieved.

The thesis is divided into two parts. In Part I we discuss the liquid-solid and gas-solid interactions, with particular emphasis placed upon the gas-solid interaction. Previous attempts[1],[2] to describe gas adsorption have usually been based upon the kinetic theory of gases - - an approach quite different than the one presented here. A discussion of the advantages and disadvantages of the kinetic theory method is presented in Chapter II. Past work involving a rigorous statistical mechanical approach has utilized the so-called B.B.G.K.Y. hierarchy. The B.B.G.K.Y. hierarchy is a set of

N equations involving the various distribution functions of statistical mechanics for a classical N-particle system. Slight variations of these equations were developed independently by Bogolyubov, Born, Green, Kirkwood, and Yvon. The n^{th} equation of the set involves not only the n^{th}-order distribution function, but also the $(n+1)^{th}$. Hence, a complete analysis of any problem would involve solving N coupled, integro-differential equations. The B.B.G.K.Y. equations are valid only if the pair-potential condition, Eq. (2.1), is satisfied.

In Chapter II we apply the B.B.G.K.Y. equations to the problem of a fluid interacting with a plane wall. Although the solution to this problem has been obtained by Fisher (Ref. 3, p. 106), we believed it instructive to formulate the equations and the statement of the problem in a manner paralleling the development of a different set of equations, presented in Chapter III. These new equations have an advantage over those obtained from the B.B.G.K.Y. approach in that their validity is in no way limited by the assumption of pair-wise interactions. They are, therefore, completely general. It is also demonstrated in Chapter III that the solution of the new equations reduces to the solution of the B.B.G.K.Y. equations when the pair-wise interaction condition of Eq. (2.1) is imposed. From these solutions one may calculate most of the important, measurable quantities associated with the adsorption process.

Part II is concerned with the liquid-vapor interface. Kirkwood and Buff[4], using the pair-potential condition, have derived formulas giving the surface tension and surface energy of a simple fluid in terms of the density and the second-order distribution function. Numerical results have been obtained[4],[5] from these equations when the microstructure of the interface is ignored. In Chapter IV we include, in an approximate manner, the effect of the microstructure and thereby improve upon these calculations.

The transition region has been analyzed by several authors[6],[7],[8],[9],[10],[11] using methods grounded in thermodynamical reasoning. The fact that the results predicted by such methods compare poorly with experiment (at least when the system is far from its critical point) supports the widely held opinion that thermodynamic theories of the interface cannot accurately explain interfacial properties. It has long been recognized that a solution of the B.B.G.K.Y. equations, applied to the liquid-vapor problem, would provide the necessary information about the transition region for a system whose total potential energy can be expressed by the sum of pair-potentials. The number of these equations must, of course, be drastically reduced so that a solution can be found without reaching the limit of present computational techniques. The simplest way to achieve this reduction is to use the superposition approximation, first introduced by Kirkwood, which approximates the third order distribution function in terms of a product of second order distribution functions. Unfortunately, even this resulting system of two equations is nearly impossible to solve.

In Chapter IV we extend the principles used to derive the equations presented in Chapter III to the liquid-vapor problem. By so doing, we derive a system of N equations that describes the transition region when the vapor density is much smaller than the liquid density. These equations, when simplified by the superposition approximation, can be solved easily. The resulting solutions are substituted into the expressions for the surface energy and surface tension, and numerical results are obtained for the liquid-vapor systems: oxygen, nitrogen, neon, and krypton.

One of the more interesting aspects of the transition region is the manner in which the density of the fluid changes as one proceeds from the vapor side to the liquid side. The theory presented in Chapter IV predicts the existence of a length scale that characterizes the density variation through the interface. This characteristic length depends on the liquid density, temperature, and the intermolecular potential. In particular, the length scale increases with temperature, decreases with liquid density, and decreases with increasing strength of the intermolecular potential. If in fact, the potential is too weak, no physical solution to the equations exists. This result suggests that a dominant factor in the formation of two phases is the existence of a sufficiently strong, attractive intermolecular potential.

Finally, in Chapter V we analyze the liquid-vapor system near the critical point. Because of the fact that the transition region becomes very broad as the critical point is approached, several authors[8],[9],[10],[11] have used thermodynamics to describe the resulting "macroscopic" interface. Using the B.B.G.K.Y.

equations, modified by certain critical point assumptions, we reproduce the thermodynamically derived results.

PART I

THE FLUID-SOLID INTERFACE

II. REVIEW AND MODIFICATION OF PREVIOUS THEORIES

A. INTRODUCTION

There exist various theories that attempt to describe the interaction between a solid and a collection of fluid molecules*. Most of these utilize the kinetic theory of gases at some stage in their development. Thus, the actual dynamics of the molecules - - in particular the molecular flux impinging on the solid and the corresponding residence time of the molecules near the surface of the solid - - is studied. To obtain reasonable results, interactions between the adsorbed molecules must be considered, and it is this consideration that inevitably leads to the use of simplifying models. For example, the Langmuir theory[1],[2] attempts to include the effect of these interactions by supposing that only one "layer" of molecules can be adsorbed. Hence, the physical presence of adsorbed molecules prevents others from being adsorbed.

It is obvious that an assumption of this type does not take into consideration the complex nature of molecular interactions. Consequently, we shall not discuss at length the usual approach to adsorption; rather our attention will be directed toward a rigorous, statistical mechanical theory of a simple** fluid interacting with a plane, solid wall.

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*Usually the density of molecules is greater near the solid than it is far away. The molecules are then said to be adsorbed by the solid.

**The potential of the interaction between molecules of a simple fluid depends only on the distances between the molecules.

B. THE B.B.G.K.Y. APPROACH

Previous attempts to construct a rigorous statistical mechanical theory of a simple fluid interacting with a plane, solid wall have been centered around the B.B.G.K.Y. equations for a non-uniform fluid (Ref. 3, p. 98). Due to inherent complexities, the search for a general solution of these equations, valid for any limiting value of the fluid number density as the distance from the solid approaches infinity, has not been successful. However, a power series solution in the asymptotic fluid density variable has been obtained (Ref. 3, p. 108). A series solution of this type is useful for the low density fluid problem, but of little value for the treatment of dense fluids - - much as the virial approach to the equation of state is useful at low densities but not at high densities.

In the following sections we develop a power series solution to our problem using a set of equations that can be derived from the B.B.G.K.Y. equations. This task is undertaken for three main reasons. First, the modified equations are of a form paralleling the development of a new set of equations to be presented in Chapter III. Thus, one is able to use similar solution techniques for both sets. Secondly, we feel that the solution method used for the modified equations is more straightforward. Thirdly, the solution presented in Ref. [3] is partially in error.

C. MODIFICATION OF B.B.G.K.Y. APPROACH

The following problem is posed. A fluid occupies the half space $z > 0$. At $z = 0$ there exists a solid wall which exerts a force on the fluid molecules given by $-\frac{dU(z)}{dz}\hat{e}_z$, where $\hat{e}_z$ is a unit vector in the z direction. $U(z)$ is the external potential applied to the fluid due to the existence of the solid wall. We would like to solve for the statistical mechanical distribution functions that describe the fluid-wall system.

Before we construct the basic equations governing the distribution functions, it is useful to cite some results from the theory of uniform fluids which will be used as boundary conditions for these equations. From the B.B.G.K.Y. equations for a uniform fluid, or from a more general approach using the modified U-functions, (Ref. 12, p. 145) one can derive a power series expansion in the fluid density parameter for the distribution functions associated with a uniform fluid. The former method is valid only if the so-called pair-potential assumption is satisfied. Namely, the total potential energy of a system of N particles, $\Phi(\underset{\sim}{r}_1, \ldots \underset{\sim}{r}_N)$, must be written as

$$\Phi(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N) = \frac{1}{2}\sum_{i\neq j=1}^{N} \varphi(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|) \quad , \tag{2.1}$$

where $\varphi(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|) = \varphi_{ij}$ is the intermolecular potential and $\underset{\sim}{r}_i$ is the position vector of the i^{th} particle. The U-function method is thus more general. In either case, if n is the density of the uniform fluid, then

$$n^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h) = \sum_{k=1}^{\infty} C_{k-1}^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h) n^{k+1} \quad , \tag{2.2}$$

where $n^{(j)}$ is the j^{th}-order distribution function $(2 \leq j \leq N)$ for an N particle system defined by

$$n^{(j)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_j) = \frac{1}{(N-j)!\,Q_N} \int e^{-\beta\Phi(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N)}\, d\underset{\sim}{r}_{j+1} \ldots d\underset{\sim}{r}_N \tag{2.3}$$

and

$$Q_N = \frac{1}{N!} \int e^{-\beta\Phi(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_N)}\, d\underset{\sim}{r}_1 \ldots d\underset{\sim}{r}_N \; .$$

β is $\frac{1}{kT}$, where k is Boltzmann's constant and T is the temperature. For a uniform fluid $n^{(h)}$ can only depend on the distances between the molecules so that we may write Eq. (2.2) as

$$n^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})\right) = \sum_{k=1}^{\infty} C_{k-1}^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})\right) n^{k+1} \quad , \tag{2.4}$$

where $r_{\ell m} = |\underset{\sim}{r}_\ell - \underset{\sim}{r}_m|$ and $\overset{h}{\underset{\ell m}{P}}(r_{\ell m})$ is an ordering operator allowing ℓ to vary from 2 to h, and for each ℓ, ordering the values of $m < \ell$ from $m = \ell - 1$ to 1. Thus, for example,

$$\overset{4}{\underset{\ell m}{P}}(r_{\ell m}) = r_{21}, r_{32}, r_{31}, r_{43}, r_{42}, r_{41} \quad .$$

For $h \geq 5$, $n^h\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})\right)$ has redundant arguments since not all the $r_{\ell m}$ listed are independent. We shall, however, list all the $r_{\ell m}$ without loss of generality. Equation (2.4) is strictly valid only in the thermodynamic limit: $N \to \infty$, $V \to \infty$ such that the ratio $N/V = n$ is finite. Hereafter this limit will be understood. Equation (2.3) must be interpreted accordingly.

For a nonuniform system of particles the B.B.G.K.Y. equations are

$$kT\nabla_{\underset{\sim}{r}_i} n^{(h)}(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h) = - n^{(h)}(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h)\nabla_{\underset{\sim}{r}_i} \Phi(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h)$$

$$- \int (\nabla_{\underset{\sim}{r}_i}(\varphi_{i,\,h+1}))n^{(h+1)}(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_{h+1})d\underset{\sim}{r}_{h+1}(h=1,2 \; . \; . \; .) \; . \tag{2.5}$$

Again, $\varphi_{ij} = \varphi(|\underset{\sim}{r}_i - \underset{\sim}{r}_j|)$ is the intermolecular potential, $\underset{\sim}{r}_i$ is any of $\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h$, and

$$\Phi(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h) = \frac{1}{2}\sum_{i \neq j}^{h}\sum \varphi_{ij} + \sum_{i=1}^{h} U(\underset{\sim}{r}_i) \; .$$

$U(\underset{\sim}{r}_i)$ is any external potential that is applied to the system. Due to the plane nature of the problem, we may write

$$n^{(h)}(\underset{\sim}{r}_1 \; . \; . \; . \underset{\sim}{r}_h) = \hat{n}^{(h)}(\overset{h}{P}_{\ell m}(r_{\ell m}), z_1, z_2, \; . \; . \; . z_h)^{\dagger} \; . \; . \; , \tag{2.6}$$

where we have again included a redundancy in the arguments of $n^{(h)}$ for $h \geq 4$ with no loss of generality. If we specialize $\nabla_{\underset{\sim}{r}_i}$ to $\hat{e}_{z_i} \frac{\partial}{\partial z_i}$ in (2.5) and for each value of h add together the several equations produced by allowing i to vary from 1 to h, we obtain, with aid of the definition,

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[†] The $\wedge$ notation is used to indicate the change in independent variables. It will be omitted hereafter.

$$n^{(h)}\left({}_{\ell m}\overset{(h)}{P}(r_{\ell m}), z_1, \ldots z_h\right) = n^{(1)}(z_1)\ldots n^{(1)}(z_h)\, g^{(h)}\left({}_{\ell m}\overset{h}{P}(r_{\ell m}), z_1, \ldots z_h\right),$$

$$kT\,\frac{dn^{(1)}(z_1)}{dz_1} = -n^{(1)}(z_1)\,\frac{dU(z_1)}{dz_1} - \int \frac{z_{12}}{r_{12}}\,\varphi'(r_{12})\,n^{(1)}(z_1)\,n^{(1)}(z_2)\,g^{(2)}(r_{12}, z_1, z_2)\,d\underset{\sim}{r}_2$$

for $h = 1$ (2.7)

and for $h \geq 2$,

$$kT\sum_{k=1}^{h} \frac{\partial}{\partial z_k}\left(n^{(1)}(z_1)\ldots n^{(1)}(z_h)\,g^{(h)}\right) + n^{(1)}(z_1)\ldots n^{(1)}(z_h)\,g^{(h)}\sum_{i=1}^{h}\frac{dU(z_i)}{dz_i}$$

$$= -n^{(1)}(z_1)\ldots n^{(1)}(z_h)\sum_{i=1}^{h}\int \frac{z_{i,h+1}}{r_{i,h+1}}\,\varphi'(r_{i,h+1})\,n^{(1)}(z_{h+1})\,g^{(h+1)}\,d\underset{\sim}{r}_{h+1}\ ,\tag{2.8}$$

where $\varphi'(r) = \dfrac{d\varphi(r)}{dr}$ and the arguments of $g^{(h)}$ are understood to be $\left({}_{\ell m}\overset{h}{P}(r_{\ell, m}), z_1, \ldots z_h\right)$. We have also employed the following:

$$\sum_{k=1}^{h}\frac{\partial}{\partial z_k}\sum_{i\neq j}^{h}\sum \varphi_{ij} = 0 \qquad \text{and} \qquad n^{(1)}(\underset{\sim}{r}_1) = n^{(1)}(z_1)\ .$$

If Eq. (2.7) is used to simplify (2.8), one obtains

$$-kT\sum_{k=1}^{h}\frac{\partial}{\partial z_k}\left(g^{(h)}\right) = \sum_{i=1}^{h}\int \frac{z_{i,h+1}}{r_{i,h+1}}\,\varphi'(r_{i,h+1})\,n^{(1)}(z_{h+1})\left[g^{(h+1)} - g^{(h)}g^{(2)}(r_{i,h+1}, z_i, z_{h+1})\right]d\underset{\sim}{r}_{h+1}\tag{2.9}$$

If we define $\rho(z_1)$ by $n^{(1)}(z_1) = \rho(z_1)e^{-\beta U(z_1)}$, and assume that the wall at $z = 0$ is ideal in the sense that $e^{-\beta U(z_1)} = H(z_1)$, where $H(z_1)$ is the Heaviside step function, (2.7) simplifies to

$$\frac{d\rho(z_1)}{dz_1} = -\frac{\rho(z_1)}{kT}\int_{z_2>0} \frac{z_{12}}{r_{12}}\,\varphi'(r_{12})\rho(z_2)g^{(2)}(r_{12}, z_1, z_2)\,d\underset{\sim}{r}_2 \quad , \tag{2.10}$$

and (2.9) simplifies to

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k}\, g^{(h)} = -\frac{1}{kT}\sum_{i=1}^{h}\int_{z_{h+1}>0} \frac{z_{i,h+1}}{r_{i,h+1}}\,\varphi'(r_{i,h+1})\rho(z_{h+1})[\,g^{(h+1)} - g^{(h)}g^{(2)}(r_{i,h+1}, z_i, z_{h+1})]\,d\underset{\sim}{r}_{h+1} \quad .^{*} \tag{2.11}$$

Equations (2.10) and (2.11) are not valid if $\rho(z_1)$ becomes infinite for $z_1 < 0$. It is known, however, that $\rho(z_1)$ possesses discontinuous derivatives if and only if the intermolecular potential function has discontinuous derivatives. Even in the case when φ_{ij} represents the hard sphere interaction, $\rho(z_1) \epsilon\ C^3$ (Ref. 13, p. II-47). Therefore, Eqs. (2.10) and (2.11) are correct.

It is of some interest to examine the question of whether or not the solution of Eqs. (2.10) and (2.11), subject to certain boundary conditions to be presented in the next section, is identical to the solution of the original B.B.G.K.Y. equations subject to the same boundary conditions. This question is discussed in Appendix A.

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[*] It should be realized that the operator $\frac{\partial}{\partial z_i}$ operates on $r_{ij} (j \neq i)$ as well as on z_i in the argument of $g^{(h)}$.

Finally, we should mention that the expression

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k} \left(g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell,m}), z_1, \ . \ . \ . z_h\right)\right) dz_o$$

is the differential change in $g^{(h)}$ as the z values of all the h points in three-space $\underset{\sim}{r}_1 \ . \ . \ . \underset{\sim}{r}_h$ are changed from z_i to $z_i + dz_o$, while the distances between the h points are held fixed. Thus, letting $z_i = z_i^o + z_o$ ($i = 1, \ . \ . \ . h$), we can use the chain rule and the fact that

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k} (r_{\ell,m}) = 0 \qquad \ell \neq m, \ \ell, m = 1, \ . \ . \ . h$$

to obtain

$$\left.\sum_{k=1}^{h} \frac{\partial}{\partial z_k} g^{(h)}\right]_{z_i = z_i^o + z_o} = \left.\left(\frac{\partial}{\partial z_1} + \cdot \frac{\partial}{\partial z_h}\right) g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h\right)\right]_{z_i = z_i^o + z_o}$$

$$= \frac{d}{dz_o} g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1^o + z_o, \ . \ . \ . z_h^o + z_o\right) . \tag{2.12}$$

Hence,

$$\int_o^{\infty} \frac{d}{dz_o} g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1^o + z_o, \ . \ . \ . z_h^o + z_o\right) dz_o =$$

$$\lim_{\substack{z_i \to \infty \\ (i=1, \ . \ . \ . h)}} \left| g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h\right) \right| - g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1^o, \ . \ . \ . z_h^o\right) . \tag{2.13}$$

Consequently, if $\left.\sum_{k=1}^{h} \frac{\partial}{\partial z_k} (g^h)\right]_{z_i = z_i^o + z_o}$ is known for all values of $z_i = z_i^o + z_o$ for $z_o > 0$ and fixed $r_{\ell, m}$, and if

$$\lim_{\substack{z_i \to \infty \\ i=1, \ldots h}} g^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h)$$

is known for the same fixed $r_{\ell, m}$, then from Eq. (2.13) we can uniquely determine

$$g^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1^o, \ldots z_h^o) \quad .$$

D. THE SERIES SOLUTION

A series solution in powers of the asymptotic fluid density n is written as

$$\rho(z) = \sum_{k=1}^{\infty} n^k \rho_k(z) \tag{2.14}$$

$$g^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h) = \sum_{k=o}^{\infty} n^k g_k^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h) \quad . \tag{2.15}$$

The boundary condition on $\rho(z)$ is simply

$$\rho(z) \to n \quad \text{as} \quad z \to \infty \quad . \tag{2.16}$$

Examining Eq. (2.14), we see that Eq. (2.16) implies

$$\begin{aligned} \rho_1(z) &\to 1 \quad \text{as} \quad z \to \infty \\ \rho_k(z) &\to 0 \quad \text{as} \quad z \to \infty \end{aligned} \tag{2.17}$$

The boundary conditions for $g_k^{(h)}$ are obtained by comparing Eq. (2.15) to Eq. (2.4) and using the definition of $g^{(h)}$. The result is

$$g_k^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h) \rightarrow C_k^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})) \tag{2.18}$$

as

$$z_1, \ldots z_h \rightarrow \infty \quad , \quad r_{\ell, m} \text{ fixed} \quad .$$

In particular, we now have in Eq. (2.13)

$$\lim_{\substack{z_i \rightarrow \infty \\ (i=1, \ldots h)}} g^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h) = \sum_{k=0}^{\infty} n^k C_k^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})) \quad . \tag{2.19}$$

We shall now substitute Eqs. (2.14) and (2.15) into Eqs. (2.10) and (2.11), and equate powers of n. For the k^th power of n we obtain a linear, first-order differential equation for ρ_k and $g_k^{(h)}$ involving $\rho_i, g_i^{(h)}, g_i^{(h+1)}, g_i^{(2)}$ for $i = 2, \ldots k-1$. Boundary conditions (2.17) and (2.18) will be used in the solution of these equations. For example, by equating terms of order n in Eq. (2.10) and of order unity in Eq. (2.11), we immediately have

$$\frac{d}{dz_1} \rho_1(z_1) = 0 \tag{2.20}$$

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k} g_o^{(h)} = 0 \quad . \tag{2.21}$$

Equation (2.20) and boundary condition (2.17) require

$$\rho_1(z_1) = 1 \quad . \tag{2.22}$$

By referring to the derivation of Eq. (2.13), we see that Eq. (2.21), subject to boundary condition (2.18), implies that

$$g_o^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h) = C_o^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})) \ . \tag{2.23}$$

By equating terms of order n^2 in Eq. (2.10) and order n in Eq. (2.11), we obtain, with the aid of Eq. (2.23),

$$\frac{d\rho_2(z_1)}{dz_1} = -\frac{1}{kT}\int_{z_2>o} \frac{z_{12}}{r_{12}}\, \varphi'(r_{12})C_o^2(r_{12})d\underset{\sim}{r}_2 \tag{2.24}$$

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k}(g_1^{(h)}) = -\frac{1}{kT}\sum_{i=1}^{h}\int_{z_{h+1}>o} \frac{z_{i,h+1}}{r_{i,h+1}}\, \varphi'(r_{i,h+1})\{C_o^{(h+1)}(\overset{h+1}{\underset{\ell m}{P}}(r_{\ell m}))$$

$$- C_o^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}))C_o^{(2)}(r_{i,h+1})\}d\underset{\sim}{r}_{h+1} \ . \tag{2.25}$$

The results of Eq. (2.13) suggest that Eqs. (2.24) and (2.25) can be treated as first order differential equations (after the substitution $z_i = z_i^o + z_o$) of the form

$$\frac{d}{dz_o} Y(\alpha, z_o) = F(\alpha, z_o)$$

with boundary conditions

$$Y(\alpha, z_o) \to Y_o(\alpha) \quad \text{as} \quad z_o \to \infty \quad ,$$

where α represents a set of constant parameters and $F(\alpha, z_o)$ may be considered a known function. Consequently, Eqs. (2.24) and (2.25), subject to the given boundary conditions, have a unique solution. Proceeding in this manner, we can construct solutions for all

ρ_k and $g_k^{(h)}$.

In general the integrals appearing in Eqs. (2.24) and (2.25) are difficult to evaluate as explicit functions of the $z_i (i = 1, \ldots h)$. Thus, the solutions to (2.24), (2.25) must usually be obtained numerically. We recall, however, that the B.B.G.K.Y. equations are valid only if the pair-potential condition, Eq. (2.1), is satisfied. By using Eq. (2.1), one calculates $C_i^{(h)}$ functions which, surprisingly, permit Eqs. (2.24) and (2.25) and the equations governing the higher order terms to be solved analytically. Some of the $C_i^{(h)}$ calculated using condition (2.1) are (Ref. 3, p. 105)

$$C_o^{(2)}(r_{12}) = e^{-\beta\varphi(r_{12})} , \tag{2.26}$$

$$C_o^{(3)}(r_{12} r_{23} r_{13}) = e^{-\beta\varphi(r_{12})} e^{-\beta\varphi(r_{23})} e^{-\beta\varphi(r_{13})} , \tag{2.27}$$

and

$$C_1^{(2)}(r_{12}) = e^{-\beta\varphi(r_{12})} \int d\underset{\sim}{r}_3 (e^{-\beta\varphi(r_{13})} - 1)(e^{-\beta\varphi(r_{23})} - 1) . \tag{2.28}$$

Relations (2.26) - (2.28) enable us to calculate

$$\rho_2(z) \quad , \quad g_1^{(2)}(r_{12}, z_1, z_2) \quad \text{and} \quad \rho_3(z_1) \quad .$$

Substituting Eq. (2.26) into Eq. (2.24) we obtain

$$\frac{d\rho_2(z_1)}{dz_1} = - \frac{1}{kT} \int_{z_2 > o} \frac{z_{12}}{r_{12}} \varphi'(r_{12}) e^{-\beta\varphi(r_{12})} d\underset{\sim}{r}_2$$

$$= \frac{d}{dz_1} \int_{z_2 > o} (e^{-\beta\varphi(r_{12})} - 1) d\underset{\sim}{r}_2 \quad .$$

Thus,

$$\rho_2(z_1) = \int_{z_2 > 0} f(r_{12})\, d\underset{\sim}{r}_2 + \alpha \quad ,$$

where α is a constant and

$$f(r_{12}) = (e^{-\beta\varphi(r_{12})} - 1) \quad .$$

However, boundary conditions (2.17) imply that

$$\alpha = -\int f(r_{12})\, d\underset{\sim}{r}_2 = -\beta_1 \quad ,$$

where β_1 is the first irreducible integral to be introduced in the virial treatment of the equation of state. Therefore,

$$\rho_2(z_1) = \int_{z_2 > 0} f(r_{12}) d\underset{\sim}{r}_2 - \beta_1 \quad . \tag{2.29}$$

Upon substituting Eqs. (2.26) and (2.27) into Eq. (2.25) we obtain

$$\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right) g_1^{(2)} = -\frac{1}{kT}\int_{z_3 > 0} d\underset{\sim}{r}_3 \frac{z_{13}}{r_{13}} \varphi'(r_{13}) e^{-\beta\varphi(r_{12})} e^{-\beta\varphi(r_{13})} f(r_{23})$$

$$-\frac{1}{kT}\int_{z_3 > 0} d\underset{\sim}{r}_3 \frac{z_{23}}{r_{23}} \varphi'(r_{23}) e^{-\beta\varphi(r_{12})} e^{-\beta\varphi(r_{23})} f(r_{13})$$

$$= \left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)\left(e^{-\beta\varphi(r_{12})} \int_{z_3 > 0} d\underset{\sim}{r}_3 f(r_{23})\, f(r_{13})\right) \tag{2.30}$$

Equation (2.30) implies that

$$g_1^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})} \int_{z_3 > 0} d\underset{\sim}{r}_3 f(r_{23}) f(r_{13}) + G(r_{12}) \quad ,$$

where $G(r_{12})$ is an arbitrary function of r_{12}. Boundary condition (2.18) coupled with Eq. (2.28) requires $G(r_{12}) = 0$. Therefore

$$g_1^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})} \int_{z_3 > 0} d\underset{\sim}{r}_3 f(r_{23}) f(r_{13}) \quad . \tag{2.31}$$

It is now possible to solve for $\rho_3(z_1)$. By equating terms of order n^3 in Eq. (2.10) and using previous results, we have that

$$\begin{aligned} \frac{d\rho_3(z_1)}{dz_1} &= -\frac{1}{kT} \rho_2(z_1) \int_{z_2 > 0} \frac{z_{12}}{r_{12}} \varphi'(r_{12}) e^{-\beta\varphi(r_{12})} d\underset{\sim}{r}_2 \\ &- \frac{1}{kT} \int_{z_2 > 0} \frac{z_{12}}{r_{12}} \varphi'(r_{12}) e^{-\beta\varphi(r_{12})} \rho_2(z_2) d\underset{\sim}{r}_2 \\ &- \frac{1}{kT} \int_{z_2 > 0} \varphi'(r_{12}) e^{-\beta\varphi(r_{12})} \left[\int_{z_3 > 0} f(r_{23}) f(r_{13}) d\underset{\sim}{r}_3 \right] d\underset{\sim}{r}_2 \\ &= \rho_2(z_1) \frac{d\rho_2(z_1)}{dz_1} + \frac{d}{dz_1} \left[\int_{z_2 > 0} f(r_{12}) \rho_2(z_2) d\underset{\sim}{r}_2 \right] \\ &+ \int_{z_2 > 0} \int_{z_3 > 0} f(r_{23}) f(r_{13}) \frac{\partial}{\partial z_1} f(r_{12}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 \quad . \end{aligned} \tag{2.32}$$

However,

$$\int_{z_2>0}\int_{z_3>0} f(r_{23})f(r_{13})\frac{\partial}{\partial z_1} f(r_{12})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3$$

$$= \frac{d}{dz_1}\int_{z_2>0}\int_{z_3>0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3$$

$$-\int_{z_2>0}\int_{z_3>0} f(r_{12})f(r_{23})\frac{\partial}{\partial z_1} f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \quad . \tag{2.33}$$

Upon interchanging indices 2 and 3, we see that the last term on the right hand side of Eq. (2.33) is equal to the left hand side of Eq. (2.33). Equation (2.33) is therefore equivalent to

$$\int_{z_2>0}\int_{z_3>0} f(r_{23})f(r_{13})\frac{\partial}{\partial z_1} f(r_{12})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 =$$

$$\frac{1}{2}\frac{d}{dz_1}\int_{z_2>0}\int_{z_3>0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \quad . \tag{2.34}$$

Hence,Eq. (2.32) simplifies to

$$\frac{d\rho_3(z_1)}{dz_1} = \frac{d}{dz_1}\left(\frac{\rho_2(z_1)}{2}\right)^2 + \frac{d}{dz_1}\int_{z_2>0} f(r_{12})\rho_2(z_2)d\underset{\sim}{r}_2$$

$$+\frac{1}{2}\frac{d}{dz_1}\int_{z_2>0}\int_{z_3>0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \quad ,$$

or

$$\rho_3(z_1) = \frac{(\rho_2(z_1))^2}{2} + \int\limits_{z_2 > o} f(r_{12})\rho_2(z_2)d\underset{\sim}{r}_2$$

$$+ \frac{1}{2}\int\limits_{z_2 > o}\int\limits_{z_3 > o} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 + \gamma \quad , \qquad (2.35)$$

where γ is a constant. From boundary condition (2.17) we see that

$$\gamma = -\frac{1}{2}\int\int f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 = -\beta_2 \quad ,$$

where β_2 is the second irreducible integral occurring in the virial theory of the equation of state. Adding together Eqs. (2.35), (2.29) and (2.22), one obtains

$$\rho(z_1) = n + n^2\left[\int\limits_{z_2 > o} f(r_{12})d\underset{\sim}{r}_2 - \beta_1\right] + n^3\left[\frac{1}{2}\left(\int\limits_{z_2 > o} f(r_{12})d\underset{\sim}{r}_2 - \beta_1\right)^2\right.$$

$$+ \int\limits_{z_2 > o}\int\limits_{z_3 > o} f(r_{12})f(r_{23})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 - \beta_1\int\limits_{z_2 > o} f(r_{12})d\underset{\sim}{r}_2 +$$

$$\left.\frac{1}{2}\int\limits_{z_2 > o}\int\limits_{z_3 > o} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 - \beta_2\right] + O(n^4) \ . \qquad (2.36)$$

Likewise, adding together Eq. (2.23) for $h = 2$ and Eq. (2.31), we have

$$g^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})} + ne^{-\beta\varphi(r_{12})}\int\limits_{z_3 > o} d\underset{\sim}{r}_3 f(r_{23})f(r_{13}) + O(n^2) \ . \qquad (2.37)$$

It is important to realize that Eqs. (2.36), (2.37) and their extensions to the higher order distribution functions are valid only if the pair-potential condition, Eq. (2.1), is satisfied. If we want to consider multi-body interactions, or if we need to generate expressions like (2.36) and (2.37) where the only assumption involved is the introduction of a suitable approximate theory of the uniform fluid state, then a completely general set of equations is needed. In the next chapter we develop these equations.

III. FORMULATION OF A NEW APPROACH

A. DERIVATION OF THE EQUATIONS

As a starting point for deriving a general set of equations describing the fluid-solid interaction, we cite the definition of the q^{th}-order distribution function in a suitable ensemble. In the Grand Canonical Ensemble[14],

$$n^{(q)}(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_q) = \frac{1}{Z} \sum_{N>q}^{\infty} \frac{1}{(N-q)!} \int \exp\{N(\lambda + \beta\mu) - \beta\,\Phi(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_N)\} d\underset{\sim}{r}_{q+1} . \; . \; . d\underset{\sim}{r}_N , \tag{3.1}$$

where $\lambda = 3/2\, \ell n(2\pi mkT/h^2)$, $\beta = \frac{1}{kT}$ and μ is the chemical potential. $\Phi(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_N)$ is the total potential energy of an N particle system and can be written as

$$\Phi(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_N) = \Phi'(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_N) + \sum_{i=1}^{N} U(\underset{\sim}{r}_i) \quad .$$

$\Phi'(r_1 . \; . \; . r_N)$ is the interaction energy of a configuration of N molecules, and $U(\underset{\sim}{r}_i)$ is the external potential that acts on the system. Z is the grand canonical partition function defined by

$$Z = \sum_{N=1}^{\infty} \frac{1}{N!} \int \exp\{N(\lambda + \beta\mu) - \beta\,\Phi(\underset{\sim}{r}_1 . \; . \; . \underset{\sim}{r}_N)\} d\underset{\sim}{r}_1 . \; . \; . d\underset{\sim}{r}_N \quad .$$

Equation (3.1) allows us to study the effect of an infinitesimal change in the external potential $U(\underset{\sim}{r}_i)$ on the $n^{(h)}$ functions.

It is easy to prove that

$$\delta n^{(1)}(\underset{\sim}{r}_1) = -\beta\delta U(\underset{\sim}{r}_1)n^{(1)}(\underset{\sim}{r}_1) + \int (-\beta\delta U(\underset{\sim}{r}_2))(n^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) - n^{(1)}(\underset{\sim}{r}_1)n^{(1)}(\underset{\sim}{r}_2))d\underset{\sim}{r}_2 \qquad (3.2)$$

and

$$\delta n^{(h)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h) = n^{(h)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h)\sum_{i=1}^{h} -\beta\,\delta U(\underset{\sim}{r}_i)$$

$$+ \int (-\beta\delta U(\underset{\sim}{r}_{h+1}))\{n^{(h+1)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_{h+1}) - n^{(h)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h)n^{(1)}(\underset{\sim}{r}_{h+1})\}d\underset{\sim}{r}_{h+1}$$

$$(h \geq 2) \quad , \qquad (3.3)$$

where δX stands for "infinitesimal change in" X. By using the definition,

$$n^{(h)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h) = n^{(1)}(\underset{\sim}{r}_1)n^{(1)}(\underset{\sim}{r}_2) . \ . \ . n^{(1)}(\underset{\sim}{r}_h)g^{(h)}(\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h) \ , \qquad (3.4)$$

one can transform Eq. (3.2) to

$$\delta n^{(1)}(\underset{\sim}{r}_1) = n^{(1)}(\underset{\sim}{r}_1)\left[-\beta\delta U(\underset{\sim}{r}_1) + \int d\underset{\sim}{r}_2\, n^{(1)}(\underset{\sim}{r}_2)(-\beta\delta U(\underset{\sim}{r}_2))(g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)-1)\right] \qquad (3.5)$$

and Eq. (3.3) to

$$\delta g^{(h)} = \int d\underset{\sim}{r}_{h+1}\, n^{(1)}(\underset{\sim}{r}_{h+1})\left[g^{(h+1)} - g^{(h)}\left(\sum_{j=1}^{h}(g^{(2)}(\underset{\sim}{r}_{h+1},\underset{\sim}{r}_j)-1)+1\right)\right](-\beta\delta U(\underset{\sim}{r}_{h+1})), \qquad (3.6)$$

where the arguments of $g^{(h)}$ are understood. If we now define $\rho(\underset{\sim}{r}_i) = n^{(1)}(\underset{\sim}{r}_i)e^{\beta U(\underset{\sim}{r}_i)}$, Eq. (3.5) and Eq. (3.6) can be written as

$$\delta\rho(\underset{\sim}{r}_1) = \rho(\underset{\sim}{r}_1)\int d\underset{\sim}{r}_2\,\rho(\underset{\sim}{r}_2)(g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)-1)\,\delta[e^{-\beta U(\underset{\sim}{r}_2)}] \tag{3.7}$$

and

$$\delta g^{(h)}(\underset{\sim}{r}_1 . \; . \; .\underset{\sim}{r}_h) = \int d\underset{\sim}{r}_{h+1}\rho(\underset{\sim}{r}_{h+1})\Bigg[g^{(h+1)}(\underset{\sim}{r}_1 . \; . \; .\underset{\sim}{r}_{h+1})$$

$$-g^{(h)}(\underset{\sim}{r}_1 . \; . \; .\underset{\sim}{r}_h)\left(1+\sum_{j=1}^{h}(g^{(2)}(\underset{\sim}{r}_{h+1},\underset{\sim}{r}_j)-1)\right)\Bigg][\delta e^{-\beta U(\underset{\sim}{r}_{h+1})}]. \tag{3.8}$$

Again we consider a semi-infinite fluid occupying the region $z > 0$ bounded by a plane, solid wall at $z = 0$ and assume that the interaction of the wall with the fluid is due to the existence of a potential field associated with the wall. To generate a new set of equations we specialize Eqs. (3.5) and (3.6) to the situation where $\delta U(r_i)$ is created by a displacement of the wall an infinitesimal distance dz toward the negative z direction. Figure (3.1) is a graph of a typical U(z) as a function of z. The dotted line represents the same function translated to the left by a distance dz. The vertical distance between the dotted and solid curves represents $\delta U(z)$. It follows that $\delta U(z)$ can be expressed as

$$\delta U(z) = U(z+dz) - U(z) = \frac{dU(z)}{dz}\,dz + O(dz^2) \quad .^{\dagger} \tag{3.9}$$

To calculate $\delta\rho(\underset{\sim}{r}_1)$ and $\delta g^{(h)}(\underset{\sim}{r}_1 . \; . \; .\underset{\sim}{r}_h)$, we use the following principle of equivalence. The value of any function, with direct physical significance, of the h points $\underset{\sim}{r}_1 . \; . \; .\underset{\sim}{r}_h$ is unchanged when

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† It is assumed that U(z) does not change as the wall displaces provided z is always measured from the wall.

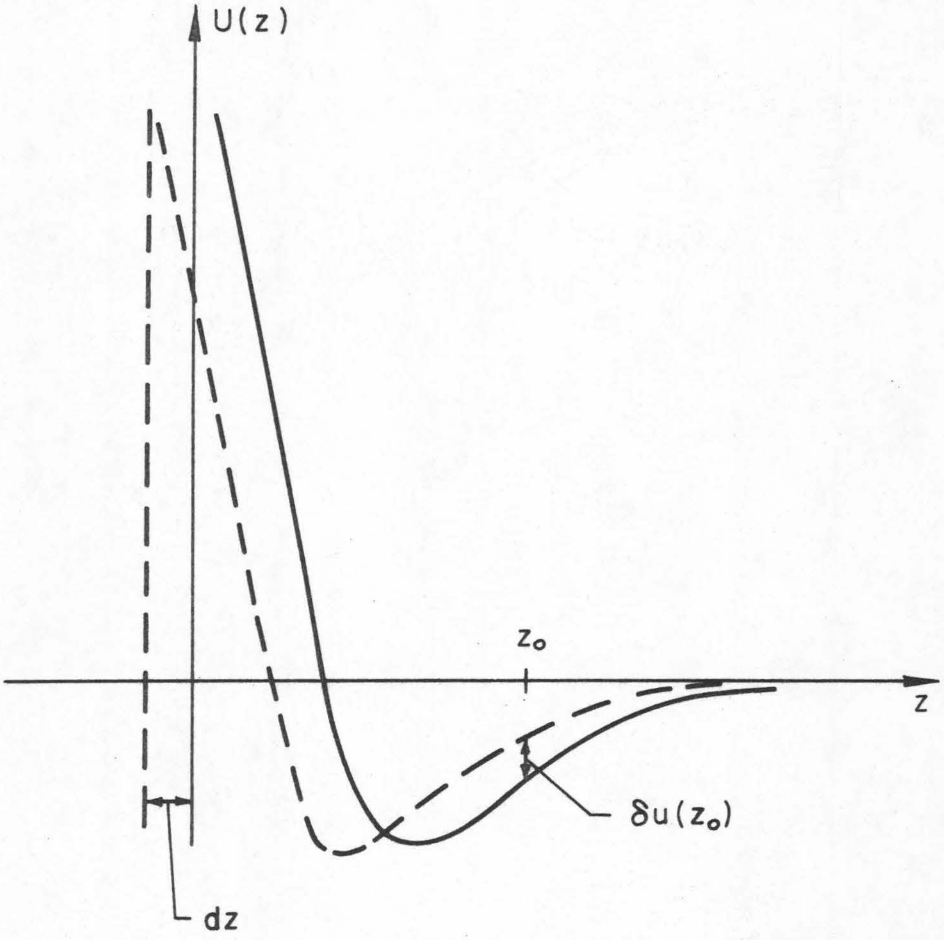

Fig. 3.1 A Typical U(z).

the wall is displaced parallel to the z axis provided the coordinate system used to evaluate $\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h$ moves with the wall. The above statement can only be true to order $1/V$, where V is the volume of the system. Since the system is infinite, the principle must be exact, unless one is attempting to describe a two-phase system. The reason for this restriction will be made clear in Part II.

Thus, defining $\underset{\approx}{\xi} = \hat{e}_z dz$, we have that

$$\delta\rho(z) = \rho(z+dz) - \rho(z) = \frac{d\rho(z)}{dz}\, dz + O(dz)^2 \qquad (3.10)$$

and

$$\begin{aligned}
\delta g^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h) &= g^{(h)}(\underset{\sim}{r}_1 + \underset{\approx}{\xi} \ldots \underset{\sim}{r}_h + \underset{\approx}{\xi}) - g^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h) \\
&= \sum_{k=1}^{h} \nabla_{\underset{\sim}{r}_k} g^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h)\cdot\underset{\approx}{\xi} + O(dz)^2 \\
&= \sum_{k=1}^{h} \frac{\partial}{\partial z_k}\left(g^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h)\right) dz + O(dz)^2 \quad . \qquad (3.11)
\end{aligned}$$

Substituting Eqs. (3.9), (3.10) and (3.11) into Eqs. (3.7) and (3.8), we obtain, in the limit $dz \to 0$,

$$\frac{d\rho(z_1)}{dz_1} = \rho(z_1) \int d\underset{\sim}{r}_2\, \rho(z_2)\left(g^{(2)}(r_{12}, z_1, z_2) - 1\right) \frac{d}{dz_2}\, e^{-\beta U(z_2)} \qquad (3.12)$$

and

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k}\left(g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h\right)\right) =$$

$$\int d\underset{\sim}{r}_{h+1}\,\rho(z_{h+1})\Big[g^{(h+1)}\Big(\overset{h+1}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_{h+1}\Big)$$

$$- g^{(h)}\Big(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h\Big)\Big(1+\sum_{j=1}^{h}\big(g^{(2)}(r_{j,h+1}, z_j, z_{h+1})-1\big)\Big)\Big]\frac{d}{dz_{h+1}}\, e^{-\beta U(z_{h+1})},$$

$$(3.13)$$

where we have used the notation of the previous chapter and where it must be realized that $\frac{\partial}{\partial z_i}$ operates on r_{ik} as well as on z_i in the indicated arguments of $g^{(h)}$.

If the wall is ideal, $e^{-\beta U(z)} = H(z)$ and the expression $\frac{d}{dz}e^{-\beta U(z)} \rightarrow \delta(z)$, where $\delta(z)$ is the Dirac delta function. Equations (3.12) and (3.13) then become

$$\frac{d\rho(z_1)}{dz_1} = \rho(z_1)\int_{z_2 = 0} dS_2\,\rho(z_2)\{g^{(2)}(r_{12}, z_1, z_2) - 1\} \qquad (3.14)$$

and,

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k}(g^{h}) = \int_{z_{h+1}=0} dS_{h+1}\,\rho(z_{h+1})\Big[g^{(h+1)}$$

$$-g^{(h)}\Big(1 + \sum_{j=1}^{h}\big(g^{(2)}(r_{j,h+1}, z_j, z_{h+1})-1\big)\Big)\Big] \quad .$$

$$(3.15)$$

We can use the divergence theorem plus the fact that the bracketed expressions in the integrals of Eqs. (3.14) and (3.15) approach zero for fixed, finite $\underset{\sim}{r}_1 . \ . \ . \underset{\sim}{r}_h$ as $\underset{\sim}{r}_{h+1}$ approaches infinity[14] to further transform Eqs. (3.14) and (3.15) to

$$\frac{d\rho(z_1)}{dz_1} = -\rho(z_1)\int_{z_2>o} d\underset{\sim}{r}_2 \, \frac{\partial}{\partial z_2}\left(\rho(z_2)(g^{(2)}(r_{12}, z_1, z_2)-1)\right) \tag{3.16}$$

and

$$\sum_{k=1}^{h} \frac{\partial}{\partial z_k}(g^h) = -\int_{z_{h+1}>o} d\underset{\sim}{r}_{h+1} \, \frac{\partial}{\partial z_{h+1}}\left[\rho(z_{h+1})\left[g^{(h+1)} - g^{(h)}\left(1+\sum_{j=1}^{h}\left(g^{(2)}(r_{h+1,j}, z_{h+1}, z_j)-1\right)\right)\right]\right]. \tag{3.17}$$

It is interesting to note the similarity between Eqs. (3.16) and (2.10) and between Eqs. (3.17) and (2.11).

Equations (3.16) and (3.17) together with the boundary conditions,

$$\rho(z_1) \to n \qquad \text{as} \qquad z_1 \to \infty \tag{3.18}$$

$$g^{(h)}\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ldots z_h\right) \to g_L^h\left(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})\right)$$

$$\text{as} \quad z_1, \ldots z_h \to \infty, \; r_{\ell m} \text{ fixed},$$

where $g_L^{(h)}$ is the modified h^{th}- order distribution function of a <u>uniform</u> fluid at density n, represent a general formulation of the problem. Like Eqs. (2.10) and (2.11), Eqs. (3.16) and (3.17) are extremely difficult to solve for any value of n. We may, however, again seek a series solution in powers of n. Thus, by substituting

Eqs. (2.14) and (2.15) into Eqs. (3.16) and (3.17) and using the boundary conditions (2.17) and (2.18), we obtain a new set of equations that is independent of the pair-potential assumption.

If the above equations are correct, the series solution of these equations in powers of n, when condition (2.1) is used to calculate the boundary conditions, must be identical to Eqs. (2.36), (2.37), etc. This fact is demonstrated in Section C of the current chapter.

B. OBSERVATIONS AND EXTENSIONS

The equations described above can be used to give some indication of the effect of the pair-potential assumption on nonuniform systems. Practially speaking, this cannot be accomplished until multi-body interactions are better understood, or until a suitable approximate theory of the uniform fluid state is extended to include nonuniformities . With respect to the latter possibility, we expect that an integral equation for $n^{(2)}$ involving $n^{(1)}$ would usually result. This integral equation, together with either Eq. (3.16) or Eq. (2.10),could be solved by using a series solution technique. A comparison of the two solutions would indicate the effects of assumption (2.1). Unfortunately, the usefulness of this approach is somewhat limited since the approximate theories mentioned above are of value mainly in the regime of relatively large n, where the series solution would converge slowly or might possibly diverge.

Still another aspect of the problem is the possibility of solving Eqs. (3.16) and (3.17) without using the series expansion approach. Obviously, the infinite set of equations must be terminated, and the easiest way to do this is to use the so-called superposition approximation,

$$g^{(3)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3) = g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) g^{(2)}(\underset{\sim}{r}_2, \underset{\sim}{r}_3) g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_3) \quad . \tag{3.20}$$

We would then have two coupled, nonlinear, integro-differential equations in the variables $\rho(z_1)$ and $g^{(2)}(r_{12}, z_1, z_2)$. If, indeed, a numerical solution of Eqs. (2.10) and (2.11) is possible using Eq. (3.20), one would also expect a numerical solution of Eqs. (3.16) and (3.17) to be possible. The latter would not be restricted to cases where condition (2.1) is applicable.

Finally, we mention some possible contributions to the theory of gas adsorption. In reality solid walls are not ideal. The potential $U(z)$ is such that the molecules are usually attracted to the wall. Equations (3.16) and (3.17) as well as Eqs. (2.10) and (2.11) can easily be extended to the case where the wall is non-ideal. Consequently, one could solve, at least numerically, for the density $n(z)$ and the distribution functions $g^{(h)}$. By computing

$$\alpha = \int_{z=0}^{\infty} (n(z)-n)dz \quad , \tag{3.21}$$

we would obtain an expression for the number of adsorbed molecules per unit area. For constant n, Eq. (3.21) yields the adsorption isochore. If we express n in terms of p and T, we obtain from Eq. (3.21) the adsorption isobar (for constant p) and the adsorption isotherm (for constant T). Since these quantities are measurable, their calculation is the aim of all adsorption theories.

The statistical mechanical approach is, in some respects, superior to other methods because the former does not involve model assumptions. In particular, the theory presented in this chapter is rigorous if the potential field produced by the wall is known. This would include taking into effect the surface irregularities that must be present on any real solid - - a task of enormous complexity. We must also rule out the case where two phases, liquid and vapor, are present. The reason for the one phase restriction is discussed in Appendix A and involves the question of uniqueness. Practically speaking, this means that for a given temperature, the pressure of the system must be less than the equilibrium vapor pressure at that temperature. Thus, if one is willing to accept the assumption of a mathematically plane wall with perhaps some simple extensions to include the effect of surface irregularities, is satisfied with his knowledge of the potential field produced by the wall,[*] and is only interested in one-phase systems, then the approaches outlined in the preceding two chapters are useful.

The equations developed above have advantages over those developed in Chapter II. Some of these advantages, especially those concerned with relation (2.1),have been detailed. When dealing with adsorption problems, one is usually concerned with rather complex molecules possessing several internal degrees of freedom.

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[*] At present such knowledge is limited.

The interaction potential is therefore quite complicated. The method developed in this chapter seems to be more easily extendable to cases involving such complicated interactions. The basic equations, (2.2) and (2.3), do not contain the two-body potential function, and it is easy to see that this will also be true of the extended equations. Thus, although the integration over molecular coordinates becomes more complicated, the complexity of molecular interactions enters only through the boundary conditions. The B.B.G.K.Y. equations, however, explicitly contain the potential function and, in the general case, appear more complicated.

C. SERIES SOLUTION USING THE PAIR-POTENTIAL CONDITION

We shall now substitute expressions (2.14) and (2.15) into Eqs. (3.16) and (3.17). Using boundary conditions (2.17) and (2.19), where the $C_{\ell}^{(h)}$ in (2.19) are calculated by using the pair-potential condition, we shall then solve Eqs. (3.16) and (3.17) and show that the results are identical to Eqs. (2.36) and (2.37).

Equating terms of order n in Eq. (3.16), we find that

$$\frac{d\rho_1(z_1)}{dz_1} = 0 \quad , \tag{3.22}$$

which, when coupled with boundary condition (2.17), proves that

$$\rho_1(z_1) = 1 \quad . \tag{3.23}$$

Equating terms of order n^2 and n^3 in Eq. (3.16) and using condition (3.23), one obtains

$$\frac{d\rho_2(z_1)}{dz_1} = -\int_{z_2>0} d\underset{\sim}{r}_2 \frac{\partial}{\partial z_2} \left(g_0^{(2)}(r_{12}, z_1, z_2) - 1\right) \tag{3.24}$$

$$\frac{d\rho_3(z_1)}{dz_1} = \rho_2(z_1) \frac{d\rho_2(z_1)}{dz_1} - \int_{z_2>0} d\underset{\sim}{r}_2 \frac{\partial}{\partial z_2} \left[\left(g_0^{(2)}(r_{12}, z_1, z_2) - 1\right)\rho_2(z_2)\right]$$

$$- \int_{z_2>0} d\underset{\sim}{r}_2 \frac{\partial}{\partial z_2} g_1^{(2)}(r_{12}, z_1, z_2) \quad . \tag{3.25}$$

Likewise, by equating terms of order unity and order n in Eq. (3.17) for $h = 2$, and order unity in Eq. (3.17) for $h = 3$, one finds that

$$\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right) g_0^{(2)}(r_{12}, z_1, z_2) = 0 \tag{3.26}$$

$$\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right) \left(g_1^{(2)}(r_{12}, z_1, z_2)\right) = -\int_{z_3>0} d\underset{\sim}{r}_3 \{g_0^{(3)}(r_{12}, r_{23}, r_{13}, z_1, z_2, z_3)$$

$$- g_0^{(2)}(r_{12}, z_1, z_2) \left(g_0^{(2)}(r_{13}, z_1, z_3) + g_0^{(2)}(r_{23}, z_2, z_3) - 1\right)\} \tag{3.27}$$

and

$$\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2} + \frac{\partial}{\partial z_3}\right) g_0^{3}(r_{12}, r_{23}, r_{13}, z_1, z_2, z_3) = 0 \quad . \tag{3.28}$$

The relevant boundary conditions, derived from Eqs. (2.17) and (2.19), are

$$\left.\begin{array}{l} \rho_2(z_1) \to 0 \\ \rho_3(z_1) \to 0 \end{array}\right. \quad \text{as} \quad z_1 \to \infty \tag{3.29}$$

$$g_0^{(2)}(r_{12}, z_1, z_2) \to e^{-\beta\varphi(r_{12})} \quad \text{as} \quad z_1, z_2 \to \infty \; , \quad \text{for fixed } r_{12} \; , \tag{3.30}$$

$$g_o^{(3)}(r_{12}, r_{23}, r_{13}, z_1, z_2, z_3) \rightarrow e^{-\beta\varphi(r_{12})} e^{-\beta\varphi(r_{23})} e^{-\beta(\varphi(r_{13})}$$

$$\text{as } z_1, z_2, z_3 \rightarrow \infty \quad \text{for fixed } r_{12}, r_{23}, r_{13} \tag{3.31}$$

and

$$g_1^{(2)}(r_{12}, z_1, z_2) \rightarrow e^{-\beta\varphi(r_{12})} \int d\underset{\sim}{r}_3 f(r_{13}) f(r_{23}) \quad ,$$

$$\text{as } z_1, z_2 \rightarrow \infty, \quad r_{12} \text{ fixed} \tag{3.32}$$

where

$$f(r_{12}) = (e^{-\beta\varphi(r_{12})} - 1) \quad .$$

Recalling the methods used in Chapter II, we immediately have

$$g_o^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})} \tag{3.33}$$

and

$$\rho_2(z_1) = \int_{z_2 > o} f(r_{12}) d\underset{\sim}{r}_2 - \beta_1 \quad , \tag{3.34}$$

where

$$\beta_1 = \int f(r_{12}) d\underset{\sim}{r}_2 \quad ,$$

and

$$g_o^{(3)}(r_{12}, r_{23}, r_{31}, z_1, z_2, z_3) = e^{-\beta\varphi(r_{12})} e^{-\beta\varphi(r_{13})} e^{-\beta\varphi(r_{23})} \quad . \tag{3.35}$$

By using Eqs. (3.33) and (3.35), we obtain from Eq. (3.27),

$$\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)\left(g_1^{(2)}(r_{12}, z_1, z_2)\right) = -\int_{z_3 > 0} \left[\frac{\partial}{\partial z_3}\left[(f(r_{12})+1)(f(r_{13})+1)(f(r_{23})+1)\right]\right.$$

$$\left. -(1+f(r_{12}))\,\frac{\partial}{\partial z_3}\,(f(r_{13})+f(r_{32})+1)\right] d\underset{\sim}{r}_3 \quad . \quad (3.36)$$

Since

$$-\frac{\partial}{\partial z_3}\left(e^{-\beta\varphi(r_{12})}e^{-\beta\varphi(r_{23})}e^{-\beta\varphi(r_{13})}\right)$$

$$= \left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)\left(e^{-\beta\varphi(r_{12})}e^{-\beta\varphi(r_{23})}e^{-\beta\varphi(r_{13})}\right)$$

and

$$\frac{\partial}{\partial z_3}\,(f(r_{13})+f(r_{23})+1) = -\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right)(f(r_{13})+f(r_{23})+1) \quad ,$$

the solution to Eq. (3.36) can be written as

$$g_1^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})}\int_{z_3 > 0} d\underset{\sim}{r}_3\, f(r_{13})f(r_{23}) + G(r_{12}) \quad ,$$

where $G(r_{12})$ is an arbitrary function of r_{12}. Boundary conditions (3.32) imply that $G(r_{12}) = 0$. Thus,

$$g_1^{(2)}(r_{12}, z_1, z_2) = e^{-\beta\varphi(r_{12})}\int_{z_3 > 0} d\underset{\sim}{r}_3\, f(r_{13})f(r_{23}) \quad . \qquad (3.37)$$

We can now write Eq. (3.25) as

$$\frac{d\rho_3(z_1)}{dz_1} = \rho_2(z_1)\,\frac{d\rho_2(z_1)}{dz_1} + \frac{d}{dz_1}\int d\underset{\sim}{r}_2\,\rho_2(z_2)f(r_{12}) - \int d\underset{\sim}{r}_2\,f(r_{12})\,\frac{d}{dz_2}\Big(\rho_2(z_2)\Big)$$

$$-\int_{z_2>0} d\underset{\sim}{r}_2\,\frac{\partial}{\partial z_2}\left[e^{-\beta\varphi(r_{12})}\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})f(r_{23})\right] \quad . \qquad (3.38)$$

However,

$$-\int_{z_2>0} dr_2\,\frac{\partial}{\partial z_2}\left[e^{-\beta\varphi(r_{12})}\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})f(r_{23})\right]$$

$$= -\int_{z_2>0} d\underset{\sim}{r}_2\,\frac{\partial}{\partial z_2}\left[f(r_{12})\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})f(r_{23})\right] - \int_{z_2>0} d\underset{\sim}{r}_2\,\frac{\partial}{\partial z_2}\left[\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})f(r_{23})\right]$$

$$= -\int_{z_2>0} d\underset{\sim}{r}_2\,\frac{\partial}{\partial z_2}\left[f(r_{12})\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})f(r_{23})\right] + \int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})\,\frac{d}{dz_3}\Big(\rho_2(z_3)\Big)$$

$$(3.39)$$

$$= \frac{d}{dz_1}\left[\int_{z_2>0} d\underset{\sim}{r}_2\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{12})f(r_{23})f(r_{13})\right]$$

$$+\int_{z_2>0} d\underset{\sim}{r}_2\,f(r_{12})\int_{z_3>0} d\underset{\sim}{r}_3\left(\frac{\partial}{\partial z_3}\;f(r_{13})\right)f(r_{23})$$

$$+\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})\,\frac{d}{dz_3}\Big(\rho_2(z_3)\Big) - \int_{z_2>0} d\underset{\sim}{r}_2\,f(r_{12})\int_{z_3>0} d\underset{\sim}{r}_3\,f(r_{13})\,\frac{\partial}{\partial z_2}\Big(f(r_{23})\Big) \quad . \qquad (3.40)$$

A comparison of Eqs. (3.39) and (3.40) indicates that Eq. (3.39) is equivalent to

$$\frac{1}{2}\frac{d}{dz_1}\int_{z_2>0} d\underset{\sim}{r}_2 \int_{z_3>0} d\underset{\sim}{r}_3 f(r_{12})f(r_{23})f(r_{13}) + \int_{z_3>0} d\underset{\sim}{r}_3 f(r_{13}) \frac{d}{dz_3}\rho_2(z_3) \quad .$$

Therefore, we may write the solution of Eq. (3. 38), subject to boundary condition (3. 29), as

$$\rho_3(z_1) = \frac{(\rho_2(z_1))^2}{2} + \int_{z_2>0} d\underset{\sim}{r}_2 f(r_{12})\rho_2(z_2) + \frac{1}{2}\int_{z_2>0}\int_{z_3>0} d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 f(r_{12})f(r_{23})f(r_{13}) - \beta_2 \quad , \tag{3.41}$$

where

$$\beta_2 = \frac{1}{2}\iint d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 f(r_{12})f(r_{13})f(r_{23}) \quad .$$

Adding together the results of this section, we see that relations (2. 36) and (2. 37), derived from the modified B. B. G. K. Y. method, have been duplicated by the current, more general method when condition (2. 1) was imposed on the latter. In Appendix B we derive Eq. (2. 36) by using a different approach based on a functional expansion technique developed by J. K. Percus (Ref. 4, p. II-54).

In reference to the adsorption of a gas by an ideal, plane wall, we may note that when condition (2. 1) is accepted,

$$\alpha = \int_{z=0}^{\infty} (n(z)-n)dz$$

$$= -\pi n^2 \int_0^{\infty} r^3 f(r)dr + O(n^3) \quad . \qquad (3.42)$$

Or, anticipating that $f(r) = g\left(\frac{r}{a_o}\right)$, where a_o is a length scale factor of the size of a molecular radius, we find that Eq. (3.42) becomes

$$\alpha = n^2 a_o^{\,6}\left[-\frac{\pi}{a_o^2}\int_0^{\infty} dx\, x^3 g(x)\right] + O(n^3 a_o^9) \quad . \qquad (3.43)$$

Finally, we should remark that Eq. (2.37), evaluated at $z_1 = 0$, yields

$$\rho(z = 0) = n - n^2 \frac{\beta_1}{2} - \frac{2n^3}{3}\beta_2 + \ldots \quad , \qquad (3.44)$$

which, for the first three terms, is identical to the series $\frac{p}{kT}$ expanded in powers of n (the virial equation of state). Actually, the equation

$$\rho(z=0) = \frac{p}{kT}$$

can be derived by using a different method (Ref. 3, p. 109).

PART II

THE LIQUID-VAPOR INTERFACE

IV: THE GENERAL LIQUID-VAPOR INTERFACE

A. THE THERMODYNAMIC APPROACH

Due to the complexities associated with a statistical mechanical study of nonuniform systems, most attempts to describe the liquid-vapor interface have, to some degree, employed thermodynamic concepts and reasoning. The pure thermodynamic theory, initiated by Gibbs and refined by Tolman[6], was the first attempt to describe surface phenomena. Tolman is careful, however, to emphasize the difficulties associated with the presence of thermodynamically undefined functions in his theory. Another approach involves the use of a free energy density for nonuniform fluids. This method has been used extensively to describe the interface near the critical point and will be discussed in Chapter V. The last basic approach was developed by Hill[7] and involves finding an expression for the chemical potential of the liquid-vapor system. Hill adopts the van der Waals description of the uniform fluid state and then generalizes this description to include nonuniform fluid regions. For a van der Waals fluid,

$$\nu = \ell n[\theta/1+\theta] + [\theta/1-\theta] - \alpha\theta \quad , \qquad (4.1)$$

where

$$\nu = [\mu - \mu^{o}(T) - kT\ell n(kT/b)]/kT \quad ,$$

$$\theta = NbN = nb \quad , \quad \alpha = 2a/bkT \quad ,$$

$$\alpha = \epsilon b \quad , \quad b = 2\pi(r^{*})^{3}/3 \quad .$$

Here, μ is the chemical potential of the fluid, a and b are the standard van der Waals constants, N is the number of molecules, V is the volume occupied by the fluid, and $\mu^{o}(T)$ is a function of T only. The quantity $-\alpha\theta kT$ is interpreted as the interaction energy of a given molecule with the rest of the molecules. The intermolecular potential is taken to be

$$\begin{aligned} \phi(r) &= -\epsilon\left(\frac{r^{*}}{r}\right)^{6} && r > r^{*} \\ &= +\infty && r < r^{*} \end{aligned} \qquad (4.2)$$

and the radial distribution function is taken to be

$$\begin{aligned} g(r) &= 1 && r > r^{*} \\ &= 0 && r < r^{*} \end{aligned} \quad . \qquad (4.3)$$

Hill suggests that Eq. (4.1) can be generalized to apply to a non-uniform fluid by changing α appropriately and letting $\theta \rightarrow \theta(r)$, where $\theta(r) = bn(r)$. The quantity $-\alpha\theta$ is replaced by $\Phi(r)$, where, specializing to a plane interface problem,

$$\Phi(z)kT = \int_{r^{*}}^{\infty}\int_{0}^{\pi}\int_{0}^{2\pi} \phi(r')n(z+z')r'^{2}\sin\theta' d\varphi' d\theta' dr' \quad . \qquad (4.4)$$

$\Phi(z)kT$ is the potential energy of interaction of a molecule at z with all the rest of the molecules under the assumption that Eqs. (4.2) and (4.3) are valid. The requirement that μ is a constant for phase equilibrium implies that ν is a constant for a given temperature T.

Equation (4.1), modified by

$$\theta \rightarrow \theta(z) = n(z)b$$

and

$$-\alpha\theta kT \rightarrow \Phi(z)kT \quad ,$$

where $\Phi(z)kT$ is given by Eq. (4.4), reduces to an integral equation for $n(z)$ when ν is set equal to a constant. For numerical calculations Hill uses Tonks' equation of state for a gas of hard spheres instead of the van der Waals equation, but treats the potential energy term in the same way as above. To calculate the surface tension, he uses an expression derived by Tolman[6]:

$$\sigma = \int_{-\infty}^{\infty} (p-p'(z))dz \quad . \tag{4.5}$$

p is the pressure of the system, and $p'(z)$ is a generalization of p in exactly the same way that μ is generalized. The surface energy, a well defined quantity involving only the potential of interaction, is also calculated. Table (4.1) compares Hill's results for argon at 90°K with those obtained from another method developed by Kirkwood and Buff[4]. The latter method will be discussed in detail in the next section.

It is clear that Hill's approach involves assumptions that are difficult to justify. In fact, the assumptions present in Eqs. (4.2) and (4.3) are simply not valid. We also note from Table (4.1) that there is considerable disagreement between the experimental results and those calculated from the theory. Thus, one is certainly encouraged to investigate the problem from a different viewpoint.

TABLE 4.1

Argon, 90°K

	Hill[7]	Kirkwood and Buff[4]	Experiment[4]
σ(ergs/cm^2)	6.0	14.9	11.9
E_s(ergs/cm^2)	19.0	27.2	35

B. THE KIRKWOOD-BUFF METHOD

The discussion in Section A of this chapter demonstrates the need for a statistical mechanical theory of the liquid-vapor interface. The first attempt in this direction was due to Fowler. He derives[15] expressions for the surface tension and surface energy under the assumption that a step interface separates the two phases. A more complete description is given by Kirkwood and Buff [4] which, in principle, eliminates the above restriction. Since their method plays an important role in obtaining the numerical results found in Section D of Chapter IV, a summary and extension of the method are presented below.

Consider a plane interface with the z-direction normal to the plane of the interface. Under the assumption that the pair-potential condition of Eq. (2.1) is valid, one can derive the following expression for the force acting in the x-direction across a strip in the (y, z) plane of unit width in the y direction and extending from $-\frac{\ell}{2}$ to $\frac{\ell}{2}$ in the z direction:

$$\Sigma_x = -kT \int_{-\frac{\ell}{2}}^{\frac{\ell}{2}} n^{(1)}(z_1)dz_1 + \frac{1}{2}\int_{-\frac{\ell}{2}}^{+\frac{\ell}{2}} dz_1 \left[\int \frac{x_{12}^2}{r_{12}} \varphi'(r_{12}) n^{(2)}(z_1, \underset{\sim}{r}_{12}) d\underset{\sim}{r}_{12}\right] , \tag{4.6}$$

where $n^{(1)}(z_1)$ is the density or first order distribution function as in Chapter II, $n^{(2)}(z_1, r_{12})$ is the second order distribution function, $\underset{\sim}{r}_{12}$ is the vector between points $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$, r_{12} is the distance between $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ and $\varphi'(r_{12}) = \frac{d\varphi(r_{12})}{dr_{12}}$ is the derivative of the intermolecular potential. Obviously,

$$\Sigma_x = -\int_{-\frac{\ell}{2}}^{\frac{\ell}{2}} p'(z_1)dz_1$$

where

$$p'(z_1) = kTn^{(1)}(z_1) - \frac{1}{2}\int \frac{x_{12}^2}{r_{12}} \varphi'(r_{12}) n^{(2)}(z_1, \underset{\sim}{r}_{12}) d\underset{\sim}{r}_{12} \quad . \tag{4.7}$$

From the mechanical definition of the surface tension, we must have

$$\sigma = \int_{-\infty}^{\infty} (p - p'(z_1))dz_1 \quad , \tag{4.8}$$

where p is the thermodynamic pressure of the system. If the pair-potential condition holds, the pressure of the system may be written in two equivalent forms (Ref. 3, p. 48):

$$p = kT n_\ell - \frac{1}{6}\int r_{12}\varphi'(r_{12})n_\ell^{(2)}(r_{12})d\underset{\sim}{r}_{12} \tag{4.9}$$

or

$$p = kT n_v - \frac{1}{6}\int r_{12}\varphi'(r_{12})n_v^{(2)}(r_{12})d\underset{\sim}{r}_{12} \quad , \tag{4.10}$$

where the subscripts ℓ and v refer to the uniform liquid and uniform vapor states respectively.* It is convenient to define the functions $n_{\ell v}$ and $n_{\ell v}^{(2)}$ as

$$\begin{aligned} n_{\ell v}(z) &= (1 - H(z-z_o))n_v + H(z-z_o)n_\ell \\ n_{\ell v}^{(2)}(z,\underset{\sim}{r}_{12}) &= (1-H(z-z_o))\, n_v^{(2)}(r_{12}) + H(z-z_o)n_\ell^{(2)}(r_{12}) \quad , \end{aligned} \tag{4.11}$$

where

$$H(z) = \begin{cases} 1 & z > 0 \\ 0 & z < 0 \end{cases} \quad .$$

The surface $z = z_o$ is an arbitrary Gibbs dividing surface. Therefore, p can be written as

$$p = kT n_{\ell v}(z_1) - \frac{1}{6}\int r_{12}\varphi'(r_{12})n_{\ell v}^{(2)}(\underset{\sim}{r}_{12}, z_1)d\underset{\sim}{r}_{12} \quad . \tag{4.12}$$

Substitution of Eqs. (4.12) and (4.7) into Eq. (4.8) yields

$$\sigma = -\Gamma_s^{(1)}kT + \frac{1}{2}\int \frac{x_{12}^2}{r_{12}}\varphi'(r_{12})\Gamma_s^{(2)}(\underset{\sim}{r}_{12})d\underset{\sim}{r}_{12} \quad , \tag{4.13}$$

---

* n_v is the uniform vapor density and n_ℓ is the uniform liquid density.

where

$$\Gamma_s^{(1)} = \int_{-\infty}^{\infty} n_s(z_1)dz_1 \quad ,$$

$$\Gamma_s^{(2)}(r_{12}) = \int_{-\infty}^{\infty} n_s^{(2)}(z_1, \underset{\sim}{r}_{12})dz_1 \quad , \tag{4.14}$$

and

$$n_s(z_1) = n^{(1)}(z_1) - n_{\ell v}(z_1)$$

$$n_s^{(2)}(z, \underset{\sim}{r}_{12}) = n^{(2)}(z_1, \underset{\sim}{r}_{12}) - n_{\ell v}^{(2)}(z_1, \underset{\sim}{r}_{12}) \quad . \tag{4.15}$$

$\Gamma_s^{(1)}$ is the Gibbs superficial density relative to the surface $z = z_o$. One can see from Eq. (4.13) that σ is independent of z_o.

If the pair-potential condition is satisfied, the functions $n^{(h)}(\underset{\sim}{r}_1 \ldots \underset{\sim}{r}_h)$ must satisfy the B.B.G.K.Y. equations. In particular

$$\frac{dn^{(1)}(z_1)}{dz_1} = + \frac{1}{kT} \int \frac{z_{12}}{r_{12}} \varphi'(r_{12}) n^{(2)}(\underset{\sim}{r}_{12}, z_1) d\underset{\sim}{r}_{12} \tag{4.16}$$

or, because

$$\int z_{12} f(r_{12}) d\underset{\sim}{r}_{12} = 0$$

for arbitrary $f(r_{12})$,

$$\frac{dn_s(z_1)}{dz_1} = (n_v - n_\ell)\delta(z_1 - z_o) + \frac{1}{kT} \int \frac{z_{12}}{r_{12}} \varphi'(r_{12}) n_s^{(2)}(z_1, \underset{\sim}{r}_{12}) d\underset{\sim}{r}_{12} \quad .$$

Multiplication of Eq. (4.17) by $(z_1 - z_o)$ and integration from $z_1 = -\infty$ to $z_1 = +\infty$ gives

$$\int_{-\infty}^{\infty}(z_1-z_o)\frac{dn_s(z_1)}{dz_1}dz_1=\frac{1}{kT}\int\frac{z_{12}}{r_{12}}\varphi'(r_{12})\int_{-\infty}^{\infty}(z_1-z_o)n_s^{(2)}(z_1,\underset{\sim}{r}_{12})dz_1d\underset{\sim}{r}_{12} ,$$

or

$$\int_{-\infty}^{\infty}\left[\frac{d}{dz_1}\Big((z_1-z_o)n_s(z_1)\Big)-n_s(z_1)\right]dz_1$$

$$=\frac{1}{kT}\int\frac{z_{12}}{r_{12}}\varphi'(r_{12})\int_{-\infty}^{\infty}(z_1-z_o)n_s^{(2)}(z_1,\underset{\sim}{r}_{12})dz_1d\underset{\sim}{r}_{12} ,$$

and by assuming $\lim\limits_{\substack{z_1\to+\infty\\ \text{or } z_1\to-\infty}} z_1n_s(z_1)\to 0$, we have that

$$\Gamma_s^{(1)}=-\frac{1}{kT}\int\frac{z_{12}}{r_{12}}\varphi'(r_{12})\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1d\underset{\sim}{r}_{12} , \tag{4.18}$$

where

$$\{\Gamma_s^{(2)}\}_1=\int_{-\infty}^{\infty}(z_1-z_o)n_s^{(2)}(z_1,\underset{\sim}{r}_{12})dz_1 . \tag{4.19}$$

Substituting Eq. (4.18) into Eq. (4.13), we obtain

$$\sigma=\int\frac{1}{r_{12}}\varphi'(r_{12})\left[z_{12}\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1+\frac{x_{12}^2}{2}\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\right]d\underset{\sim}{r}_{12} . \tag{4.20}$$

The Gibbs surface energy is, by definition,

$$E_s=\frac{1}{2}\int\varphi(r_{12})\Gamma_s^{(2)}(\underset{\sim}{r}_{12})d\underset{\sim}{r}_{12} , \tag{4.21}$$

where z_o, in the definition of $\Gamma_s^{(2)}$, is determined by the condition

$$\int_{-\infty}^{z_o} (n^{(1)}(z_1)-n_v)dz_1 + \int_{z_o}^{\infty} (n^{(1)}(z_1)-n_\ell)dz_1 = 0 \quad .$$

In other words, z_o is chosen so that $\Gamma_s^{(1)} = 0$.

Thus, σ and E_s can be determined if $n^{(1)}(z_1)$ and $n^{(2)}(z_1,\underset{\sim}{r}_{12})$ are known. Unfortunately, these functions can be determined only by solving the B.B.G.K.Y. equations. Progress can be made, however, if one assumes a particular $n^{(1)}(z_1)$ and $n^{(2)}(z_1,\underset{\sim}{r}_{12})$ and then substitutes these quantities into Eqs. (4.20) and (4.21). The step interface model is defined as

$$n^{(1)}(z_1) = \begin{cases} n_\ell & z_1 > 0 \\ n_v & z_1 < 0 \end{cases} \tag{4.22}$$

$$g^{(2)}(z_1,\underset{\sim}{r}_{12}) = \frac{n^{(2)}(z_1,\underset{\sim}{r}_{12})}{n^{(1)}(z_1)n^{(1)}(z_2)} = \begin{cases} g_\ell(r_{12}) & z_1 > 0 \ , \quad z_2 > 0 \\ g_v(r_{12}) & z_1 < 0 \ , \quad z_2 < 0 \\ & \\ g_{\ell v}(r_{12}) & z_1 < 0 \ , \quad z_2 > 0 \\ g_{\ell v}(r_{12}) & z_1 > 0 \ , \quad z_2 < 0 \end{cases} \quad , \tag{4.23}$$

where $z_1 = 0$ is the position of the step interface. If we choose*

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*If $n^{(1)}(z_1)$ and $n^{(2)}(z_1,\underset{\sim}{r}_{12})$ are related by Eq. (4.16), then σ, as expressed by (4.20), is independent of z_o. For the step model, σ is likewise independent of z_o. For a general model, however, σ will depend on z_o. This problem is not present in the expression for the surface energy, Eq. (4.21).

$z_o = 0$, $\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1$ and $\Gamma_s^{(2)}(\underset{\sim}{r}_{12})$ can be calculated from relations (4.22) and (4.23). Substituting the results into Eq. (4.20), we obtain

$$\sigma = \frac{\pi}{8}\int_0^\infty r^4\varphi'(r)\,\{(n_\ell)^2 g_\ell(r) + (n_v)^2 g_v(r) - 2n_\ell n_v g_{\ell v}(r)\}dr \quad . \tag{4.24}$$

Since $z_o = 0$ is the surface where $\Gamma_s^{(1)} = 0$, expression (4.21) for the surface energy, with the step interface assumption, becomes

$$E_s = -\frac{\pi}{2}\int_0^\infty r^3\varphi(r)\{(n_\ell)^2 g_\ell(r) + (n_v)^2 g_v(r) - 2n_\ell n_v g_{\ell v}(r)\}dr \quad . \tag{4.25}$$

Kirkwood and Buff[4] assume $\frac{n_v}{n_\ell} \ll 1$ and, in the low vapor density limit, obtain

$$\sigma = \frac{\pi}{8}(n_\ell)^2\int_0^\infty r^4\varphi'(r)g_\ell(r)dr \tag{4.26}$$

$$E_s = -\frac{\pi}{2}(n_\ell)^2\int_0^\infty r^3\varphi(r)g_\ell(r)dr \quad . \tag{4.27}$$

Equations (4.26) and (4.27) can be evaluated if the intermolecular potential and the liquid pair-correlation function are known. Table (4.1) contains the results calculated from Eqs. (4.26) and (4.27) for Argon[4] at 90°K. Shoemaker, Paul, and Marc de Chazal[5] have recently evaluated Eqs. (4.26) and (4.27) using more accurate $g_\ell(r)$ data for several simple liquid-vapor systems. Their results compare favorably with experiment and will be presented in Section D of this chapter.

An interesting problem concerning the two expressions for the surface tension, Eqs. (4.20) and (4.13), exists. Instead of substituting Eqs. (4.22) and (4.23) into Eq. (4.20) and evaluating the surface tension, we could just as easily substitute these relations into Eq. (4.13). One then obtains, for the low-vapor-density approximation,

$$\sigma = - \frac{\pi}{8} (n_{\ell})^2 \int_{0}^{\infty} r^4 \varphi'(r) g_{\ell}(r) dr \quad , \tag{4.28}$$

or exactly the negative of Eq. (4.26). Since the surface tension derived from Eq. (4.26) is usually close to the experimental results, one must conclude that the surface tension values derived from Eq. (4.28) are nonphysical . Fowler[15] computes the surface tension for the step interface model (low vapor density) by defining the surface tension to be one half the work of adhesion between two columns of liquid phase of unit cross sectional area. His results are identical to those derived from Eq. (4.20) when the same approximations are employed. Since the two definitions of the surface tension must be compatible, one must consider σ as defined by Eq. (4.20) to be the proper expression to use with model assumptions like Eqs. (4.22) and (4.23). As a final remark, we should note that Eq. (4.21) for the surface energy is free from any such ambiguity.

C. STRUCTURE OF THE INTERFACE

The structure of the liquid-vapor interface can be determined if the distribution functions of classical statistical mechanics are known. The most commonly suggested method of solution involves solving the B.B.G.K.Y. equations under the superposition hypothesis, Eq. (3.20). The solution of the resulting system of two equations is extremely difficult and must be accomplished numerically. To our knowledge, no solution has been obtained for a nonuniform problem such as the liquid-vapor interface.

There exists another set of equations, mentioned in Chapter III, that will prove useful in dealing with the liquid-vapor interface. We have derived a set of equations describing the infinitesimal change produced in the various distribution functions by an arbitrary, infinitesimal change in the external potential function. Recall that

$$\delta n^{(1)}(\underset{\sim}{r}_1) = n^{(1)}(\underset{\sim}{r}_1)\left[\left(-\beta\,\delta U(\underset{\sim}{r}_1)\right) + \int d\underset{\sim}{r}_2\, n^{(1)}(\underset{\sim}{r}_2)(g^{(2)}(\underset{\sim}{r}_1\,\underset{\sim}{r}_2)-1)(-\beta\,\delta U(\underset{\sim}{r}_2))\right] \tag{3.5}$$

and

$$\delta g^{(h)} = \int d\underset{\sim}{r}_{h+1}\, n^{(1)}(\underset{\sim}{r}_{h+1})\left[g^{(h+1)} - g^{(h)} \sum_{j=1}^{h} (g^{(2)}(\underset{\sim}{r}_{h+1}, \underset{\sim}{r}_j)+1)\right](-\beta\delta U(\underset{\sim}{r}_{h+1})), \tag{3.6}$$

where

$$n^{(h)}(\underset{\sim}{r}_1 \,.\,.\,. \underset{\sim}{r}_h) = n^{(1)}(\underset{\sim}{r}_1).\,.\,. n^{(1)}(\underset{\sim}{r}_h) g^{(h)}(\underset{\sim}{r}_1.\,.\,. \underset{\sim}{r}_h) \quad .$$

Equations (3.5) and (3.6) will now be applied to a particular two-phase problem described below. A liquid-vapor system is contained in a very large box with ideal walls. We assume that a plane interface exists between the liquid and vapor phases, located near z^*, where z^* is the point of inflection of the density profile. An ideal wall is located at $z = z_o$, bounding the vapor phase, and another ideal wall, bounding the liquid phase, is at $z \to \infty$. The distance $z^* - z_o$ is arbitrary and can be made as large as desired. A qualitative picture of the density profile is indicated in Fig. (4.1). Notice that near the wall located at $z = z_o$, the vapor density changes from its asymptotic value. An interesting set of equations results from Eqs. (3.5) and (3.6) if the change in the external potential corresponds to a displacement of the ideal wall, located at $z = z_o$, an infinitesimal distance dz_o in the minus z direction.

The density must change in response to the displacement of the wall. We assume that the density profile in the region near z^* translates a distance $\frac{n_v}{n_\ell} dz_o$ in the positive z direction when the wall is moved an infinitesimal distance dz_o in the negative z direction.[†] This assumption implies that the structure of the interface is independent of the volume of the system at a given temperature, and that the total number of particles contained in the changing volume is a constant. If the microstructure of the interface and, in particular, the density profile changed in a more complicated manner, then the surface tension and surface energy would in general depend on the volume of the system. This dependence is certainly not observed. One might also note that the assumption above is not true near $z = z_o$, since the analysis in Chapter III demonstrated that the density profile near the wall translates a distance dz_o in the negative z direction. Thus,

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[†] We have assumed that $n_v \ll n_\ell$.

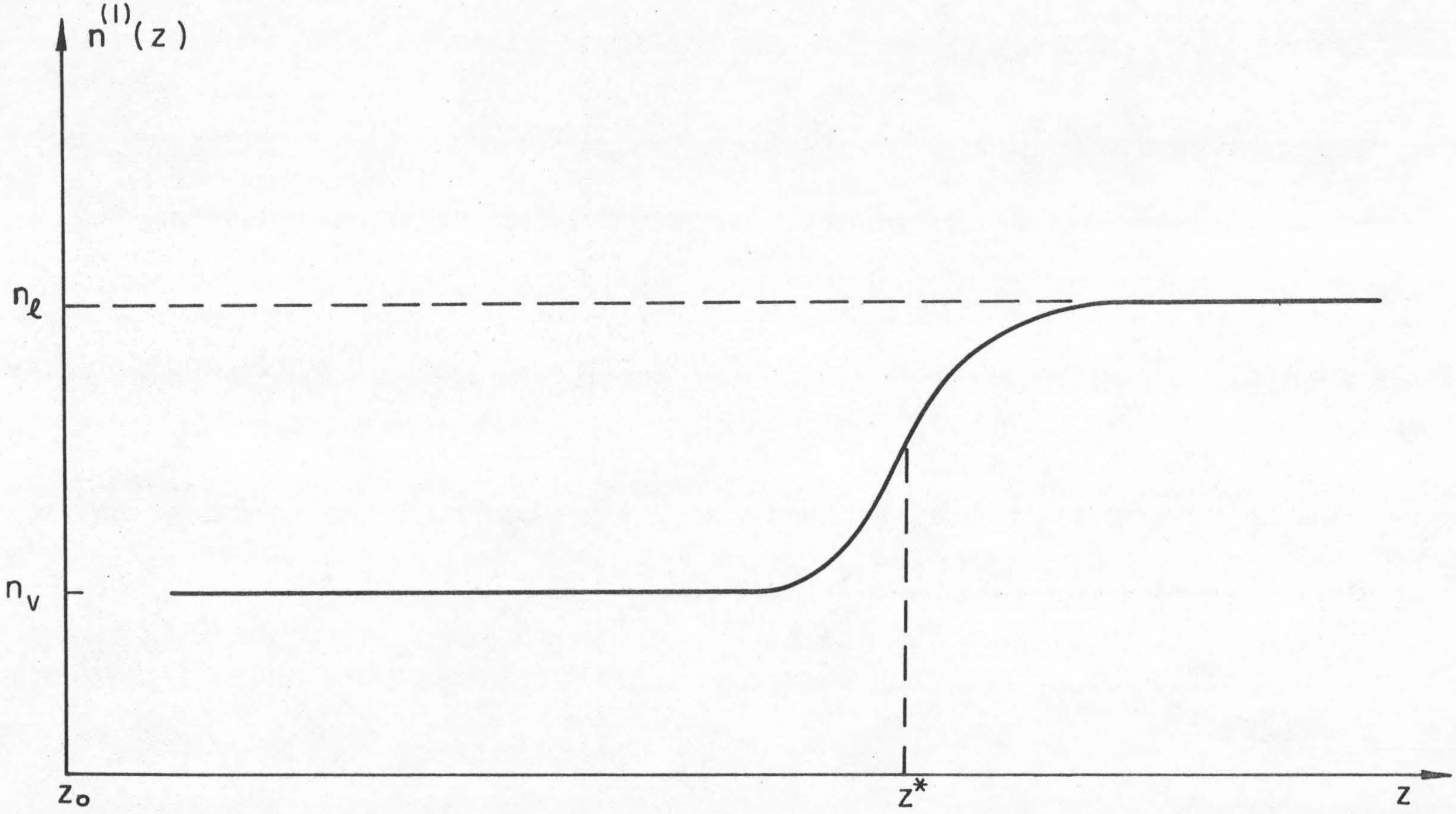

Fig. 4.1 The Density Profile

$$\delta U(z) = U(z+dz_o) - U(z)$$

$$= \frac{dU}{dz}(z)\, dz_o + O(dz_o^2)$$

and by assumption

$$\delta n^{(1)}(z) = n^{(1)}\left(z - \frac{n_v}{n_\ell}\, dz_o \right) - n^{(1)}(z)$$

$$= - \frac{dn^{(1)}(z)}{dz} \frac{n_v}{n_\ell}\, dz_o + O(dz_o^2) \quad .$$

Equation (3.5), with the substitution

$$\rho(z) = n^{(1)}(z) e^{\beta U(z)}$$

becomes

$$\frac{n_v}{n_\ell} \frac{d\rho(z_1)}{dz_1} = - \rho(z_1) \int d\underset{\sim}{r}_2 (g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - 1) \rho(z_2) \frac{d}{dz_2}\, e^{-\beta U(z_2)} \quad , \tag{4.29}$$

and with the ideal-wall assumption, Eq. (4.29) simplifies to

$$\frac{n_v}{n_\ell} \frac{d\rho(z_1)}{dz_1} = - \rho(z_1) \rho(z_o) \int_{z_2 = z_o} dS_2 (g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - 1) \quad , \tag{4.30}$$

where the surface integral is over the surface of the wall and $\rho(z_o)$ is the density at the surface of the wall ($\rho(z) = n^{(1)}(z)$ for $z > z_o$). From symmetry, we have that

$$g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - 1 = f^{(2)}(z_1, z_2, \xi_{12}) \quad ,$$

where

$$\xi_{12}^{\ 2} = (\underset{\sim}{r}_2 - \underset{\sim}{r}_1) \cdot (\underset{\sim}{r}_2 - \underset{\sim}{r}_1) - (z_2 - z_1)^2 \quad .$$

Equation (4.30) therefore becomes equal to

$$\frac{n_v}{n_\ell}\frac{d\rho(z_1)}{dz_1} = -\rho(z_1)\rho(z_o)\int_o^\infty 2\pi\xi_{12}d\xi_{12}f^{(2)}(z_1,z_o,\xi_{12}) \quad . \tag{4.31}$$

Equation (4.30) or Eq. (4.31) illustrate an interesting property of the function $(g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)-1)$ for a two-phase system. For the usual one phase system, $g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)-1 \to 0$ as $|\underset{\sim}{r}_1-\underset{\sim}{r}_2| \to \infty$ (Ref.13, p. II-39). The function $g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ is said to approach unity beyond an effective correlation length. Since (z^*-z_o) can be as large as desired and $\frac{d\rho(z^*)}{dz}$ is finite, Eq. (4.30) implies that no effective correlation length exists for this two-phase system.

The dependence of $f^{(2)}(z_1,z_{12},\xi_{12})$ on ξ_{12} can be examined by using a simple physical argument. Suppose that the volume of the system is bounded by the right circular cylinder, $x^2+y^2=R_o^2$, $z_o<z<\infty$, instead of having infinite extent in the x and y directions. R_o is of macroscopic dimensions, and we shall later take the limit as $R_o\to\infty$. The interface at $z=z_1$ will remain plane for any values of x and y except near the boundary, $x^2+y^2=R_o^2$. If we focus attention on the z dependence of the density when $x=y=0$, the same analysis as before will lead to the equation,

$$\frac{n_v}{n_\ell}\frac{d\rho(z_1)}{dz_1} = -\rho(z_1)\rho(z_o)\int_o^{R_o} 2\pi\xi_{12}d\xi_{12}f^{(2)}(z_1,z_o,\xi_{12}) \quad . \tag{4.32}$$

Suppose now that the wall at $z=z_o$ is constructed with a movable circular piston of radius R, where $R<R_o$. If the piston is

retracted a distance dz_o, then the density profile must translate to the right a distance, $\frac{n_v}{n_\ell} dz_o \frac{\pi R^2}{\pi R_o^2}$. In this case the equation for the density profile when $x = y = 0$ is

$$\frac{n_v}{n_\ell} \frac{\pi R^2}{\pi R_o^2} \frac{d\rho(z_1)}{dz_1} = -\rho(z_1)\rho(z_o) \int_o^R 2\pi\xi_{12} d\xi_{12} f^{(2)}(z_1, z_o, \xi_{12}) \quad . \qquad (4.33)$$

Since $\rho(z_1)$ is the same function in both Eq. (4.32) and Eq. (4.33), we must have that

$$\frac{R^2}{R_o^2} = \frac{\int_o^R \xi_{12} d\xi_{12} f^{(2)}(z_1, z_o, \xi_{12})}{\int_o^{R_o} \xi_{12} d\xi_{12} f^{(2)}(z_1, z_o, \xi_{12})} \quad , \qquad (4.34)$$

where R is arbitrary. Equation (4.34) can be satisfied for arbitrary R if and only if $f^{(2)}$ does not depend on ξ_{12}. Equation (4.32) therefore simplifies to

$$\frac{n_v}{n_\ell} \frac{d\rho(z_1)}{dz_1} = -\rho(z_1)\rho(z_o)\Sigma_o f^{(2)}(z_1, z_o) \quad , \qquad (4.35)$$

where Σ_o is the area of the wall at $z = z_o$. In particular, one is interested in the situation when the vapor density is small. From our discussion in Chapters II and III, we know that the gas density at the surface of an ideal, plane wall is of the form

$$\rho(z_o) = n_v + O(n_v^2)$$

so that, neglecting terms of $O(n_v)^2$, we can write Eq. (4.35) as

$$\frac{d\rho(z_1)}{dz_1} = -\rho(z_1)n_\ell\Sigma_o f^{(2)}(z_1,z_o) \quad . \qquad (4.36)$$

We must now determine the function, $f^{(2)}(z_1,z_o) = g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) - 1$. Simplifying Eq. (3.6) by using the superposition approximation, $g^{(3)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) = g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)\, g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_3)\, g^{(2)}(\underset{\sim}{r}_2,\underset{\sim}{r}_3)$, and specializing to plane symmetry, we have

$$\delta g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2) = g(\underset{\sim}{r}_1,\underset{\sim}{r}_2)\int d\underset{\sim}{r}_3\,\rho(z_3)(g(\underset{\sim}{r}_1,\underset{\sim}{r}_3)-1)(g(\underset{\sim}{r}_2,\underset{\sim}{r}_3)-1)\,\frac{d}{dz_3}\,(e^{-\beta U(z_3)})dz_o \;.^{\dagger} \qquad (4.37)$$

If the wall is ideal, Eq. (4.37) becomes

$$\frac{\delta g^{(2)}(\underset{\sim}{r}_1,\underset{\sim}{r}_2)}{dz_o} = g(\underset{\sim}{r}_1,\underset{\sim}{r}_2)\rho(z_o)\int_{z_3=z_o} dS_3(g(\underset{\sim}{r}_1,\underset{\sim}{r}_3)-1)(g(\underset{\sim}{r}_2,\underset{\sim}{r}_3)-1) \quad . \qquad (4.38)$$

By examining Eq. (4.38) when $\underset{\sim}{r}_1$, $\underset{\sim}{r}_2$ are both near the interface region, one can obtain an equation describing the change in $g(\underset{\sim}{r}_1,\underset{\sim}{r}_2)$ when $z_1 \approx z^*$, $z_2 \approx z^*$. Likewise, when $\underset{\sim}{r}_1$ is near the interface region and $\underset{\sim}{r}_2$ lies on $z_2 = z_o$, one can obtain an equation involving the function $f^{(2)}(z_1,z_o)$.

If $\underset{\sim}{r}_1$ is a point near the interface region and $\underset{\sim}{r}_2$ is a point on the surface of the wall at $z_2 = z_o$, Eq. (4.38) becomes

$$\left.\frac{\delta f^{(2)}(z_1,z_2)}{dz_o}\right]_{z_2=z_o} = \rho(z_o)(f^{(2)}(z_1,z_o)+1)f^{(2)}(z_1,z_o)\int_{z_3,\,z_2=z_o} dS_3(g(\underset{\sim}{r}_2,\underset{\sim}{r}_3)-1) \;. \qquad (4.39)$$

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†The superscript notation is understood.

To determine $\delta f^{(2)}(z_1, z_2)$, we apply Eq. (4.36) to the case where the wall is at $z = z_o - dz_o$. If the wall is at $z = z_o$, Eq. (4.36) implies that

$$\frac{d\rho(z_1)}{dz_1} = -\rho(z_1) n_\ell \Sigma_o f^{(2)}(z_1, z_o) \quad .$$

If the wall is moved to $z = z_o - dz_o$, Eq. (4.36) becomes

$$\frac{d\rho'(z_1)}{dz_1} = -\rho'(z_1) n_\ell \Sigma_o f'^{(2)}(z_1, z_o - dz_o) \quad , \tag{4.40}$$

where $\rho'(z_1)$ is the new density function and $f'^{(2)}(z_1, z_o - dz_o)$ the new correlation function. From the previous discussion, we have noted that

$$\rho'\left(z_1 + \frac{n_v}{n_\ell} dz_o\right) = \rho(z_1) \quad . \tag{4.41}$$

Evaluating Eq. (4.40) at $z_1 = z_1 + \frac{n_v}{n_\ell} dz_o$, one obtains

$$\frac{d\rho'}{dz_1}\left(z_1 + \frac{n_v}{n_\ell} dz_o\right) = -\rho'\left(z_1 + \frac{n_v}{n_\ell} dz_o\right) n_\ell f'^{(2)}\left(z_1 + \frac{n_v}{n_\ell} dz_o, z_o - dz_o\right) \quad . \tag{4.42}$$

Substitution of Eq. (4.41) into Eq. (4.42) yields

$$\frac{d\rho(z_1)}{dz_1} = -\rho(z_1) n_\ell f'^{(2)}\left(z_1 + \frac{n_v}{n_\ell} dz_o, z_o - dz_o\right) \quad . \tag{4.43}$$

Comparing Eq. (4.43) to Eq. (4.36),one concludes that

$$f^{(2)}(z_1, z_0) = f'^{(2)}\left(z_1 + \frac{n_v}{n_\ell}\, dz_0,\ z_0 - dz_0\right) . \tag{4.44}$$

Thus,

$$\frac{\delta f^{(2)}(z_1, z_0)}{dz_0} = \lim_{dz_0 \to 0} \frac{f'^{(2)}(z_1, z_0) - f^{(2)}(z_1, z_0)}{dz_0}$$

is equal to

$$\lim_{dz_0 \to 0} \frac{f'^{(2)}(z_1, z_0) - f'^{(2)}\left(z_1 + \frac{n_v}{n_\ell}\, dz_0, z_0 - dz_0\right)}{dz_0} ,$$

or

$$\frac{\delta f^{(2)}(z_1, z_0)}{dz_0} = -\frac{n_v}{n_\ell} \frac{\partial f^{(2)}(z_1, z_0)}{\partial z_1} + \frac{\partial f'^{(2)}}{\partial z_2}\left(z_1 + \frac{n_v}{n_\ell}\, dz_0, z_2\right)\Bigg]_{z_2 = z_0 - dz_0} .$$

Equation (4.39) therefore reduces to

$$\frac{\partial f^{(2)}(z_1, z_0)}{\partial z_1} - \frac{n_\ell}{n_v} \frac{\partial f'^{(2)}}{\partial z_2}\left(z_1 + \frac{n_v}{n_\ell}\, dz_0, z_2\right)\Bigg]_{z_2 = z_0 - dz_0}$$

$$= -n_\ell (1 + f^{(2)}(z_1, z_0)) f^{(2)}(z_1, z_0) \int_{z_2, z_3 = 0} dS_3 (g(\underset{\sim}{r}_2, \underset{\sim}{r}_3) - 1) , \tag{4.45}$$

where we have again neglected terms of order $(n_v)^2$. Equation (4.45) can be further simplified by considering the z_2 dependence of $f^{(2)}(z_1, z_2)$. If $z_2 \approx z_0$, we assume that the only reason for $f^{(2)}(z_1, z_2)$ to depend upon z_2 is the nonuniformity in the gas phase due to the presence of the wall. This nonuniformity is conveniently described by the inverse length scale, $\frac{1}{\ell(z)} = \frac{1}{\rho(z)} \frac{d\rho(z)}{dz}$. As $\frac{1}{\ell(z)} \rightarrow 0$, the nonuniformity vanishes, and if $\ell(z)$ is small, the nonuniformity is large. Thus, we assume that

$$f^{(2)}(z_1, z_2) = h^{(2)}\left(z_1, \frac{1}{\rho(z_2)} \frac{d\rho(z_2)}{dz_2}\right) = h^{(2)}(z_1, \xi(z_2))$$

and, taking the derivative with respect to z_2, one obtains

$$\frac{\partial f^{(2)}}{\partial z_2}(z_1, z_o) = \frac{\partial h^{(2)}}{\partial \xi}(z_1, \xi(z_o)) \quad \frac{d}{dz_2}\left(\frac{1}{\rho(z_2)} \frac{d\rho(z_2)}{dz_2}\right)\Bigg]_{z_2 = z_o} .$$

From Eq. (3.14), one obtains the relation

$$\frac{1}{\rho(z_2)} \frac{d\rho(z_2)}{dz_2} = \int_{z_3 = z_o} dS_3 \rho(z_3)\{g^{(2)}(r_{23}, z_2, z_3) - 1\}$$

$$= n_v \int_{z_3 = z_o} dS_3 \left(e^{-\beta\varphi(r_{23})} - 1 \right) + O(n_v^2) \quad .$$

Therefore,

$$\frac{d}{dz_2}\left(\frac{1}{\rho(z_2)} \frac{d\rho(z_2)}{dz_2}\right) = n_v \int_{z_3 = o} dS_3 \frac{(z_2 - z_o)}{r_{23}} \frac{d}{dr_{23}} e^{-\beta\varphi(r_{23})} + O(n_v^2) \quad ,$$

or

$$\frac{d}{dz_2}\left(\frac{1}{\rho(z_2)} \frac{d\rho(z_2)}{dz_2}\right)\Bigg]_{z_2 = z_o} = O(n_v^2) \quad .$$

Thus, with neglect of terms of $O(n_v^2)$, Eq. (4.45) simplifies to

$$\frac{\partial f^{(2)}}{\partial z_1}(z_1, z_o) = -n_\ell (f^{(2)}(z_1, z_o)+1)f^{(2)}(z_1, z_o)C \ , \qquad (4.46)$$

where

$$C = \lim_{n_v \to o} \int_{z_2, z_3 = o} dS_3(g(\underset{\sim}{r}_3, \underset{\sim}{r}_2)-1) = \int_o^\infty 2\pi r \, dr(e^{-\beta\varphi(r)}-1) \ .$$

In the following discussion C will be assumed positive. Equation (4.46) is a first-order, ordinary differential equation. The relevant boundary condition is $f^{(2)}(z_1, z_o) \to 0$ as $z_1 \to \infty$.

We expect (See Eq. (4.36)) that $f^{(2)}(z_1, z_o) \sim \frac{1}{\Sigma_o}$ and hence in the limit $\Sigma_o \to \infty$, $f^{(2)}(z_1, z_o)$ should be small compared to unity. Assuming that this is the case, we can simplify Eq. (4.46) to

$$\frac{\partial f^{(2)}(z_1, z_o)}{\partial z_1} = -n_\ell C f^{(2)}(z_1, z_o) \ , \qquad (4.47)$$

which has the solution

$$f^{(2)}(z_1, z_o) = De^{-n_\ell C z_1} \ , \qquad (4.48)$$

with D being an arbitrary constant. Substituting Eq. (4.48) into Eq. (4.36), one obtains

$$\frac{d\rho(z_1)}{dz_1} = -\rho(z_1) n_\ell \Sigma_o De^{-n_\ell C z_1} \ . \qquad (4.49)$$

The constant D can be expressed in terms of the point of inflection for the density profile. Taking the derivative of Eq. (4.49), we have

$$\frac{d^2\rho(z_1)}{dz_1^2} = -\frac{d\rho(z_1)}{dz_1}\, n_\ell \Sigma_o D\, e^{-n_\ell C z_1}$$

$$+ \rho(z_1)(n_\ell)^2 \Sigma_o DC\, e^{-n_\ell C z_1}$$

$$= \rho(z_i) n_\ell \Sigma_o D\, e^{-n_\ell C z_1} (n_\ell \;\; \Sigma_o D\, e^{-n_\ell C z_1} + n_\ell C) \quad .$$

Thus,

$$D = -\frac{C}{\Sigma_o}\, e^{+n_\ell C z^*} \quad ,$$

where z^* is the point of inflection. Equation (4.48) implies that

$$f^{(2)}(z_1, z_o) = -\frac{C}{\Sigma_o}\, e^{-n_\ell C(z_1 - z^*)} \quad , \qquad (4.50)$$

and in the limit $\Sigma_o \to \infty$ we see that $f^{(2)}$ is indeed small compared to unity. Equation (4.49) becomes

$$\frac{1}{\rho(z_1)} \frac{d\rho(z_1)}{dz_1} = + n_\ell C\, e^{-n_\ell C\, z_1} \quad , \qquad (4.51)$$

where we have fixed the point of inflection to be $z^* = 0$. The solution of Eq. (4.51), subject to the boundary condition $\rho(z_1) \to n_\ell$ as $z_1 \to \infty$, is

$$\rho(z_1) = n_\ell \exp(-e^{-n_\ell C z_1}) \quad . \qquad (4.52)$$

Figure (4.2) is a plot of $\rho\left(\frac{z_1}{\delta}\right) / n_\ell$, where $\delta = \frac{1}{n_\ell C}$.

If both $\underset{\sim}{r}_1$ and $\underset{\sim}{r}_2$ lie in the region of the interface, Eq. (4.38)

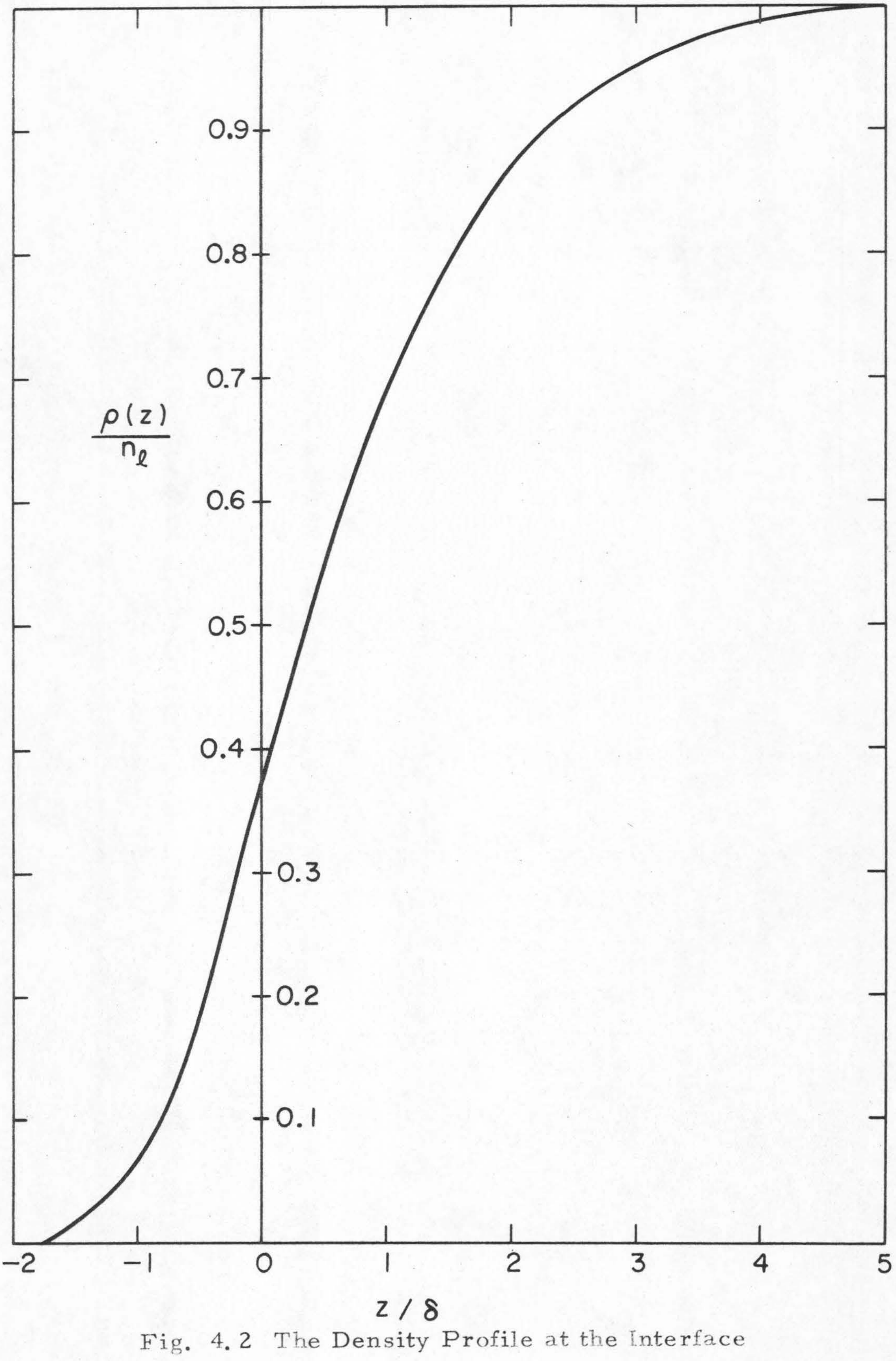

Fig. 4.2 The Density Profile at the Interface

transforms to

$$\frac{\delta g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)}{dz_o} = g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) n_v f^{(2)}(z_1, z_o) f^{(2)}(z_2, z_o) \Sigma_o \quad . \qquad (4.53)$$

To determine $\delta g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)$, we suppose that the two points $\underset{\sim}{r}_1, \underset{\sim}{r}_2$ are physically equivalent points if they both translate with the interface. Thus,

$$g^{(2)'}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = g^{(2)}\left(\underset{\sim}{r}_1 - \frac{n_v}{n_\ell} dz_o \hat{e}_z \ , \ \underset{\sim}{r}_2 - \frac{n_v}{n_\ell} dz_o \hat{e}_z\right)$$

and

$$\frac{\delta g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)}{dz_o} = \lim_{dz_o \to o} \frac{g^{(2)'}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - g^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)}{dz_o}$$

$$= - \frac{n_v}{n_\ell}\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right) g^{(2)}(r_{12}, z_1, z_2) \ .$$

Therefore, Eq. (4.53) becomes, to order $(n_v)^2$,

$$-\left(\frac{\partial}{\partial z_1} + \frac{\partial}{\partial z_2}\right) g^{(2)}(r_{12}, z_1, z_2) = g^{(2)}(r_{12}, z_1, z_2) n_\ell f^{(2)}(z_1, z_o) f^{(2)}(z_2, z_o) \Sigma_o$$

$$= g^{(2)}(r_{12}, z_1, z_2) n_\ell \left[\frac{C^2}{\Sigma_o} \exp\{-n_\ell C(z_1 - z^*) - n_\ell C(z_2 - z^*)\}\right] . \qquad (4.54)$$

From the analysis presented in Chapter III, one can conclude that Eq. (4.54) is equivalent to

$$\frac{d}{dz} g^{(2)}(r_{12}, z_1^o + z, z_2^o + z)$$

$$= -g^{(2)}(r_{12}, z_1^o + z, z_2^o + z) \, n_\ell \left[\frac{C^2}{\Sigma_o} \exp\{2n_\ell C z^* - n_\ell C(z_1^o + z) - n_\ell C(z_2^o + z)\}\right] , \qquad (4.55)$$

where r_{12} is fixed and z_1^o and z_2^o are constants. Integrating Eq. (4.55) from $z = 0$ to $z \to \infty$ and supplying the boundary condition,

$$\lim_{z\to\infty} g^{(2)}(r_{12}, z_1^o+z, z_2^o+z) = g_\ell(r_{12}) \quad , \tag{4.56}$$

where $g_\ell(r_{12})$ is the radial distribution function for the uniform liquid state, we have that

$$\log \frac{g^{(2)}(r_{12}, z_1^o, z_2^o)}{g_\ell(r_{12})} = \int_0^\infty dz\, n_\ell \frac{C^2}{\Sigma_o} \exp\{2n_\ell C z^* - n_\ell C(z_1^o+z) - n_\ell C(z_2^o+z)\}$$

$$= \frac{C}{2\Sigma_o} \exp\{-n_\ell C(z_1^o - z^*) - n_\ell C(z_2^o - z^*)\} \quad . \tag{4.57}$$

Hence, in the limit $\Sigma_o \to \infty$, we have

$$g(r_{12}, z_1^o, z_2^o) \to g_\ell(r_{12}) \; , \tag{4.58}$$

if z_1^o and z_2^o are both near z^*. Equation (4.58) and Eq. (4.52) form the basic results of this section. In the next section we shall use the two expressions to evaluate the surface properties of simple molecular systems.

Several observations can be made at this point. First, it is important to realize that the equations derived above to describe $\rho(z_1)$ and $g(r_{12}, z_1, z_2)$ are approximate ones. The approximations involved are:

(a) The superposition approximation.

(b) The low-vapor-density approximation.

(c) The approximate nature of the equations describing $\rho(z_1)$, $g(r_{12}, z_1, z_2)$ when z_1, z_2 approach the vapor side of the interface.

Approximation (c) obviously results from the fact that the expressions for $\delta\rho(z_1)$ and $\delta g(r_{12}, z_1, z_2)$ are not correct if $z_1 \ll z^*$ or $z_2 \ll z^*$, as the analysis in Chapter III concerning the change in those functions near a plane ideal wall indicates. For this reason, one is not disturbed by the fact that $g(r_{12}, z_1, z_2)$ does not tend to its known value as the vapor phase is approached from the interface region. In addition to these approximations we have made the following assumptions:

(a) The assumption that the properties of the vapor near the ideal wall are not affected by the presence of the interface.

(b) The assumption that

$$\frac{\partial f^{(2)}(z_1, z_o)}{\partial z_2} = O(n_v)^2 ,$$

where z_o is the position of the ideal wall.

(c) The basic assumption that the density profile shifts a distance $dz_o \frac{n_v}{n_\ell}$ in the positive z direction when the wall moves a distance dz_o in the negative z direction.

(d) The assumption that

$$g^{(2)'}(r_{12}, z_1, z_2) = g^{(2)}\left(r_{12}, z_1 - \frac{n_v}{n_\ell} dz_o , z_2 - \frac{n_v}{n_\ell} dz_o\right) ,$$

where $g^{(2)}(r_{12}, z_1, z_2)$ is the pair-correlation function for $z_1 \approx z^*$ and $z_2 \approx z^*$, when the position of the ideal wall is $z = z_o$, and $g^{(2)'}(r_{12}, z_1, z_2)$ is the pair-correlation function for $z_1 \approx z^*$, $z_2 \approx z^*$, when the wall is located at $z = z_o - dz_o$.

(e) The assumption that C is positive.

The last assumption has interesting implications. Recall that

$$C = 2\pi \int_o^\infty r dr \,(e^{-\beta\varphi(r)} - 1) \qquad ,$$

where $\varphi(r)$ is the intermolecular potential, and that $\delta = \frac{1}{n_\ell C}$ is a characteristic length-scale describing the interface. From Fig. (4.2) we see that the density changes from zero to approximately $0.95\, n_\ell$ in a distance of 5δ. It is evident that the sign of C (and hence δ) is related to the intermolecular potential function. For a "hard sphere" system

$$\begin{aligned}(e^{-\beta\varphi(r)} - 1) &= -1 \quad \text{if} \quad r < a_o \\ &= 0 \quad \text{if} \quad r > a_o\end{aligned}$$

so that $C = -\pi a_o^2$, and therefore is negative. To insure that C is positive, the intermolecular potential must be sufficiently attractive (relative to the energy kT). If C is negative, the analysis above indicates that no solution to the equations with physical meaning exists. This fact suggests that the intermolecular force must be sufficiently attractive if a molecular system is to exhibit two-phase behavior. We also note that δ decreases with increasing n_ℓ and increases with increasing temperature (see Table (4.4)). Consequently, δ behaves qualitatively as one would expect. The expression for C even predicts the existence of a critical temperature. Since the low-vapor-density approximation is not valid in the critical region, one does not, however, expect that the condition $C = 0$ will determine the actual critical point.

D. NUMERICAL RESULTS

The numerical methods used here are closely associated with those developed by Shoemaker, Paul, and Marc de Chazal[5]. They calculate the surface tension and surface energy from expressions (4.26) and (4.27), derived by Kirkwood and Buff[4], for the liquid-vapor systems: argon, krypton, xenon, neon, nitrogen, oxygen and methane at certain selected temperatures. To employ Eqs. (4.26) and (4.27) one must know $g_\ell(r)$ and the intermolecular potential. The former can be measured by using X-ray or neutron diffraction data. The intermolecular potential is assumed to be of the Lennard-Jones (L-J) form

$$\varphi(r) = -4\epsilon\left[\left(\frac{r_o}{r}\right)^6 - \left(\frac{r_o}{r}\right)^{12}\right], \tag{4.59}$$

where ϵ and r_o are constants that must be determined. In Ref. [5], the L-J parameters are calculated by using the relationships

$$p = n_\ell kT - \frac{2}{3}\pi(n_\ell)^2 \int_0^\infty g_\ell(r)\varphi'(r)r^3 dr \tag{4.60}$$

and

$$u = 2\pi n_\ell N \int_0^\infty g_\ell(r)\varphi(r)r^2\, dr \quad , \tag{4.61}$$

where $\varphi(r)$ is given by Eq. (4.59), p is the pressure, u is the configurational part of the internal energy per mole, and N is Avogadro's number, together with the experimental values of p and u at a particular temperature. The L-J parameters should be independent of temperature. A slight temperature dependence is, however, observed. Moreover, when ϵ and r_o are determined by gas viscosity data or second virial coefficient data, the results differ considerably from those derived in Ref. [5] . The values of surface tension and surface energy, when the potential is calculated from Eqs. (4.60) and (4.61), are much closer to the experimental results than those obtained by using any other set of experimentally determined L-J parameters. Table (4.2) contains L-J parameters for various molecular systems. The $g_\ell(r)$ data are taken from Ref. [16] for krypton, Ref. [17] for neon and Ref. [18] for oxygen and nitrogen.

Once values of ϵ, r_o, and n_ℓ are available, one can calculate δ from the equation

$$\delta = 1/2\pi n_\ell r_o^2 \int_0^\infty \frac{r}{r_o}\left(\frac{dr}{r_o}\right)(e^{-\beta\varphi(r/r_o)}-1) \quad , \qquad (4.62)$$

where,for numerical purposes,we take

$$\int_0^\infty \frac{r}{r_o}\, d\left(\frac{r}{r_o}\right)(e^{-\beta\varphi(r/r_o)}-1) \approx \int_0^{0.8} \frac{r}{r_o}\, d\left(\frac{r}{r_o}\right)(-1)$$

$$+\int_{0.8}^{6} \frac{r}{r_o}\, d\left(\frac{r}{r_o}\right)(e^{-\beta\varphi(r/r_o)}-1) - \int_6^\infty \beta\varphi\left(\frac{r}{r_o}\right)\frac{r}{r_o}\, d\left(\frac{r}{r_o}\right) \quad .$$

Table (4.3) gives values of δ for some of the L-J parameters in Table (4.2) along with the critical temperatures of the systems in

TABLE (4.2) - - L-J PARAMETERS

			From $g_\ell(r)$, p, u Data		From Second Virial Data		From Gas Viscosity Data	
	n_ℓ ($\AA^{-3}$)	T(°K)	r_o (Å)	ϵ/k(°K)	r_o (Å)	ϵ/k(°K)	r_o (Å)	ϵ/k(°K)
Krypton	0.0176	117.	3.599	168.51	3.827(a)	164.0(a)	3.721(c)	165.02(c)
					3.597(b)	158.0(b)		
Neon	0.0325	33.1	2.761	34.44	2.749(b)	35.60(b)	2.789(b)	35.7(b)
							2.858(b)	27.5(b)
Nitrogen	0.0186	64.	3.341	146.43	3.745(a)	95.2(a)	3.722(c)	85.23(c)
							3.749(b)	79.8(b)
Nitrogen	0.0174	77.	3.339	146.78				
Oxygen	0.0239	64.	3.026	197.72	3.46(b)	118.(b)	3.433(b)	113.(b)
							3.541(b)	88.(b)
Oxygen	0.0228	77.	3.032	199.30	3.46(b)	118.(b)		

(a) A.E. Sherwood and J. M. Brausnitz, J. Chem. Phys. 41, 429 (1964).

(b) Ref. 12, pp. 1110 - 1111.

(c) L.S. Tee, S. Gotoh, and W.E. Stewart, Ind. Eng. Chem. Fundamentals 5, 356 (1966).

TABLE (4.3) - - δ

	T(°K)	r_o(Å)	ϵ/k(°K)	δ(Å)	T_c°(K)[a]
Krypton	117.	3.599	168.51	0.78	209.4
		3.597	158.	0.91	
Neon	33.1	2.761	34.44	1.66	44.8
		2.858	27.5	3.53	
Nitrogen	64.	3.749	79.8	0.96	126.0
		3.341	146.43	0.29	
Nitrogen	77.	3.749	79.8	1.71	126.0
		3.339	146.78	0.48	
Oxygen	64.	3.541	88.0	0.66	154.3
		3.026	197.72	0.13	
Oxygen	77.	3.541	88.0	1.11	154.3
		3.032	199.30	0.21	

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[a] Ref. 19 , p. 136

question.

Recalling that the "width" of the interface is approximately 5δ, we notice that the values of δ associated with L-J parameters determined from $g_\ell(r)$ data appear much too small. Indeed, we will see that the corrections to the step-model calculations of the surface tension and surface energy are extremely small when those values of δ are used. We also note that δ involves an integral of the pair-correlation function for the vapor. This fact suggests that the best values of δ

would be obtained by using L-J parameters determined from second virial coefficients or gas viscosity measurements. In any case, since δ is so sensitive to variations in ϵ and r_o, we shall treat δ as a variable. It is also of interest to examine the temperature dependence of δ. Table (4.4) contains values of δ for the molecular system, oxygen, at several temperatures ranging from 77°K to 65°K under the assumption that n_ℓ is a constant.

Substituting Eqs. (4.52) for the density and (4.58) for the pair-correlation function into Eqs. (4.21) for the surface energy and (4.20) for the surface tension*, one can arrive at new expressions for these quantities reflecting the fact that the transition region has a finite width. The surface energy is, according to Eq. (4.21), given by

$$E_s = \frac{1}{2}\int \varphi(r_{12})\Gamma_s^{(2)}(\underset{\sim}{r}_{12})d\underset{\sim}{r}_{12} \quad , \qquad (4.21)$$

where

$$\Gamma_s^{(2)}(\underset{\sim}{r}_{12}) = \int_{-a}^{\infty} (n^{(2)}(z_1, \underset{\sim}{r}_{12}) - n_{\ell v}^{(2)}(z_1, \underset{\sim}{r}_{12}))dz_1 \; .$$

$\Gamma_s^{(2)}(\underset{\sim}{r}_{12})$, according to Eq. (4.58), is equal to

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[*] Although the relationship , $g(r_{12}, z_1, z_2) = g_\ell(r_{12})$, can only be justified if z_1 and z_2 are near the interface region or on the liquid side of the interface, the extension of the relationship to all z_1, z_2 results in negligible error for the numerical calculations that follow. This is because the important quantity in these calculations is $\rho(z_1)\rho(z_2)g(r_{12}, z_1, z_2)$, where $\rho(z_1)$ is extremely small as z_1 approaches the vapor side of the interface.

TABLE (4.4)

Temperature Dependence of δ for Oxygen ($n_\ell^{(1)} = 0.0228\text{Å}^{-3}$)

(L-J Parameters: $r_o = 3.433\text{Å}$, $\epsilon/k = 113.0\ ^\circ\text{K}$)

T(°K)	δ(Å)
77	0.63
75	0.60
73	0.56
71	0.52
69	0.49
67	0.46
65	0.43

$$\int_{-\infty}^{x} \rho(z_1)\rho(z_1+z_{12}) g_\ell(r_{12}) dz_1 + \int_{x}^{\infty} [\rho(z_1)\rho(z_1+z_{12}) - (n_\ell)^2] g_\ell(r_{12}) dz_1 \quad , \qquad (4.63)$$

where x is determined by the equation

$$\int_{-\infty}^{x} \rho(z)dz = \int_{x}^{\infty} (n_\ell - \rho(z))dz$$

or, if

$$\rho(z) = n_\ell \exp(-e^{-z/\delta}) \quad ,$$

$$\int_{-\infty}^{x} \exp(-e^{-z/\delta})dz = \int_{x}^{\infty} (1 - \exp(-e^{-z/\delta}))dz \quad .$$

It is easily demonstrated that

$$\mathbf{x} = \gamma\delta \quad (\gamma = 0.5772\ .\ .\ .)\quad ,$$

where γ is Euler's Constant. Equation (4.63) then becomes

$$\Gamma_s^{(2)}(\underset{\sim}{r}_{12}) = (n_\ell)^2 g_\ell(r_{12})\left[\int_0^\infty \exp\{-e^{-z_1/\delta}(1+e^{-z_{12}/\delta})\}dz_1\right.$$

$$\left.+\int_0^\infty (\exp\{-e^{-z_1/\delta}(1+e^{-z_{12}/\delta})\}-1)dz_1+\gamma\delta\right], \tag{4.64}$$

which is equivalent to

$$\Gamma_s^{(2)}(\underset{\sim}{r}_{12}) = -(n_\ell)^2 g_\ell(r_{12})\delta\log(1+e^{-z_{12}/\delta}) \tag{4.65}$$

so that the surface energy becomes

$$E_s = -\pi(n_\ell)^2\delta\int_0^\infty r^2\varphi(r)g_\ell(r)dr\int_0^\pi \sin\theta\log(1+e^{-r\cos\theta/\delta})d\theta$$

or

$$E_s = -\pi(n_\ell)^2\delta^2\int_0^\infty r\varphi(r)g_\ell(r)dr\int_{-r/\delta}^{r/\delta}\log(1+e^{-u})du\quad . \tag{4.66}$$

Letting

$$E_{so} = -\frac{\pi}{2}(n_\ell)^2\int_0^\infty r^3\varphi(r)g_\ell(r)dr$$

be the surface energy based on the step-interface, low-vapor-density model, we have

$$\Delta E_s = E_s - E_{so} = -\pi(n_\ell)^2\delta^2\int_0^\infty r\varphi(r)g_\ell(r)dr\left[\int_{-r/\delta}^{r/\delta}\log(1+e^{-u})du - \frac{r^2}{2(\delta)^2}\right]\quad . \tag{4.67}$$

ΔE_s represents a correction to the surface energy determined from the step interface model used by previous authors[4],[5]. As expected, the correction depends on the width of the interface through the parameter δ. For numerical purposes, we write Eq. (4.67) as

$$\Delta E_s = -\pi(n_\ell)^2 \delta^2 \int_0^\infty r\varphi(r) g_\ell(r) dr \left[\int_{-r/\delta}^{0} (\log(1+e^{-u}) + u) du + \int_0^{r/\delta} (\log(1+e^{-u})) du \right] . \qquad (4.68)$$

Both integrals approach a constant value rapidly as r/δ becomes large. The u integrations were evaluated for each value of r at which $g_\ell(r)$ data were available. Both the $g_\ell(r)$ data and the point function of r resulting from the integration over u were fitted with a ninth order polynomial curve (centered on the sub-range of integration) and then the integration over r was performed using Simpson's rule. The L-J parameters for the intermolecular potential in Eq. (4.68) were determined from the $g_\ell(r)$, p, and u data. $g_\ell(r)$ was set equal to unity for values of r greater than the maximum r for which $g_\ell(r)$ data were available. Since negative $g_\ell(r)$ values are unphysical, $g_\ell(r)$ was set equal to zero for all r less than the largest r where $g_\ell(r)$ was zero or negative.

In Table (4.5) we present the values of E_{so} as calculated in Ref. [5] as well as from our own calculations. Table (4.5) also contains the ΔE_s results for several values of δ (for each molecular system) and the experimental values of E_s[5]. The second smallest value of δ included in Table (4.5) is, with the exception of neon and krypton, the largest one available from Table (4.3). The values of δ calculated from the $g_\ell(r)$, p and u data lead to rather small corrections in the surface energy - - less than 1.0 erg/cm^2 in all cases. The values of δ obtained from gas experiments lead to more significant corrections, and even larger values of δ yield E_s values very close to the experimental ones. These larger values of δ imply an interface thickness of about the size that one would expect intuitively (one or two molecular diameters).

To calculate the surface tension from Eq. (4.20), we need $\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1$. Choosing* $z_o = 0$ and using Eq. (4.58) we have

$$\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1 = \int_{-\infty}^{o} z_1 \rho(z_1)\rho(z_1+z_{12}) g_\ell(r_{12}) dz_1 + \int_{o}^{\infty} z_1[\rho(z_1)\rho(z_1+z_{12}) - (n_\ell)^2] g_\ell(r_{12}) dz_1 \ . \qquad (4.69)$$

Substituting Eq. (4.52) into Eq. (4.69), we find that

$$\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1 = (n_\ell)^2 g_\ell(r_{12})\delta^2 \left[\int_{-\infty}^{o} \frac{z_1}{\delta} \exp\{-e^{-z_1/\delta}(1+e^{-z_{12}/\delta})\} \frac{dz_1}{\delta} + \int_{o}^{\infty} \frac{z_1}{\delta} (\exp\{-e^{-z_1/\delta}(1+e^{-z_{12}/\delta})\}-1) \frac{dz_1}{\delta} \right] . \qquad (4.70)$$

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*The dependence of σ on z_o for the following model was found to be negligible.

TABLE (4.5) $\Delta E_s (\mathrm{erg/cm^2})$

							Experimental		
	T(°K)	$E_{so}^{(5)}$	E_{so}	δ(Å)	ΔE_s	E_s	$E_s^{(5)}$	r_o(Å)	ε/k(°K)
Krypton	117	33.44	33.49	0.96	3.74	37.23(37.18)	40.1	3.599	168.51
				1.3	6.57	40.06(40.01)			
Neon	33.1	8.05	8.02	1.71	3.99	12.01(12.04)	14.3	2.761	34.44
				2.2	6.00	14.02(14.05)			
Nitrogen	64.	22.93	22.93	0.83	1.99	24.92(24.92)	27.5	3.341	146.43
				0.96	2.66	25.59(25.59)			
				1.3	4.71	27.64(27.64)			
				1.43	5.63	28.56(28.56)			
Nitrogen	77.	19.79	19.76	1.43	4.78	24.54(24.57)	26.4	3.339	146.78
				1.71	6.55	26.31(26.34)			
				1.9	7.89	27.65(27.68)			
Oxygen	64.	33.91	33.97	0.39	0.81	34.78(34.72)	?	3.026	197.72
				0.66	2.27	36.24(36.18)			
Oxygen	77.	30.85	30.96	0.63	1.85	32.81(32.70)	37.1	3.032	199.30
				1.11	5.50	36.46(36.35)			
				1.3	7.41	38.37(38.26)			
				1.5	9.61	40.57(40.46)			

If we let $u = \frac{z_1}{\delta}$ and $v = e^{-u}$, and define $A = 1 + e^{-z_{12}/\delta}$, Eq. (4.70) becomes

$$\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1 = (n_\ell)^2 g_\ell(r_{12})\delta^2 \left[\int_\infty^1 \frac{\log v}{v} e^{-Av} dv + \int_1^0 \frac{\log v}{v} (e^{-Av} - 1) dv \right] .$$

Defining

$$F(A) = \int_\infty^1 \frac{\log v}{v} e^{-Av} dv + \int_1^0 \frac{\log v}{v} (e^{-Av} - 1) dv \quad ,$$

we have that

$$F'(A) = \frac{dF(A)}{dA} = \int_0^\infty \log v \, e^{-Av} dv$$

$$= - \frac{\gamma}{A} - \frac{\log A}{A} \quad ,$$

where γ is Euler's constant. Thus,

$$F(A) = -\gamma \log A - \frac{1}{2} (\log A)^2 + \alpha \quad ,$$

where α is a constant. Therefore,

$$\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1 = -(n_\ell)^2 g_\ell(r_{12})\delta^2 \left[\gamma \log(1 + e^{-r_{12}\cos\theta/\delta}) + \frac{1}{2} (\log(1 + e^{r_{12}\cos\theta/\delta}))^2 + \alpha \right] .$$

The constant α may be set equal to zero since

$$\int \frac{1}{r_{12}} \varphi'(r_{12}) z_{12} (-(n_\ell)^2 g_\ell(r_{12}) \delta^2 \alpha) d\underset{\sim}{r}_{12} = 0$$

for any value of α. The expression for $\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1$ then becomes

$$\{\Gamma_s^{(2)}(\underset{\sim}{r}_{12})\}_1 = -(n_\ell)^2 g_\ell(r_{12})\delta^2\left[\gamma\log(1+e^{-r_{12}\cos\theta/\delta}) - \frac{1}{2}(\log(1+e^{-r_{12}\cos\theta/\delta}))^2\right] . \tag{4.71}$$

From Eqs. (4.64) and (4.65) it follows that $\Gamma_s^{(2)}(\underset{\sim}{r}_{12})$, evaluated for the dividing surface $z_0 = 0$, is given by

$$\Gamma_s^{(2)}(\underset{\sim}{r}_{12}) = -(n_\ell)^2 g_\ell(r_{12})\delta(\log(1+e^{r_{12}\cos\theta/\delta})+\gamma) . \tag{4.72}$$

Substituting Eqs. (4.71) and (4.72) into Eq. (4.20), we obtain

$$\sigma = -(n_\ell)^2\delta^2 2\pi\int_0^\infty r^2\varphi'(r)g_\ell(r)dr\int_0^\pi \sin\theta\cos\theta\Big[\gamma\log(1+e^{-r\cos\theta/\delta})$$

$$+\frac{1}{2}(\log(1+e^{-r\cos\theta/\delta}))^2\Big]d\theta$$

$$-(n_\ell)^2\frac{\delta}{2}\int_0^\infty r^3\varphi'(r)g_\ell(r)dr\int_0^{2\pi}\sin^2\varphi\, d\varphi\int_0^\pi \sin^3\theta(\log(1+e^{-r\cos\theta/\delta})+\gamma)d\theta$$

or

$$\sigma = -(n_\ell)^2\delta^4\pi\int_0^\infty \varphi'(r)g_\ell(r)dr\int_{-r/\delta}^{r/\delta} u\Big[2\gamma\log(1+e^{-u})$$

$$+(\log(1+e^{-u}))^2 - \frac{u}{2}\log(1+e^{-u})\Big]du$$

$$-(n_\ell)^2\gamma\delta\frac{2\pi}{3}\int_0^\infty r^3\varphi'(r)g_\ell(r)dr$$

$$-(n_\ell)^2\frac{\delta^2\pi}{2}\int_0^\infty r^2\varphi'(r)g_\ell(r)dr\int_{-r/\delta}^{r/\delta}(\log(1+e^{-u}))du .$$

Recalling that

$$\sigma_o = \frac{\pi}{8}(n_\ell)^2 \int_0^\infty r^4 \varphi'(r)dr \quad ,$$

where σ_o is the surface tension based on the step model, low-vapor-density approximation, one can derive the following expression for $\sigma - \sigma_o$:

$$\begin{aligned}
\Delta\sigma = \sigma - \sigma_o = & -(n_\ell)^2\delta^4\pi \int_0^\infty \varphi'(r)g_\ell(r)dr \int_0^{r/\delta} u\Big[2\gamma \log(1+e^{-u}) - \frac{u}{2}(\log(1+e^{-u})) \\
& \qquad + (\log(1+e^{-u}))^2\Big] du \\
& -(n_\ell)^2\delta^2\frac{\pi}{2}\int_0^\infty r^2\varphi'(r)g_\ell(r)dr \int_0^{r/\delta} \log(1+e^{-u})du \\
& -(n_\ell)^2\delta^4\pi \int_0^\infty \varphi'(r)g_\ell(r)dr \int_{-r/\delta}^{0} u\Big[2\gamma(\log(1+e^{-u})+u) \\
& \qquad - \frac{u}{2}\log(1+e^{-u}) + (\log(1+e^{-u}))^2 - \frac{3}{2}u^2\Big] du \\
& -(n_\ell)^2\delta^2\frac{\pi}{2}\int_0^\infty r^2\varphi'(r)g_\ell(r)dr \int_{-r/\delta}^{0} (\log(1+e^{-u})+u)du \quad . \qquad (4.73)
\end{aligned}$$

Each integral above approaches a constant value for large r/δ and is therefore easy to evaluate numerically. The methods and assumptions employed to evaluate Eq. (4.73) are the same as those used in the ΔE_s calculations. Table (4.6) contains the values of $\Delta\sigma$ for the same values of δ used in Table (4.5). The experimental values of σ are also listed.

It is interesting to note that the correction $\Delta\sigma$ to σ_o is positive for small δ and then becomes negative as δ increases. This behavior is indicated in Figs. (4.8) - (4.12) where σ is plotted against δ for the molecular systems: oxygen (77°K), nitrogen (64°K), nitrogen (77°K), krypton (117°K), and neon (33.1°K). Figures (4.3) - (4.7) illustrate the δ-dependence of E_s for the same systems. The degree to which one can predict the correct surface tension and surface energy depends on the value of δ. Since δ is rather sensitive to changes in the L-J parameters and presumably even to variations of the potential-model, more work is needed to determine the best model and model-parameters for this application. An investigation into the potential model dependence of σ_o and E_{so} would also be worthwhile*. If model and model-parameter improvements do not significantly change the value of δ from the range indicated in Table (4.3), then the results of the above interfacial theory imply small to moderate improvement in the surface energy calculations and a slight increase in the surface tension away from the experimental values (except for neon at 33.1°K). If, on the other hand, larger values of δ result from potential model improvements, or if δ is treated as a variable, it is possible to calculate surface energy values extremely close to the experimental results while also improving upon the surface tension predictions. In connection with this possibility one should note that the difference between the surface tension calculated from the step model and the experimental results is much smaller than the corresponding difference for the surface energy. Consequently, for larger values of δ the above

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*See Ref. [20] for a discussion of potential models.

TABLE (4.6) $\Delta\sigma$(dyne/cm)

	T(°K)	$\sigma_o^{(5)}$	σ_o	δ(Å)	$\Delta\sigma$	σ	Experimental σ	r_o(Å)	ϵ/k(°K)
Krypton	117.	17.09	17.7	0.96	0.27	17.97(17.36)	16.1	3.599	168.51
				1.3	-0.17	17.64(16.92)			
Neon	33.1	4.49	4.43	1.71	-0.66	3.77(3.86)	2.7	2.761	34.44
				2.2	-1.06	3.37(3.43)			
Nitrogen	64.	12.73	12.73	0.83	0.58	13.31(13.31)	12.0	3.341	146.43
				0.96	0.51	13.24(13.24)			
				1.3	0.07	12.80(12.80)			
				1.43	-0.19	12.54(12.54)			
Nitrogen	77.	11.47	11.33	1.43	-0.20	11.13(11.27)	8.9	3.339	146.78
				1.71	-0.69	10.62(10.76)			
					-1.04	10.29(10.33)			
Oxygen	64.	18.64	18.71	0.39	0.58	19.29(19.22)	?	3.026	197.72
				0.66	0.95	19.66(19.59)			
Oxygen	77.	17.62	17.69	0.63	0.92	18.61(18.54)	16.5	3.032	199.30
				1.11	0.38	18.00(17.93)			
				1.3	-0.20	17.49(17.42)			
				1.5	-0.81	16.88(16.81)			

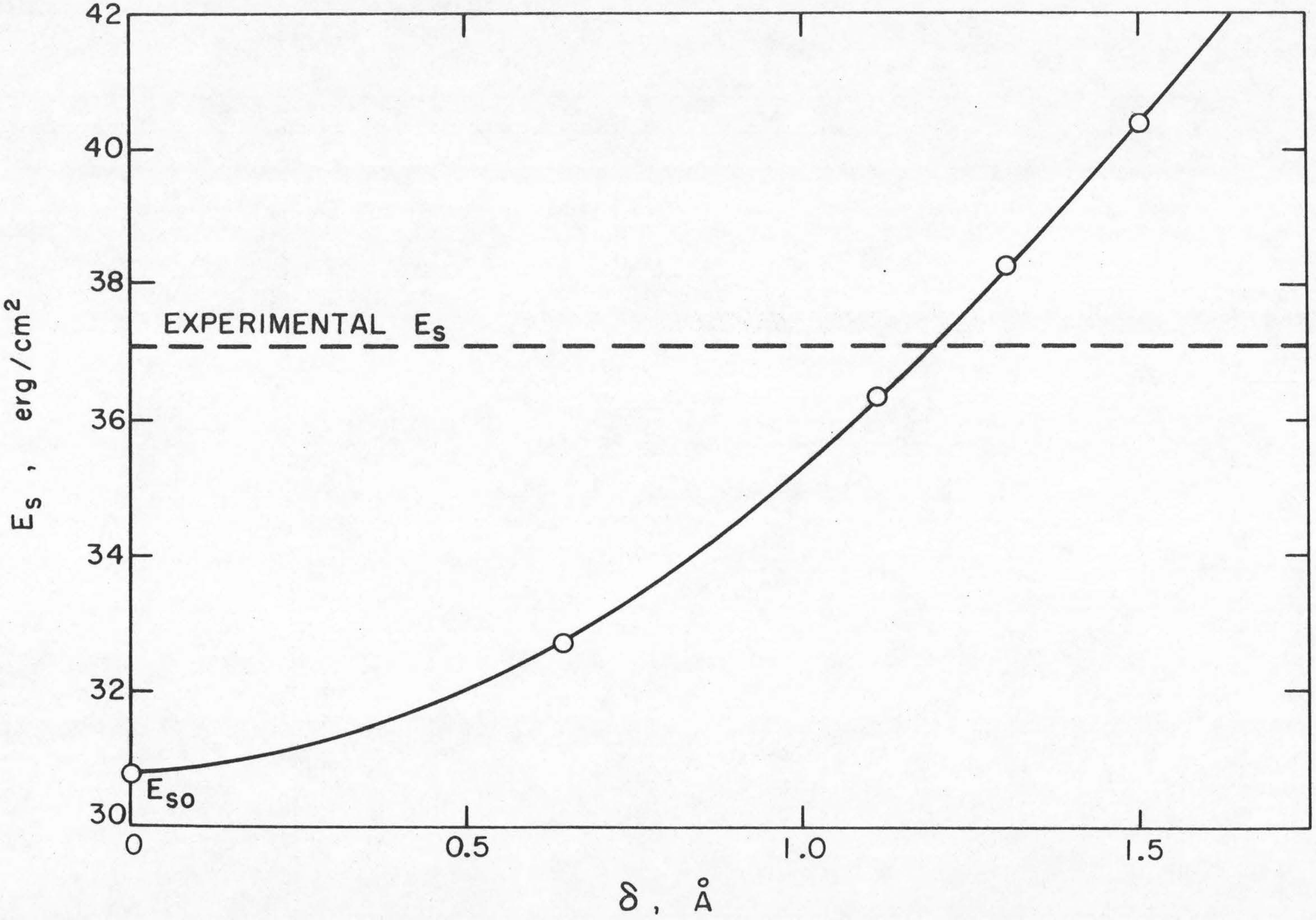

Fig. 4.3 $E_s(\delta)$ for Oxygen at 77°K

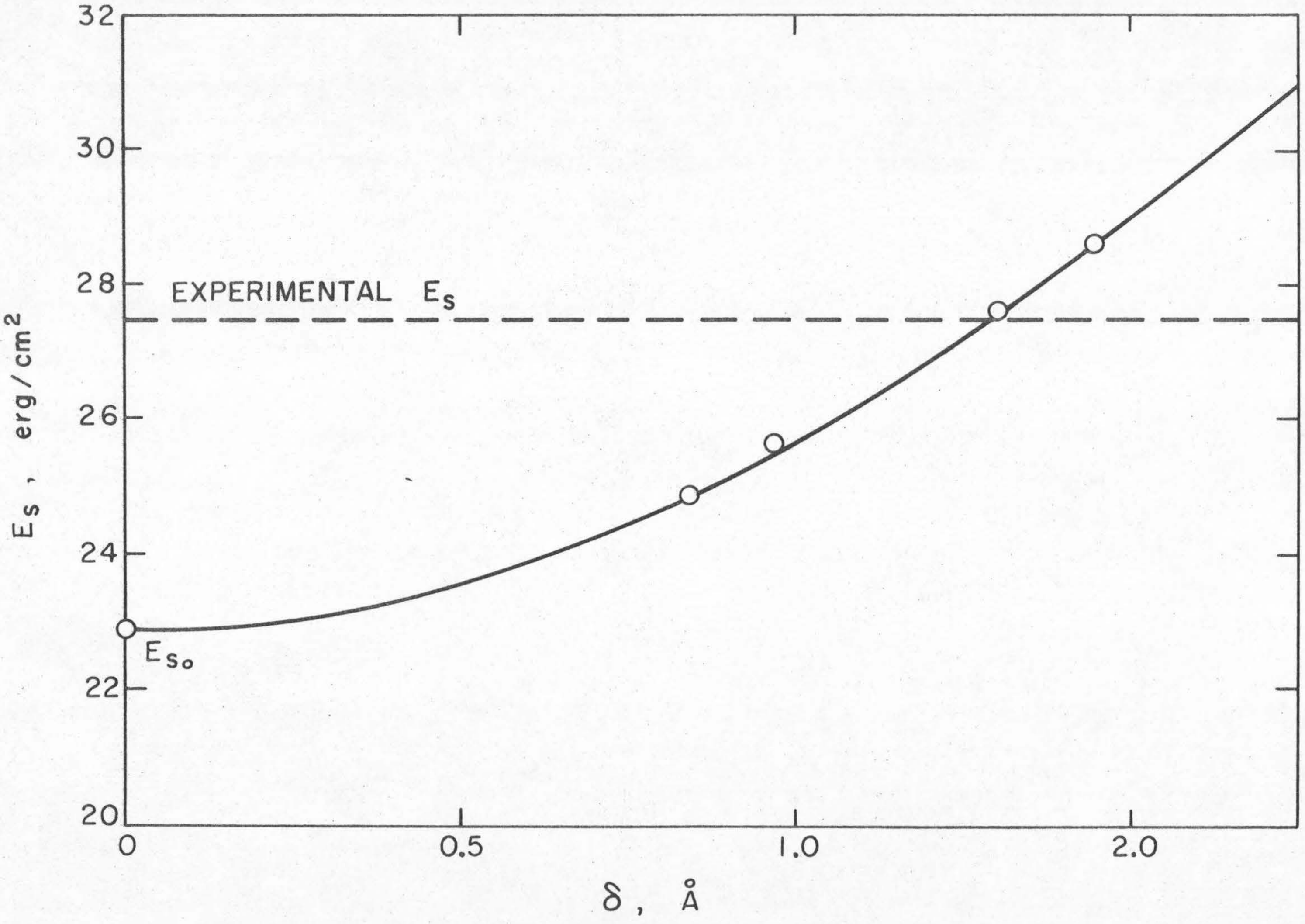

Fig. 4.4 $E_s(\delta)$ for Nitrogen at 64°K

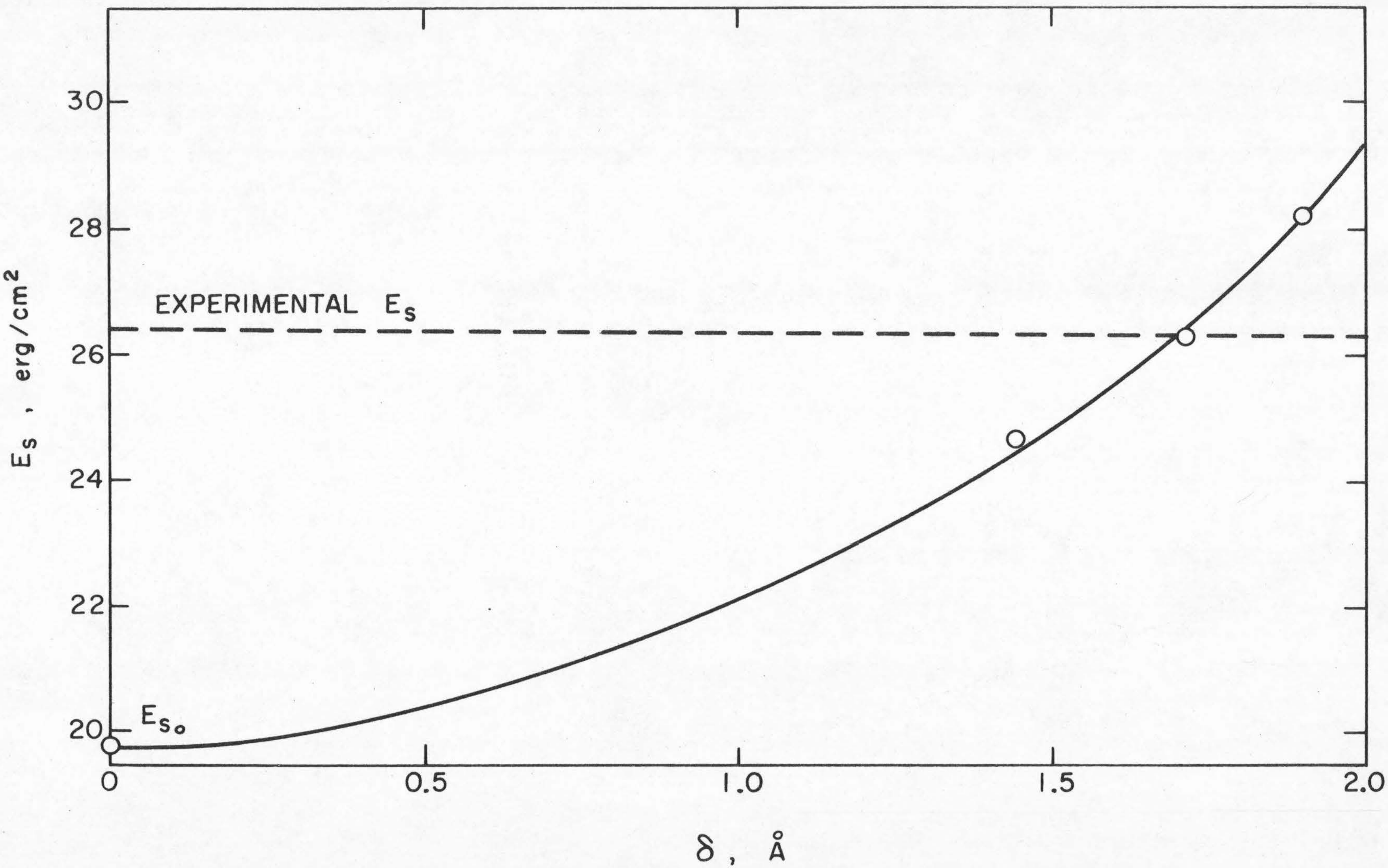

Fig. 4.5 $E_s(\delta)$ for Nitrogen at 77°K

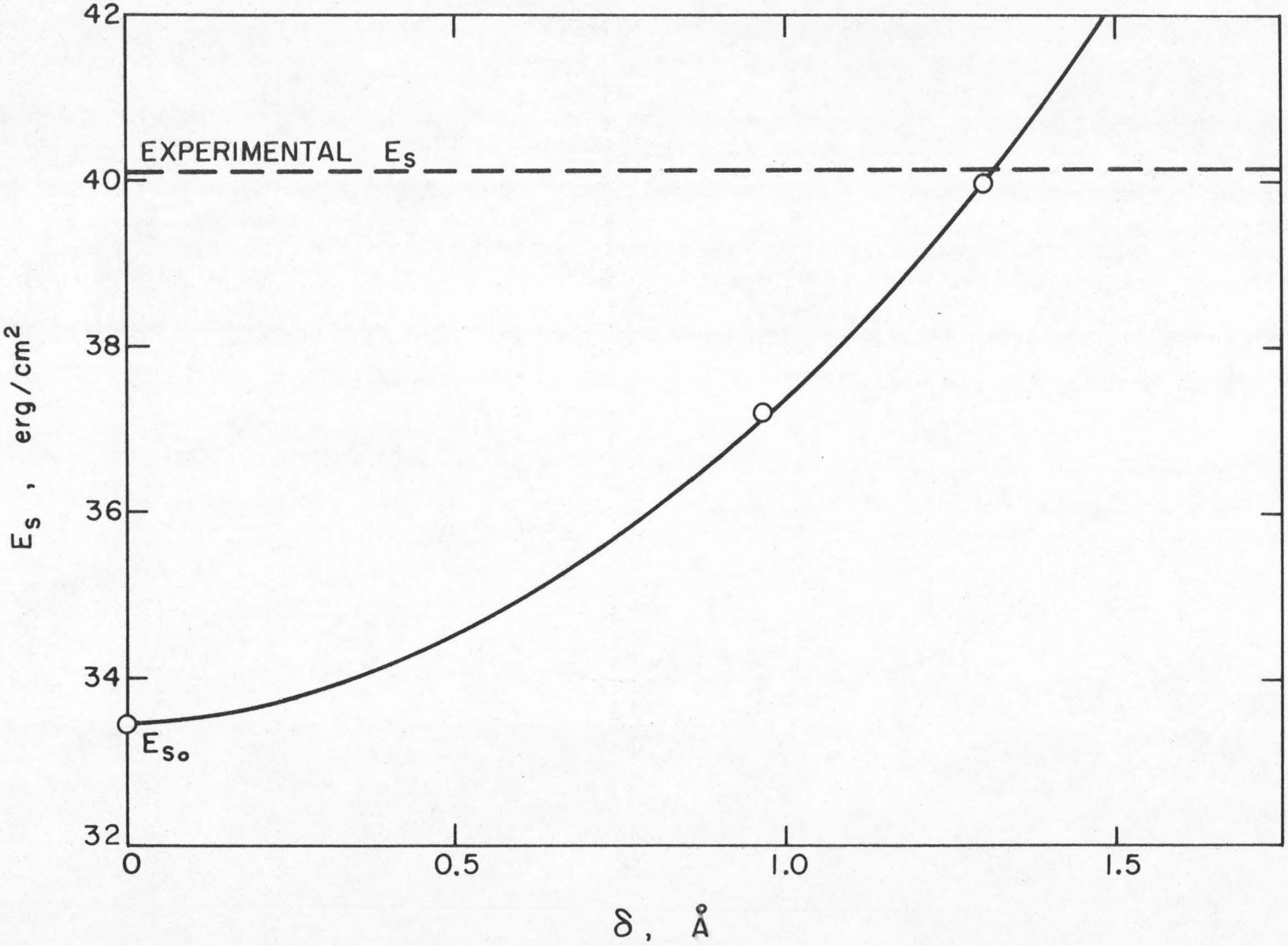

Fig. 4.6 $E_s(\delta)$ for Krypton at 117°K

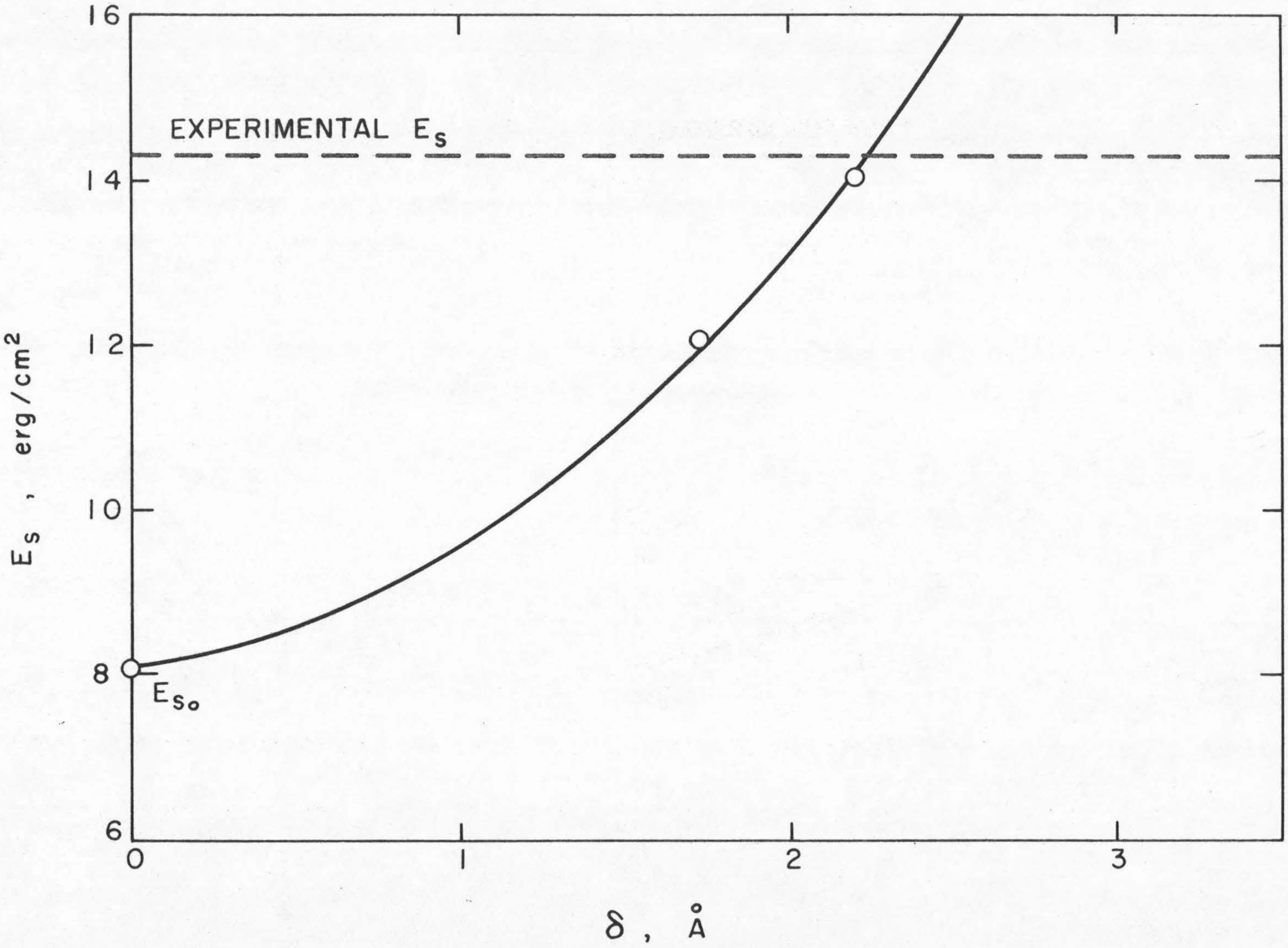

Fig. 4.7 $E_s(\delta)$ for Neon at 33.1°K

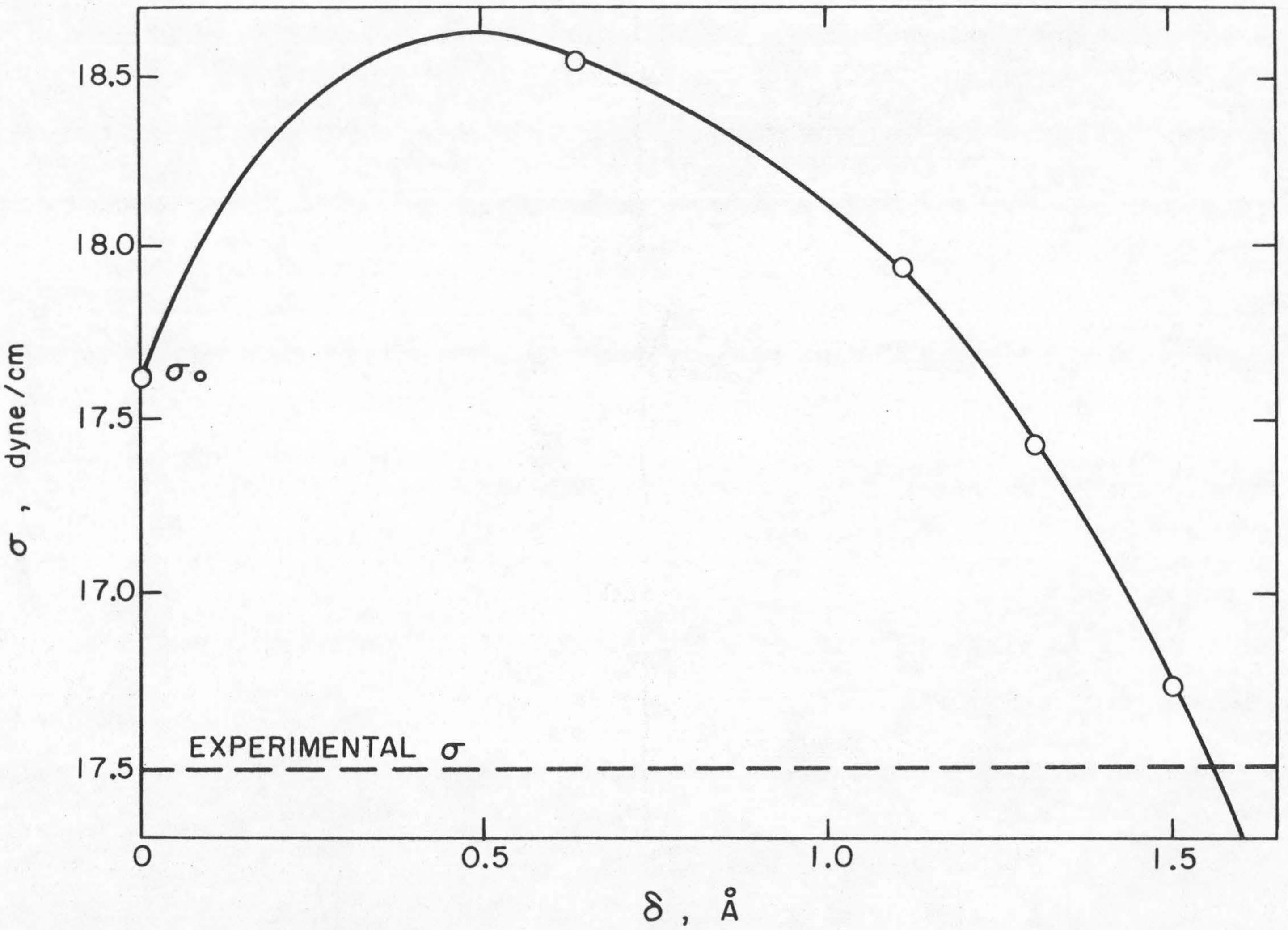

Fig. 4.8 $\sigma(\delta)$ for Oxygen at 77°K

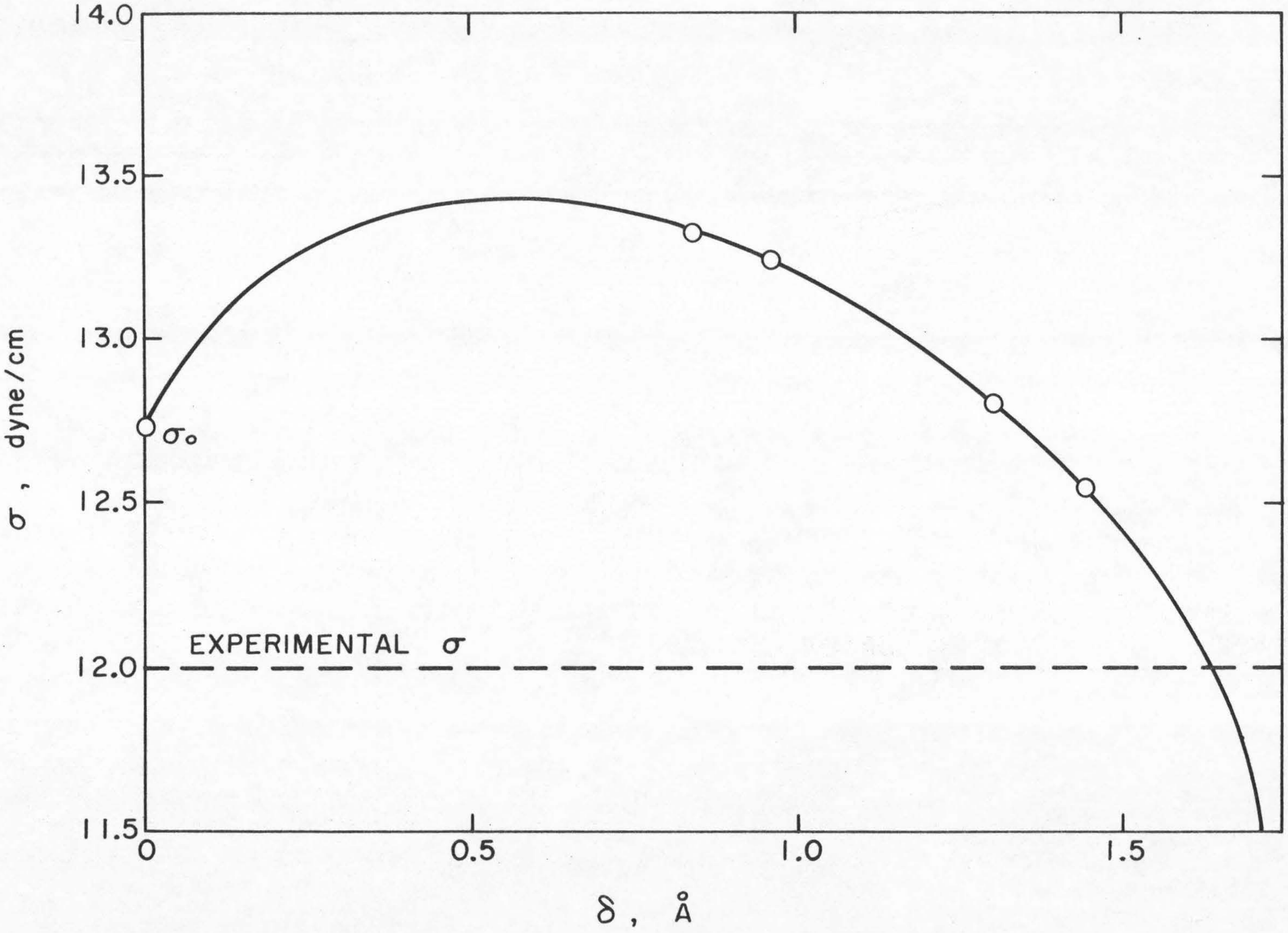

Fig. 4.9 $\sigma(\delta)$ for Nitrogen at 64°K

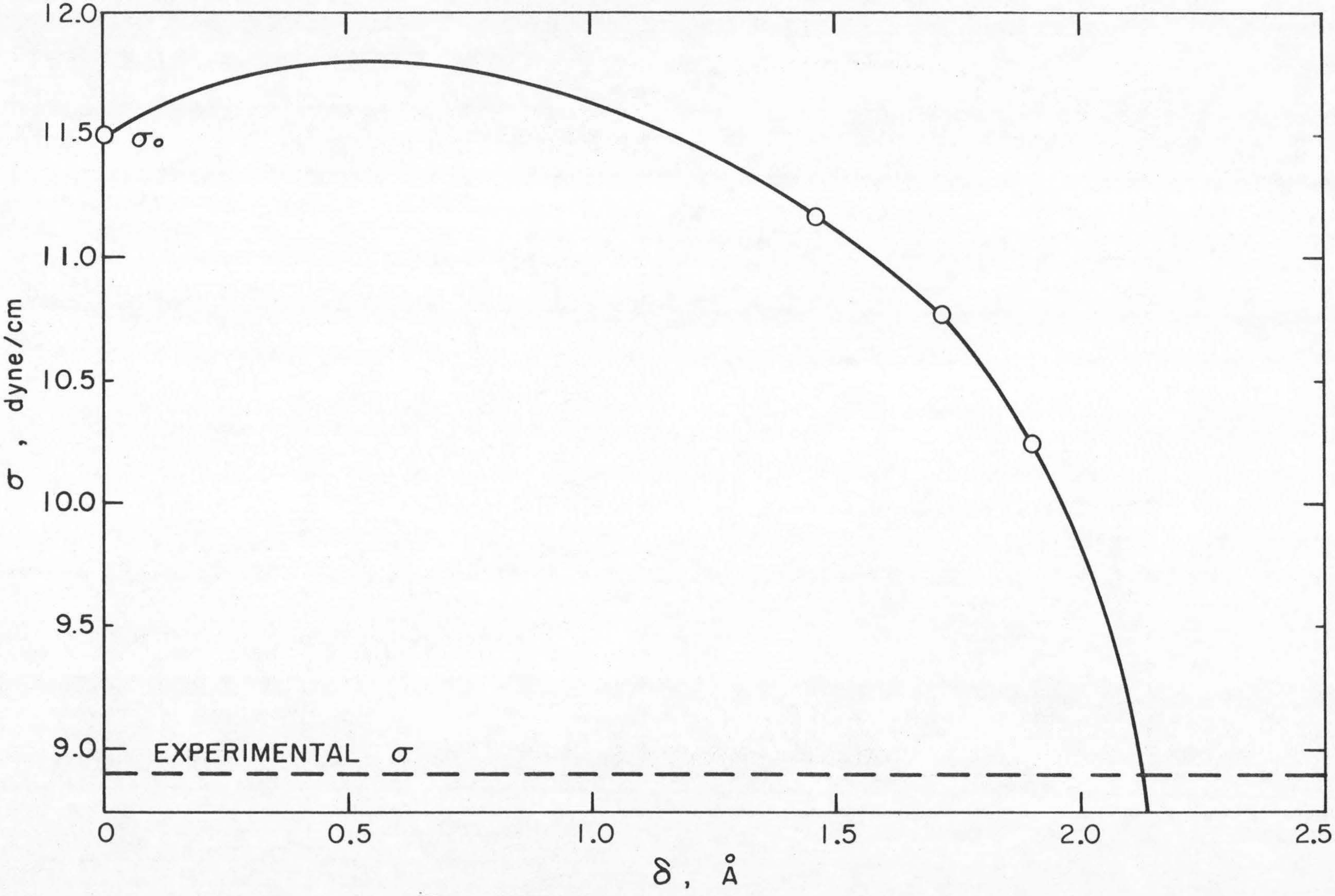

Fig. 4.10 σ(δ) for Nitrogen at 77°K

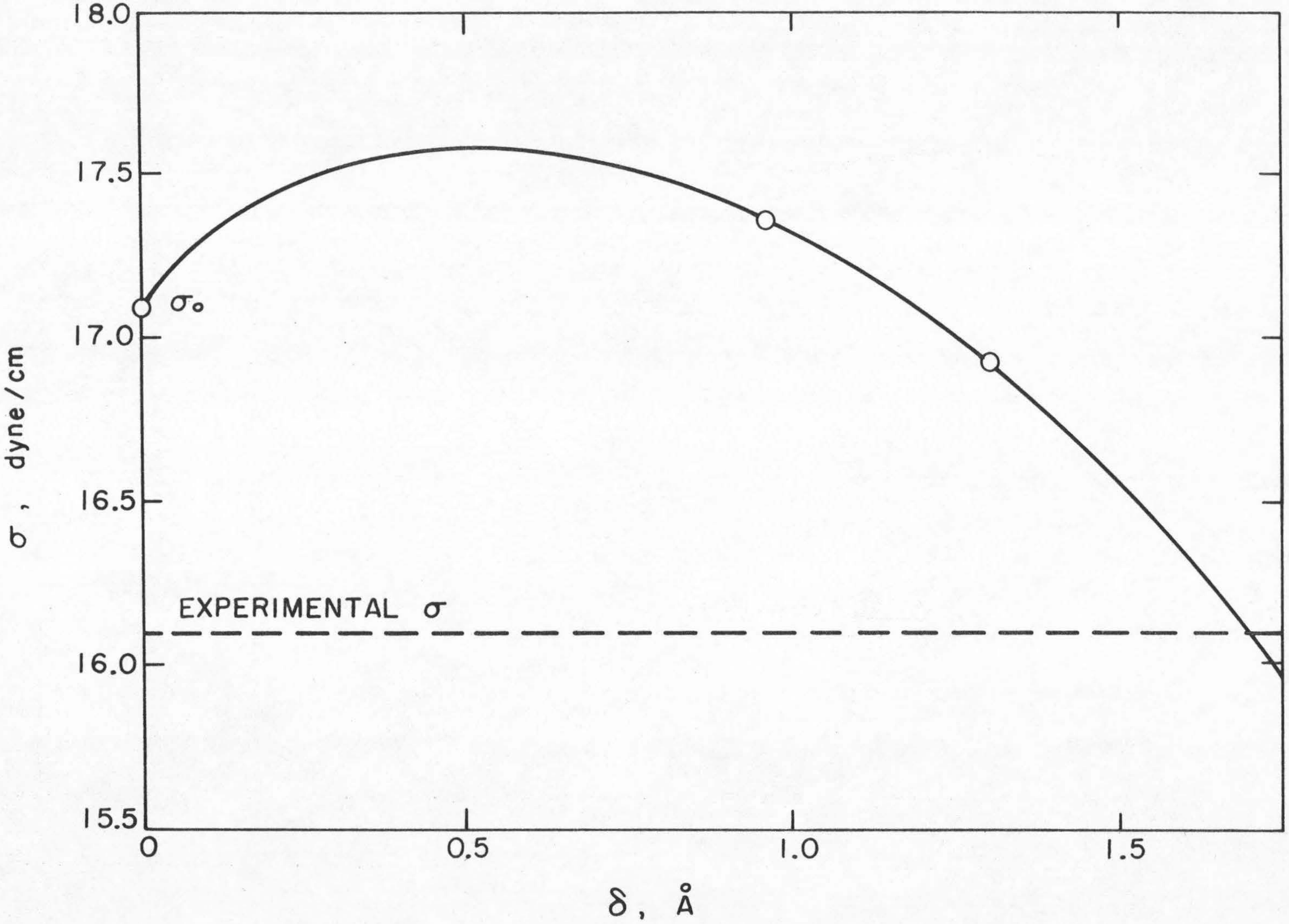

Fig. 4.11 $\sigma(\delta)$ for Krypton at 117°K

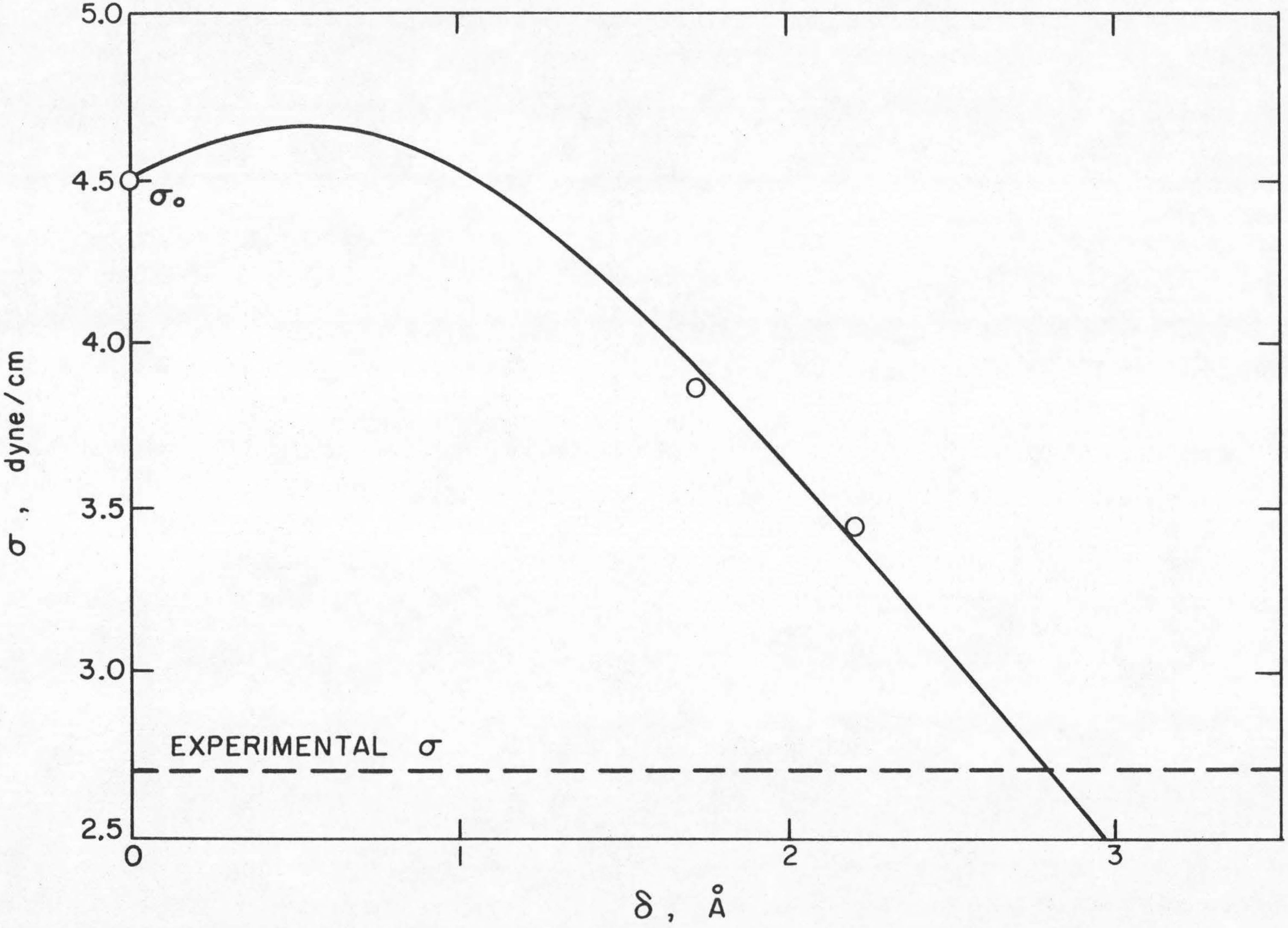

Fig. 4.12 $\sigma(\delta)$ for Neon at 33.1°K

theory represents a significant improvement over the step-interface theory.

E. SUMMARY AND CONCLUSIONS

The main result of this chapter is the development of a non-trivial model for the liquid-vapor transition region. By studying the functional relationship between the statistical mechanical distribution functions and an externally applied potential, we have been able to derive, with the aid of the superposition approximation, approximate equations that describe the variations in these functions near the transition region. In particular, the resulting density function contains a parameter that characterizes the width of the interface region. This parameter exhibits a physically reasonable dependence on temperature, liquid density, and strength of the intermolecular potential.

In order to test the solutions, we numerically evaluated the statistical mechanical expressions for the surface energy and surface tension. The results offer an improvement over the step-interface calculations; however, the degree of improvement depends on the aforementioned length parameter. The parameter δ in turn depends on the assumed potential model and the constants associated with the model. For the Lennard-Jones model we found that δ varied considerably, depending upon which set of experimentally determined parameters were used. The smaller values of δ in this range produced very small corrections to the step-model results. The larger values of δ produced considerable improvement in the surface energy, while the surface tension calculations did not agree with experiment as well as the corresponding step-interface values. Better results were obtained with even larger (though physically reasonable) values of δ. In this case the surface energy predictions were close to the experimental values, and the surface tension calculations improved slightly.

Suggestions for further research include an examination of the potential-model problem, particularly as it applies to the determination of δ. It is also suggested that the original step-interface calculations be examined in the light of different potential-model assumptions. Efforts to eliminate some of the approximations used to derive the transition region model appear difficult and not especially fruitful. Rather, we feel that solutions to the non-uniform B.B.G.K.Y. equations would yield more insight into the complexities of the liquid-vapor interface than any extension of the current theory. Finally, the effect of the pair-potential assumption on the expressions for the surface energy and surface tension should be examined.

V. THE LIQUID-VAPOR SYSTEM NEAR THE CRITICAL POINT

A. INTRODUCTION

In this chapter we consider a macroscopic system composed of simple molecules enclosed in a volume V, where:

(a) both liquid and vapor phases are present,

(b) the state of the system is near the critical state.

We assume that a plane interface exists between the two phases so that the particle density, $n = n(z)$, is only a function of z. Figure (5.1) qualitatively illustrates the z dependence of the density. The uniform liquid density is denoted by n_ℓ, and the uniform vapor density is denoted by n_v. As the critical point is approached, $(n_\ell - n_v)/n_c$ will become small, and the width of the interface region will become large. It is observed that sufficiently close to the critical point the density profile is symmetric in the following sense. Let $n = n_c + n'$, $p = p_c + p'$, and $T = T_c - T'$, where n_c, p_c, T_c are the critical density, pressure, and temperature respectively. Then

$$n_\ell = n_c + n'_{co}(T')$$

and

$$n_v = n_c - n'_{co}(T') \quad . \tag{5.1}$$

Figure (5.2) is a standard p-n diagram for the above system at two temperatures, $T = T_c - T'_1$ and $T = T_c - T'_2$, where $\frac{T'_1}{T_c} \ll 1$ and $T'_2 < T'_1$. The locus of points, X and Y, form the coexistence curve. We shall frequently refer to its projection on to the n-T plane. This

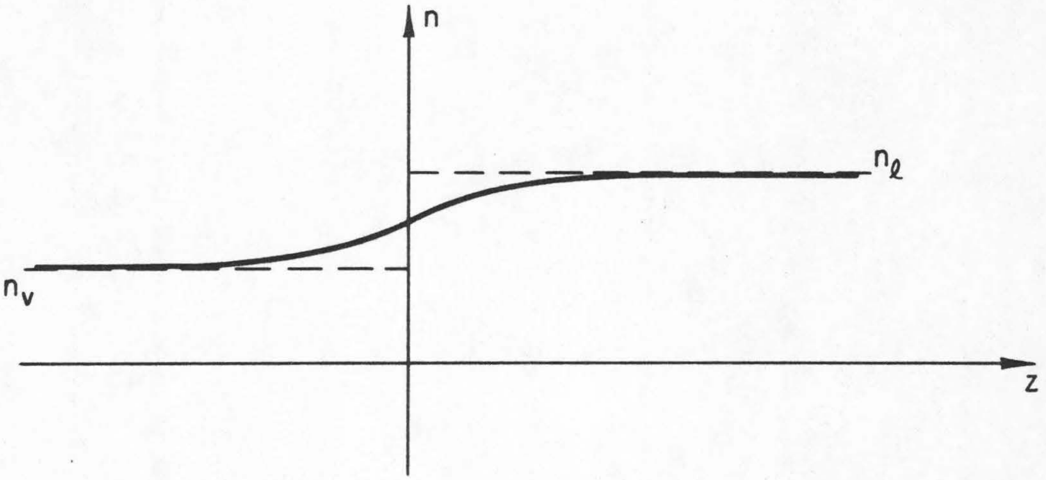

Fig. 5.1 The Density Profile Near the Critical Point

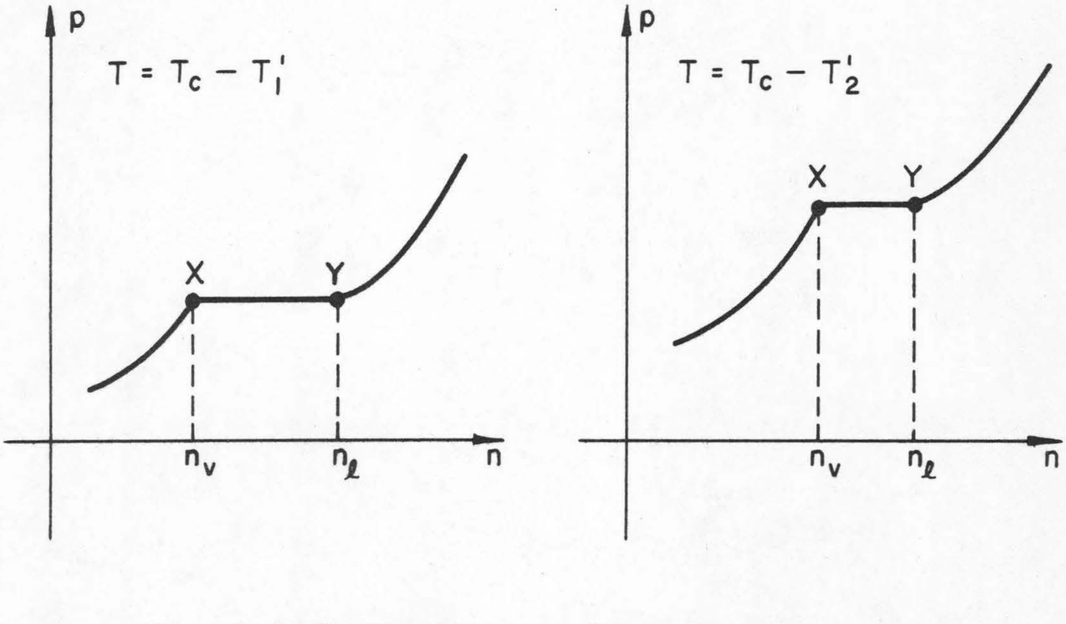

Fig. 5.2 Qualitative p-n Diagrams

projection is qualitatively depicted in Fig. (5.3). At any temperature, $T = T_c - T'$, below T_c, one can determine $n'_{co}(T')$ from the relationship

$$n'_{co} = n_{\ell}(T') - n_c$$

or

$$n'_{co} = n_c - n_v(T') \quad .$$

There have been several attempts to treat the macroscopic inhomogeneities that characterize the liquid-vapor interface near the critical point as a nonuniform, thermodynamic system. In 1958, Cahn and Hilliard [8], refining a theory originally due to van der Waals presented their "square gradient" approach to nonuniform systems. In 1965, Widom [9] modified the Cahn-Hilliard Theory to circumvent some theoretical difficulties associated with the equation of state of the system, and in 1969, Fisk and Widom [10] extended the "square gradient" concept to include more realistic limiting forms of the equation of state. Cahn and Hilliard assumed that the classical van der Waals equation of state is a valid description of a molecular system near its critical point. This assumption, however, leads to results which do not agree with experiment.

Since the "square gradient" approach has been used extensively to analyze critical point behavior of nonuniform systems, it is of interest to present a summary of the theory, below. If the origin of the system, $z = 0$, is defined as the location of the Gibbs dividing surface of vanishing superficial density, i.e.

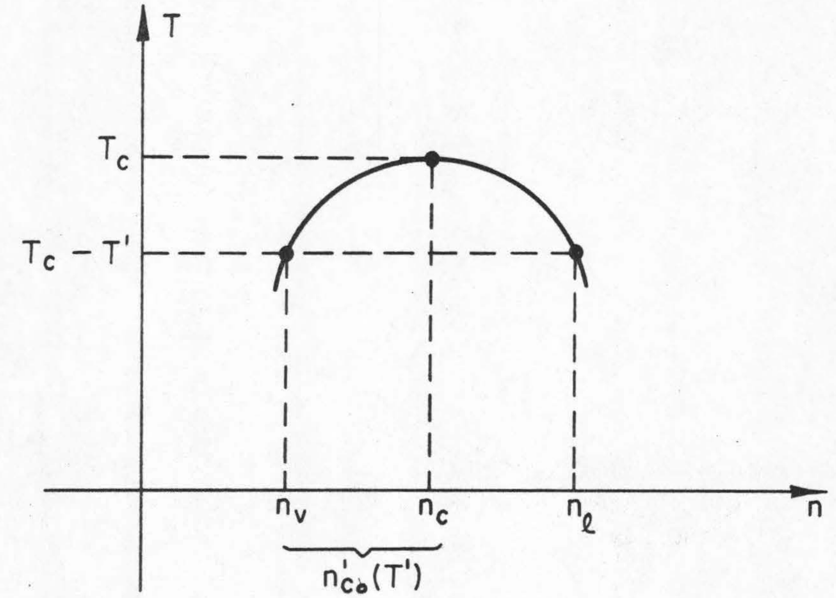

Fig. 5.3 The Projection of the Coexistence Curve

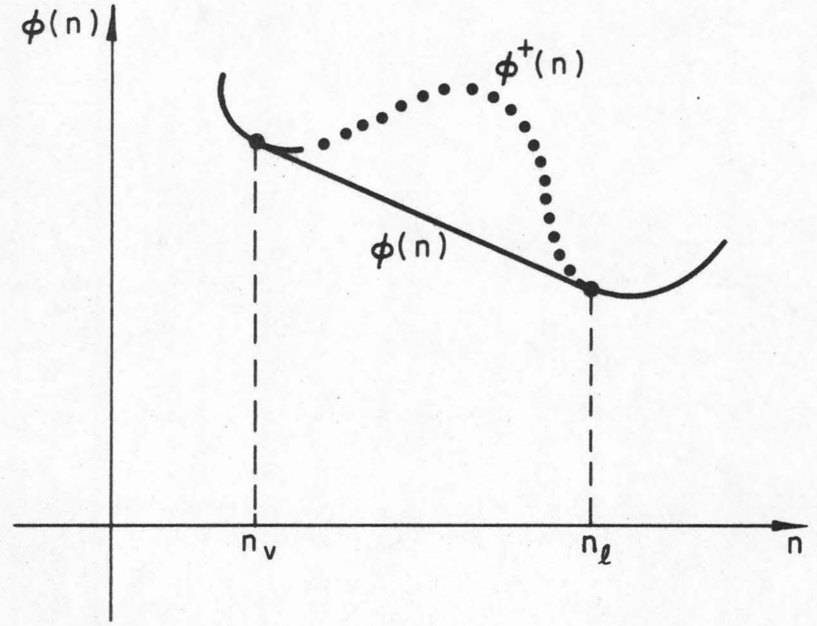

Fig. 5.4 The Free Energy Density

$$\int_{-\infty}^{0}(n(z) - n_v)dz + \int_{0}^{\infty}(n(z) - n_\ell)dz = 0 \quad , \tag{5.2}$$

then the surface tension σ becomes equal to the superficial density of the Helmholtz free energy. Thus, if $\psi(z)$ can be identified as the local free energy per unit volume in the nonuniform fluid, and if $\phi(n)$ is the thermodynamic free energy density for a uniform fluid of density n, then

$$\sigma = \int_{-\infty}^{0}(\psi(z)-\phi(n_v))dz + \int_{0}^{\infty}(\psi(z)-\phi(n_\ell))dz \quad . \tag{5.3}$$

Whereas $\phi(n)$ is a well-defined thermodynamic function, one must make the assumption that $\psi(z)$ exists. The chemical potential $\mu(n)$ and the isothermal compressibility $\chi(n)$ are defined by

$$\mu(n) = \frac{d\phi(n)}{dn} \quad , \quad \frac{1}{n^2\chi(n)} = \frac{d^2\phi(n)}{dn^2} \quad .$$

In Fig. (5.4) we plot $\phi(n)$ as a function of n for a typical two-phase system. A basic assumption present in the Cahn-Hilliard Theory is that $\phi(n)$, a well-defined function for $n < n_v$ and $n > n_\ell$, can be analytically continued into the region, $n_v < n < n_\ell$. The analytic continuation of $\phi(n)$, $\phi^+(n)$, is represented by the dotted curve in Fig. (5.4). One further assumes that, for a two-phase system near its critical point, $\psi(z)$ is the sum of two terms. The first term is $\phi^+(n(z))$, and the second term is proportional to the square of the density gradient $\left(\frac{dn(z_1)}{dz_1}\right)^2$. Thus,

$$\psi(z) = \phi^+(n(z)) + \frac{1}{2}\gamma\left(\frac{dn(z)}{dz}\right)^2 , \tag{5.4}$$

where γ is an unknown, positive constant. Expression (5.4) can be interpreted as a truncated expansion of the free energy density. One would expect Eq. (5.4) to become more accurate as the inhomogenities in the system become smaller. We now consider σ, given by Eq. (5.3), when $\psi(z)$ is given by Eq. (5.4), to be a functional of $n(z)$ and assume that the physical $n(z)$ minimizes σ subject to the constraint of Eq. (5.2). The resulting Euler-Lagrange equation is

$$\begin{aligned}\frac{\gamma d^2n(z)}{dz^2} &= \mu^+(n(z)) - \mu(n_\ell) \\ &= \mu^+(n(z)) - \mu(n_v) \quad ,\end{aligned} \tag{5.5}$$

and the boundary conditions are

$$\begin{aligned} n(z) &\rightarrow n_\ell \quad \text{as} \quad z \rightarrow +\infty \\ n(z) &\rightarrow n_v \quad \text{as} \quad z \rightarrow -\infty \quad . \end{aligned}$$

We shall obtain the solution of Eq. (5.5) when $\mu^+(n)$ is determined from the classical van der Waals theory in Section B of this Chapter.

Widom and Fisk[10] modify the Cahn-Hilliard Theory with the following generalizations:

(a). They assume that γ may exhibit a weak temperature dependence near the critical point.

(b). They let

$$\mu^+(n) - \mu(n_\ell) = (n-n_c)(T-\tau(n))(T_c-T)^{\alpha-1}\, h\left[\frac{T_c-\tau(n)}{T_c-T}\right] ,$$

where $\tau(n) = T_c - a|n-n_c|^{1/\beta}$ is the equation giving the projection of the coexistence curve, α and β are constants, and h is an arbitrary function.

(c). They require only that

$$\frac{d\phi^+}{dn}(n_\ell) = \frac{d\phi^+}{dn}(n_v) = \frac{d\phi}{dn}(n_\ell) = \frac{d\phi}{dn}(n_v)$$

and

$$\frac{d^2\phi^+}{dn^2}(n_\ell) = \frac{d^2\phi}{dn^2}(n_\ell) \quad , \quad \frac{d^2\phi^+}{dn^2}(n_v) = \frac{d^2\phi}{dn^2}(n_v) \quad .$$

Other modifications of the "square gradient" approach are discussed in Ref. [21].

The theory presented above is subject to criticism for two reasons. First, it is necessary to deal with $\phi^+(n)$ for the values of n in the range $n_v < n < n_\ell$, where the function can never be determined by experiment. Secondly, the validity of Eq. (5.4) is questionable[14],[22],[23],[24],[25]. In Section B we shall analyze the problem by using a statistical mechanical approach which circumvents some of these difficulties.

B. A STATISTICAL MECHANICAL APPROACH

The first statistical treatment of the liquid-vapor interface is due to Fowler[15]. He assumed that the interface can be treated as a step discontinuity and, by making mathematical assumptions concerning the temperature dependence of the pair-correlation function, deduced the temperature dependence of the surface tension near the critical point. From the discussion in Section A of this chapter, we note that the assumption of a step interface is certainly incorrect. Consequently, there must be limits to the validity of Fowler's theory.

Before we analyze the system with the aid of the first B.B.G.K.Y. equation, it is necessary to discuss the limiting form of the equation of state. Van der Waals assumed that the equation of state $p(n, T)$ can be expanded in a Taylor series about the critical parameters, T_c and n_c. He further assumed that $\frac{\partial^3 p}{\partial n^3}$ is finite and

$$\frac{\partial p}{\partial n} = \frac{\partial^2 p}{\partial n^2} = 0$$

at the critical point, and concluded that

$$p' = \frac{AkT_c}{n_c^2} n'^3 - Bkn'T' - Cn_c kT' + O(n'^2 T') + O(n'^4) \quad , \tag{5.6}$$

where $A, B,$ and C are positive constants. By using the condition that the chemical potentials of both phases are equal, one can demonstrate that the coexistence curve is symmetric as discussed above. Furthermore, Eq. (5.6) implies that the equation describing the projection of the coexistence curve is

$$\left(\frac{n'}{n_c}\right)^2 = \frac{B}{A} \frac{T'}{T_c} \quad . \tag{5.7}$$

Equation (5.7) does not agree with experiment. This fact implies that the classical van der Waals assumptions are not correct. We shall, however, use the van der Waals equation of state since the algebraic expressions encountered will be simplified by its use. The possibility of using more physical equations of state will be discussed later.

In the spirit of the van der Waals theory, we assume that the pair correlation function for a uniform fluid near the critical point can be expanded as a Taylor series in the variables T' and n'. Thus,

$$g(r,n,T) = g_c(r) + 2a'(r)\left(\frac{n'}{n_c}\right) + (2b'(r) + c'(r))\left(\frac{n'}{n_c}\right)^2$$
$$+ 2(d'(r) + e'(r))\left(\frac{n'}{n_c}\right)^3 + f'(r)\left(\frac{T'}{T_c}\right) + 2g'(r)\left(\frac{T'}{T_c}\right)\left(\frac{n'}{n_c}\right)$$
$$+ O\left[\left(\frac{n'}{n_c}\right)^4\right] + O\left[\left(\frac{T'}{T_c}\right)\left(\frac{n'}{n_c}\right)^2\right] , \qquad (5.8)$$

where $g_c(r)$ is the pair-correlation function for a system in its critical state. This assumption can be extended to a nonuniform fluid by writing

$$g(r, z_1, z_2) = g^+(r, n(z_1), n(z_2), T)$$

and assuming that g^+ can be expanded as a Taylor series in $n'(z_1)$, $n'(z_2)$, and T'. Therefore,

$$g^+(r, n(z_1), n(z_2), T) = g_c(r) + a(r)[y(z_1) + y(z_2)]$$
$$+ b(r)[y(z_1)^2 + y(z_2)^2] + c(r)[y(z_1)y(z_2)]$$
$$+ d(r)[y(z_1)^3 + y(z_2)^3] + e(r)[y(z_1)^2 y(z_2) + y(z_2)^2 y(z_1)]$$
$$+ f(r)\left(\frac{T'}{T_c}\right) + g(r)\left(\frac{T'}{T_c}\right)[y(z_1) + y(z_2)] + O(y^4) + O\left[y^2\left(\frac{T'}{T_c}\right)\right], \qquad (5.9)$$

where $y(z_1) = n'(z_1)/n_c$. Note that the symmetry condition, $g(r, z_1, z_2) = g(r, z_2, z_1)$, has been satisfied. The requirement

$$g(r, z_1, z_2) \rightarrow g(r, n, T)\Big]_{\frac{n'}{n_c} = \left(\frac{B}{A}\left(\frac{T'}{T_c}\right)\right)^{\frac{1}{2}}} \tag{5.10}$$

as

$$z_1 \rightarrow +\infty, \quad z_2 \rightarrow \infty \left[y(z_1) \rightarrow \left(\frac{B}{A}\left(\frac{T'}{T_c}\right)\right)^{\frac{1}{2}} \quad , \quad y(z_2) \rightarrow \left(\frac{B}{A}\left(\frac{T'}{T_c}\right)\right)^{\frac{1}{2}} \right]$$

implies that $a(r) = a'(r)$, $2b(r) + c(r) = 2b'(r) + c'(r)$, etc., provided we require Eq. (5.10) to hold independently of the value of A/B. At this point the $a'(r)$, etc. are unknown. By using the relationship between the pressure and the pair-correlation function,

$$\frac{nkT - p}{n^2} = \frac{2\pi}{3} \int_0^{\infty} r^3 \varphi'(r) g(r, n, T) dr \quad , \tag{5.11}$$

one can obtain useful relations involving these unknown functions. Expansion of the left hand side of Eq. (5.11) about the critical parameters and substitution of Eq. (5.8) into Eq. (5.11) give

$$\left.\begin{aligned}
&\frac{2\pi}{3}\int_0^\infty r^3\varphi'(r)g_c(r)dr = \lambda\left(1 - \frac{p_c}{n_c kT_c}\right)\\
&\frac{4\pi}{3}\int_0^\infty r^3\varphi'(r)a'(r)dr = \lambda\left(\frac{2p_c}{n_c kT_c} - 1\right)\\
&\frac{2\pi}{3}\int_0^\infty r^3\varphi'(r)(2b'(r) + c'(r))dr = \lambda\left(1 - \frac{3p_c}{n_c kT_c}\right)\\
&\frac{2\pi}{3}\int_0^\infty r^3\varphi'(r)f'(r)dr = \lambda(C-1)\\
&\frac{4\pi}{3}\int_0^\infty r^3\varphi'(r)(d'(r) + e'(r))\,dr = \lambda\left(\frac{4p_c}{n_c kT_c} - 1 - A\right)\\
&\frac{4\pi}{3}\int_0^\infty r^3\varphi'(r)g'(r)dr = \lambda(1+B-2C) \quad ,
\end{aligned}\right\} \qquad (5.12)$$

where $\lambda = \frac{kT_c}{n_c}$. Note that the relations (5.12) also hold if $a'(r)$ is replaced by $a(r)$, $2b'(r) + c'(r)$ is replaced by $2b(r) + c(r)$, etc.

To determine the differential equation for the density, one can employ the first B.B.G.K.Y. equation

$$\frac{1}{n(z_1)}\frac{dn(z_1)}{dz_1} + \frac{1}{kT}\int n(z_2)g(r, z_1, z_2)\frac{\partial}{\partial z_1}\varphi(r)d\underset{\sim}{r}_2 = 0 \quad ,$$

where $r = |\underset{\sim}{r}_1 - \underset{\sim}{r}_2|$. A more convenient form is

$$\frac{1}{n(z_1)}\frac{dn(z_1)}{dz_1} = \frac{2\pi}{kT}\int_0^\infty \varphi'(r)\left[\int_{z_1-r}^{z_1+r} g(r,z_1,z_2)n(z_2)(z_2-z_1)dz_2\right]dr \quad . \tag{5.13}$$

We can express Eq. (5.13) as

$$\frac{1}{n(z_1)}\frac{dn(z_1)}{dz_1} = \frac{2\pi}{kT}\int_0^\alpha \varphi'(r)\left[\int_{z_1-r}^{z_1+r} g(r,z_1,z_2)n(z_2)(z_2-z_1)dz_2\right]dr$$

$$+ \frac{2\pi}{kT}\int_\alpha^\infty \varphi'(r)\left[\int_{z_1-r}^{z_1+r} g(r,z_1,z_2)n(z_2)(z_2-z_1)dz_2\right]dr \quad . \tag{5.14}$$

Form (5.14) is useful if the system is close to the critical point because one can choose α large compared to the non-zero range of the intermolecular potential but small compared to the length scale characterizing the nonuniformities in $n(z_1)$ and $g(r,z_1,z_2)$. For α large

$$\varphi'(r) \to \frac{c}{a}\left(\frac{a}{r}\right)^7 \quad ,$$

where c is a constant and a is a length characteristic of the molecular diameter. Therefore, the second term on the right hand side of Eq. (5.14) can be expressed as

$$\frac{2\pi}{kT}\int_\alpha^\infty \frac{c}{a}\left(\frac{a}{r}\right)^7\left[\int_{z_1-r}^{z_1+r} g(r,z_1,z_2)n(z_2)(z_2-z_1)dz_2\right]dr \quad . \tag{5.15}$$

We shall assume, and shall later verify, that Eq. (5.15) is negligible compared to other terms in Eq. (5.14). With this assumption, Eq. (5.14) becomes

$$\frac{1}{n(z_1)}\,\frac{dn(z_1)}{dz_1} = \frac{2\pi}{kT}\int_0^{\alpha}\varphi'(r)\left[\int_{z_1-r}^{z_1+r} g(r,z_1,z_2)n(z_2)(z_2-z_1)dz_2\right]dr \quad . \tag{5.16}$$

Since the range of z_2 is $z_1 - a < z_2 < z_1 + a$, and a is small compared to the length scale characterizing the nonuniformity of $n(z_1)$ and $g(r, z_1, z_2)$, we are justified in expanding these quantities in a Taylor series in z_2 about $z_2 = z_1$. Consequently,

$$n(z_2) = n(z_1) + \frac{dn(z_1)}{dz_1}(z_2-z_1) + \frac{1}{2}\frac{d^2n(z_1)}{dz_1^2}(z_2-z_1)^2 + \frac{1}{6}\frac{d^3n(z_1)}{dz_1^3}(z_2-z_1)^3 + \ldots \tag{5.17}$$

and

$$g(r,z_1,z_2) = g(r,z_1,z_1) + \frac{\partial g(r,z_1,z_1)}{\partial z_2}(z_2-z_1) + \frac{1}{2}\frac{\partial^2 g(r,z_1,z_1)}{\partial z_2^2}(z_2-z_1)^2 + \frac{1}{6}\frac{\partial^3 g(r,z_1,z_1)}{\partial z_2^3}(z_2-z_1)^3 + \ldots \quad . \tag{5.18}$$

Substituting Eqs. (5.18) and (5.17) into Eq. (5.16), and letting $n(z) = n_c + n'(z)$ and $g(r, z_1, z_2) = g_c(r) + g'(r, z_1, z_2)$, we obtain

$$\frac{1}{n(z_1)}\frac{dn(z_1)}{dz_1} = \frac{4\pi}{3kT}\int_0^\alpha r^3\varphi'(r)\left[n(z_1)\frac{\partial g'(r,z_1,z_1)}{\partial z_2} + g(r,z_1,z_1)\frac{dn'(z_1)}{dz_1}\right]dr$$

$$+\frac{4\pi}{30kT}\int_0^\alpha r^5\varphi'(r)\left[\frac{d^3n'(z_1)}{dz_1^3}\,g(r,z_1,z_1)+n(z_1)\frac{\partial^3 g'(r,z_1,z_1)}{\partial z_2^3}\right]dr$$

$$+\frac{4\pi}{10kT}\int_0^\alpha r^5\varphi'(r)\left[\frac{d^2n'(z_1)}{dz_1^2}\frac{\partial g'(r,z_1,z_1)}{\partial z_2}+\frac{dn'(z_1)}{dz_1}\frac{\partial^2 g'(r,z_1,z_1)}{\partial z_2^2}\right]dr$$

$$+\,O\left[\frac{d^5n'(z_1)}{dz_1^5}\right] . \qquad (5.19)$$

Expansion of $n(z_1)$ about n_c and T about T_c, and substitution of Eq. (5.9) into Eq. (5.19) give

$$\frac{1}{n_c}\left[1-\frac{n'(z_1)}{n_c}+\left(\frac{n'(z_1)}{n_c}\right)^2\right]\frac{dn'(z_1)}{dz_1} \approx$$

$$\frac{4\pi}{3kT_c}\,\frac{dn'(z_1)}{dz_1}\int_0^\alpha \varphi'(r)r^3\left[g_c(r)+a(r)+(2b(r)+c(r)+3a(r))\left(\frac{n'(z_1)}{n_c}\right)\right.$$

$$\left.+(3d(r)+3e(r)+4b(r)+2c(r))\left(\frac{n'(z_1)}{n_c}\right)^2+\left(\frac{T'}{T_c}\right)(f(r)+g(r))\right]dr$$

$$+\frac{4\pi}{3kT_c}\left(\frac{T'}{T_c}\right)\frac{dn'(z_1)}{dz_1}\int_0^\alpha r^3\varphi'(r)(a(r)+g_c(r))dr$$

$$+\frac{4\pi}{30kT_c}\,\frac{d^3n'(z_1)}{dz_1^3}\int_0^\alpha \varphi'(r)r^5\,(a(r)+g_c(r))dr \quad , \qquad (5.20)$$

where we have neglected terms of $O\left[\left(\frac{n'}{n_c}\right)^3 \frac{dn'}{dz_1}\right]$, $O\left[\left(\frac{n'}{n_c}\right)\left(\frac{T'}{T_c}\right)\frac{dn'}{dz_1}\right]$, $O\left[\frac{d^5n'}{dz_1^5}\right]$, and the nonlinear part of the third term on the right hand side of Eq. (5.19). If, in addition, we replace α in Eq. (5.20) by infinity and assume that the resulting error can be neglected, we obtain, with the aid of the integral relations of Eq. (5.12),

$$3A\left(\frac{n'(z_1)}{n_c}\right)^2 - B\left(\frac{T'}{T_c}\right)\frac{1}{n_c}\frac{dn'(z_1)}{dz_1}$$

$$= \left[\frac{4\pi}{30kT_c}\int_0^\infty \varphi'(r)r^5(g_c(r) + a(r))dr\right]\frac{d^3n'(z_1)}{dz_1^3} \quad . \tag{5.21}$$

If we define a_o^2 by

$$\frac{4\pi}{30kT_c}\int_0^\infty \varphi'(r)r^5(g_c(r) + a(r)) = \frac{a_o^2}{n_c} \quad ,$$

Eq. (5.21) becomes

$$\frac{d}{dz}\left[A\left(\frac{n'(z)}{n_c}\right)^3 - B\left(\frac{T'}{T_c}\right)\left(\frac{n'(z)}{n_c}\right)\right] = \frac{d}{dz}\left[a_o^2\frac{d^2}{dz^2}\left(\frac{n'(z)}{n_c}\right)\right]. \tag{5.22}$$

Therefore,

$$a_o^2\frac{d^2y(z)}{dz^2} = Ay(z)^3 - B\left(\frac{T'}{T_c}\right)y(z) + \beta \quad , \tag{5.23}$$

where $y(z) = \frac{n'(z)}{n_c}$ and β is a constant. However, as $z \to \pm\infty$, $\frac{dy^2(z)}{dz^2} \to 0$ and $y \to \pm\sqrt{\frac{BT'}{AT_c}}$. This implies that $\beta = 0$. Letting $z' = z/a_o$ and defining $f(z')$ by

$$y(z) = \sqrt{\frac{B}{A}\left(\frac{T'}{T_c}\right)}\, f(z') \quad ,$$

one obtains

$$\frac{d^2 f(z')}{dz'^2} = B\left(\frac{T'}{T_c}\right) f(z')\left[f(z')^2 - 1\right] \quad , \tag{5.24}$$

with the boundary conditions

$$f(z') \to 1 \quad \text{as} \quad z' \to +\infty$$

$$f(z') \to -1 \quad \text{as} \quad z' \to -\infty \quad .$$

The solution of Eq. (5.25) subject to these boundary conditions is

$$f(z') = \tanh\left(\left(\frac{BT'}{2T_c}\right)^{\frac{1}{2}} z'\right)$$

or

$$n(z) = n_c\left[1 + \left(\frac{B}{A}\left(\frac{T'}{T_c}\right)\right)^{\frac{1}{2}} \tanh\left(\left(\frac{BT'}{2T_c}\right)^{\frac{1}{2}} \frac{z}{a_o}\right)\right] \quad . \tag{5.25}$$

Since $n'(z)/n_c$ is proportional to $(T'/T_c)^{\frac{1}{2}}$, and each derivative with respect to z introduces a multiplicative factor of $(T'/T_c)^{\frac{1}{2}}$, we see that the terms in Eq. (5.21) are of order $(T'/T_c)^2$. It is easy to verify that all the terms that have been neglected are at least of order $(T'/T_c)^{5/2}$. For example, Eq. (5.15) becomes

$$\frac{2\pi}{kT}\int_{\alpha}^{\infty} \frac{c}{a}\left(\frac{a}{r}\right)^7\left[\int_{z_1-r}^{z_1+r} (g_c(r)+g'(r,z_1,z_2))(n_c+n'(z_2))(z_2-z_1)dz_2\right] dr$$

$$= \frac{2\pi}{kT}\int_{\alpha}^{\infty} \frac{c}{a}\left(\frac{a}{r}\right)^7\left[\int_{z_1-r}^{z_1+r} (n_c g'(r,z_1,z_2)+n'(z_2)g_c(r)+n'(z_2)g'(r,z_1,z_2))(z_2-z_1)dz_2\right] dr \ ,$$

which can be bounded by

$$\frac{2\pi}{kT}\,\frac{c}{a}\int_{\alpha}^{\infty}\left(\frac{a}{r}\right)^{7}\left[\int_{z_1-r}^{z_1+r}\left|(n_c g'(r,z_1,z_2)+n'(z_2)g_c(r)+n'(z_2)g'(r,z_1,z_2))\right|\left|z_2-z_1\right|dz_2\right]dr\ . \tag{5.26}$$

If $r > \alpha$ and α is large compared to a molecular diameter*, the term within the absolute value signs in Eq. (5.26) can be bounded by a term proportional to $(T'/T_c)^{\frac{1}{2}}$. Thus, if the constant of proportionality is D, Eq. (5.26) is less than or equal to

$$\frac{4\pi}{kT}\,\frac{c}{a}\,D\left(\frac{T'}{T_c}\right)^{\frac{1}{2}}\int_{\alpha}^{\infty}\left(\frac{a}{r}\right)^{7} r^2 dr = \frac{\pi}{kT}\ cD\left(\frac{T'}{T_c}\right)^{\frac{1}{2}}\left(\frac{a}{\alpha}\right)^{4}\ . \tag{5.27}$$

However, since the length scale characterizing the nonuniformity in $n(z)$ is, from Eq. (5.25),

$$a_o\left(\frac{2T_c}{BT'}\right)^{\frac{1}{2}}\ ,$$

we can choose $\alpha = \kappa(T'/T_c)^{-\frac{1}{2}}$, where $\kappa \ll a_o\left(\frac{2}{B}\right)^{\frac{1}{2}}$. Therefore, Eq. (5.27) demonstrates that Eq. (5.15) is of order $(T'/T_c)^{5/2}$. Likewise, the nonlinear terms in Eq. (5.19) and the error terms involved in the replacement of α by ∞ in Eq. (5.20) are of order $(T'/T_c)^{5/2}$.

We note that the approach due to Cahn and Hilliard essentially reproduces the result of Eq. (5.25). If the quantity $\mu^+(n(z)) - \mu(n_\ell)$ is computed by using the van der Waals theory, we obtain

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*Note that the requirements $g(r, z_1, z_2) \to 1$ and $g_c(r) \to 1$ as $r \to \infty$ imply that the $a(r)$, etc., of Eq. (5.9) must be $o(1)$ as $r \to \infty$.

$$\mu^{+}(n(z)) - \mu(n_\ell) = n'(z)\left[\frac{AT_c}{Bn_c^{2}}\, n'(z)^2 - T'\,\frac{Bk}{n_c}\right] .$$

Substitution of this result into Eq. (5.5) yields an equation for the density of the same form as Eq. (5.24).

C. TEMPERATURE DEPENDENCE OF THE SURFACE TENSION

As a two-phase system is allowed to approach its critical point, the surface tension of the system vanishes. A primary goal of critical point theory is to predict the temperature dependence of the surface tension near the critical point. Toward this end, we recall the definition of the surface energy per unit area introduced in Chapter IV,

$$\begin{aligned} E_s &= \frac{1}{2}\int\left[\int_{z_0}^{\infty} (n(z_1)n(z_2)g(r, z_1, z_2)-n_\ell^2\, g_\ell(r))\varphi(r)dz_1\right] d\underset{\sim}{r} \\ &+ \frac{1}{2}\int\left[\int_{-\infty}^{z_0} (n(z_1)n(z_2)g(r, z_1, z_2)-n_v^2\, g_v(r))\varphi(r)dz_1\right] d\underset{\sim}{r} \quad , \qquad (5.28) \end{aligned}$$

where $z_1 = z_0$ is the Gibbs dividing surface of zero superficial density. The surface tension is related to the surface energy per unit area by

$$\sigma - T\,\frac{d\sigma}{dT} = E_s \quad . \qquad (5.29)$$

Integrating Eq. (5.29) and using the condition, $\sigma(T_c) = 0$, we find that

$$\sigma = T\int_{T}^{T_c} \frac{E_s(\tau)d\tau}{\tau^2} \quad . \qquad (5.30)$$

Substituting Eqs. (5.25) and (5.9) into Eq. (5.28), with $z_0 = 0$, we have

$$\begin{aligned} E_s = \pi \int_0^\infty \varphi(r) r^2 dr \int_0^\pi \sin\theta \, d\theta \int_0^\infty \{ & \beta n_c^2 (g_c(r)+a(r))(\tanh\alpha z_1 + \tanh\alpha z_2 - 2) \\ & + n_c^2 \beta^2 [(g_c(r)+2a(r)+c(r))(\tanh\alpha z_1 \tanh\alpha z_2) \\ & + (a(r)+b(r))(\tanh\alpha z_1 - 1)^2 + (\tanh\alpha z_2 - 1)^2)] + O(\beta^3) \} dz_1 \\ + \pi \int_0^\infty \varphi(r) r^2 \, dr \int_0^\pi \sin\theta \, d\theta \int_{-\infty}^0 \{ & \beta n_c^2 (g_c(r)+a(r))(\tanh\alpha z_1 + \tanh\alpha z_2 + 2) \\ & + n_c^2 \beta^2 [(g_c(r)+2a(r)+c(r))(\tanh\alpha z_1 \tanh\alpha z_2 - 1) \\ & + (a(r)+b(r))((\tanh\alpha z_1 - 1)^2 + (\tanh\alpha z_2 - 1)^2)] + O(\beta^3) \} dz_1 , \qquad (5.31) \end{aligned}$$

where

$$\beta = \left(\frac{BT'}{AT_c}\right)^{\frac{1}{2}} \quad , \quad \alpha = \frac{1}{a_o}\left(\frac{BT'}{2T_c}\right)^{\frac{1}{2}} ,$$

and

$$z_2 = z_1 + r\cos\theta \quad .$$

Integration over z_1 of the terms proportional to β gives no contribution. The terms proportional to β^2 are of two types:

$$(g_c(r) + 2a(r) + c(r)) \int_{-\infty}^{\infty} (\tanh\alpha z_1 \tanh\alpha z_2 - 1) dz_1 \quad , \qquad (5.32)$$

and

$$(a(r) + b(r)) \left[\int_{-\infty}^{\infty} (\tanh\alpha z_1 - 1)^2 dz_1 + \int_{-\infty}^{\infty} (\tanh\alpha z_2 - 1)^2 \, dz_1 \right] . \qquad (5.33)$$

Equation (5.33) is seen to be equal to

$$4(a(r) + b(r)) \int_{0}^{\infty} (\tanh^2 \alpha z_1 - 1) dz_1 \quad ,$$

which integrates to

$$- \frac{4}{\alpha} (a(r) + b(r)) \quad . \tag{5.34}$$

Equation (5.34), when integrated over θ in Eq. (5.31), gives

$$- \frac{8}{\alpha} (a(r) + b(r)) \quad .$$

Equation (5.32) is more complicated to analyze. From the identity,

$$(\tanh \alpha z_1 \tanh \alpha z_2 - 1) = \frac{\tanh^2 \alpha z_1 - 1}{1 + \tanh \alpha z_1 \tanh \alpha r \cos \theta} = \frac{\tanh^2 \alpha z_1 - 1}{1 + \tanh \alpha z_1 \eta} \quad ,$$

where $\eta = \tanh \alpha r \cos \theta$, we have that

$$- \frac{1}{\alpha} \int_{-\infty}^{\infty} \frac{\alpha \operatorname{sech}^2 \alpha z_1}{1 + \eta \tanh \alpha z_1} dz_1 = \int_{-\infty}^{\infty} (\tanh \alpha z_1 \tanh \alpha z_2 - 1) dz_1$$

$$= - \frac{1}{\alpha \eta} \log(1 + \eta)/(1 - \eta) \quad .$$

Therefore, we must consider

$$- \frac{1}{\alpha^2 r} \int_{0}^{\pi} \frac{\alpha r \sin \theta}{\tanh(\alpha r \cos \theta)} \log \left(\frac{1 + \tanh \alpha r \cos \theta}{1 - \tanh \alpha r \cos \theta} \right) d\theta \quad . \tag{5.35}$$

Equation (5.35) can be transformed to

$$- \frac{2}{\alpha^2 r} \int_0^{\tanh \alpha r} \frac{dv}{v(1-v^2)} \log\left(\frac{1+v}{1-v}\right) \quad . \qquad (5.36)$$

With regard to the integration over r in Eq. (5.31), we assume that, because of the presence of the potential function $\varphi(r)$, the integrand is effectively zero for r greater than a few molecular diameters. Therefore, the upper limit of integration can be replaced by δ, where δ can be several hundred molecular diameters. Since r is then bounded from above, and α is very small near the critical point, we can treat αr in Eq. (5.36) as a small quantity. Equation (5.36) can then be replaced by

$$- \frac{4}{\alpha} + O(\alpha) \quad . \qquad (5.37)$$

Equation (5.31) therefore becomes equal to

$$E_s = - \frac{4\pi}{\alpha} n_c^2 \beta^2 \int_0^\infty r^2 \varphi(r)(g_c(r)+4a(r)+c(r)+2b(r))dr + O(\beta^2) \quad . \qquad (5.38)$$

From Eq. (5.30), we find that

$$\sigma = - \frac{8}{3} \pi \frac{n_c^2}{A} \sqrt{2B}\, a_o \left(\frac{T'}{T_c}\right)^{3/2} \int_0^\infty r^2 \varphi(r)(g_c(r)+4a(r)+c(r)+2b(r))dr + O\left[\left(\frac{T'}{T_c}\right)^2\right] \quad . \qquad (5.39)$$

The integral in Eq. (5.39) can be determined by using the relationship for the configurational internal energy per molecule,

$$u = 2\pi n \int_0^\infty r^2 \varphi(r) g(r, n, T) dr \quad . \qquad (5.40)$$

We can find the limiting form of u from the equation of state, Eq. (5.6). Substitution of Eq. (5.8) into Eq. (5.40) yields the following integral relationships:

$$\frac{1}{n_c}\left(\frac{p_c}{n_c} - CkT_c\right) = 2\pi \int_0^\infty \varphi(r) r^2 (g_c(r) + 2a(r))dr \quad , \tag{5.41}$$

and

$$-\frac{1}{n_c}\left(\frac{p_c}{n_c} + \frac{BkT_c}{2} - CkT_c\right) = 2\pi \int_0^\infty r^2 \varphi(r)(2a(r)+2b(r)+c(r))dr \ . \tag{5.42}$$

From these equations, we see that

$$2\pi n_c \int_0^\infty r^2\varphi(r)(g_c(r)+4a(r)+2b(r)+c(r))dr = -\frac{BkT_c}{2} \quad .$$

Therefore, Eq. (5.39) becomes

$$\sigma = n_c k T_c a_o \left(\frac{8}{9}\right)^{\frac{1}{2}} \frac{B^{3/2}}{A} \left(\frac{T'}{T_c}\right)^{3/2} + O\left[\left(\frac{T'}{T_c}\right)^2\right] \quad . \tag{5.43}$$

We note that the theory of Cahn and Hilliard, when the van der Waals limiting form of the equation of state is employed, yields the same three-halves power law for the temperature dependence of the surface tension. The prediction that

$$\sigma \sim \left(\frac{T'}{T_c}\right)^{3/2}$$

is reasonably close to the approximate experimental result (Ref. 19, p. 164)

$$\sigma \sim \left(\frac{T'}{T_c}\right)^{11/9} \quad .$$

D. SUMMARY AND CONCLUSIONS

In this chapter we have demonstrated that the first B. B. G. K. Y. equation can be reduced to a simple equation for the density profile if the pair-correlation function is assumed to be an analytic function of the temperature and density. This assumption is in the spirit of the van der Waals approach to the limiting form of the equation of state. We have also remarked that the thermodynamic theory of Cahn and Hilliard predicts essentially the same results as those derived from the statistical mechanical theory. The latter theory has the following advantages over the former:

(a). In the thermodynamic theory, it is necessary to introduce a phenomenological constant. In the statistical mechanical theory, every constant is expressible in terms of well-defined quantities.

(b). In the thermodynamic theory, one must deal with the analytic extension of the free energy density into the two-phase region. This problem does not arise in the statistical mechanical theory.

(c). It is not necessary to introduce the concept of a free energy density expansion in the derivation of the statistical mechanical theory.

The theory based on the first B. B. G. K. Y. equation can be modified, in certain cases, to include more realistic forms of the equation of state. Unfortunately, the exact behavior of the critical isotherm, the coexistence curve, and the equation of state is difficult to determine[26],[27],[28],[29]. If the equation of state is assumed to be[27],[28]

$$p' = An'|n'|^{\nu} - BT'n' - CT' \quad ,$$

where ν is some positive number greater than or equal to 2, one could alter the density expansions in Section B to include terms of order $(n')^{\nu+1}$. However, if n is not an integer, the algebra involved becomes complicated. At best, extensions of this type appear awkward.

APPENDIX A

COMMENTS ON UNIQUENESS

Specialized to the plane ideal wall problem, the B. B. G. K. Y. equations become

$$\frac{d\rho(z_1)}{dz_1} = -\frac{\rho(z_1)}{kT}\int_{z_2>0}\frac{z_{12}}{r_{12}}\varphi'(r_{12})\rho(z_2)g^{(2)}(r_{12},z_1,z_2)d\underset{\sim}{r}_2 \qquad \text{(A-1)}$$

and

$$\frac{\partial}{\partial z_i}g^{(h)} = -\frac{1}{kT}\Bigg[\int_{z_{h+1}>0}\frac{z_{i,h+1}}{r_{i,h+1}}\varphi'(r_{i,h+1})\rho(z_{h+1})\Big[g^{(h+1)} - g^{(h)}g^{(2)}(r_{i,h+1},z_i,z_{h+1})\Big]d\underset{\sim}{r}_{h+1} + g^{(h)}\frac{\partial}{\partial z_i}\sum\sum_{k<j=1}^{h}\varphi_{jk}\Bigg], \qquad \text{(A-2)}$$

where the arguments of $g^{(h)}$ are understood. The modified equations are

$$\frac{d\rho(z_1)}{dz_1} = -\frac{\rho(z_1)}{kT}\int_{z_2>0}\frac{z_{12}}{r_{12}}\varphi'(r_{12})\,\rho(z_2)g^{(2)}(r_{12},z_1,z_2)d\underset{\sim}{r}_2 \qquad \text{(A-3)}$$

and

$$\sum_{k=1}^{h}\frac{\partial}{\partial z_k}(g^{(h)}) = -\frac{1}{kT}\sum_{k=1}^{h}\int_{z_{h+1}>0}\frac{z_{k,h+1}}{r_{k,h+1}}\varphi'(r_{k,h+1})\rho(z_{h+1})\Big[g^{(h+1)} - g^{(h)}g^{(2)}(r_{k,h+1},z_k,z_{h+1})\Big]d\underset{\sim}{r}_{h+1}\;. \qquad \text{(A-4)}$$

Suppose that ρ_a and $g_a^{(h)}$ are solutions to Eqs. (A-1) and (A-2), and that ρ_b and $g_b^{(h)}$ are solutions to Eqs. (A-3) and (A-4), subject to the boundary conditions

$$\left.\begin{array}{l} \rho_a(z_1) \\ \\ \rho_b(z_1) \end{array}\right\} \rightarrow n \quad \text{as} \quad z_1 \rightarrow +\infty \qquad \text{(A-5)}$$

and

$$\left.\begin{array}{l} g_a^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h) \\ \\ g_b^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m}), z_1, \ . \ . \ . z_h) \end{array}\right\} \begin{array}{c} \rightarrow g_\ell^{(h)}(\overset{h}{\underset{\ell m}{P}}(r_{\ell m})) \quad , \\ \text{as } z_1, \ . \ . \ . z_h \rightarrow \infty \\ r_{\ell m} \ \text{ fixed} \end{array} \qquad \text{(A-6)}$$

where n and $g_\ell^{(h)}$ are given functions. Then, is it true that $\rho_a(z_1) = \rho_b(z_1)$ and $g_a^{(h)} = g_b^{(h)}$? One can easily see that $\rho_a = \rho_b$ and $g_a^{(h)} = g_b^{(h)}$, if ρ_b and $g_b^{(h)}$ are unique, and ρ_a and $g_a^{(h)}$ exist. Since Eq. (A-4) is just a sum over i of Eq. (A-3), any solution, ρ_a and $g_a^{(h)}$, to Eqs. (A-1) and (A-2) is also a solution of Eqs. (A-3) and (A-4). If the solution to Eqs. (A-3) and (A-4) is unique, then we must have that:

a. ρ_a and $g_a^{(h)}$ are unique.

b. $\rho_a = \rho_b$ and $g_a^{(h)} = g_b^{(h)}$.

Physically, we expect that the solution of Eqs. (A-3) and (A-4), subject to the boundary conditions (A-5) and (A-6), will be unique, provided two phases are not present. There is experimental evidence, for two-phase systems, that supports the conclusion that no unique solution of Eqs. (A-3) and (A-4), subject to the boundary conditions (A-5) and (A-6), exists. We must, therefore, exclude two-phase systems from the considerations of Chapter II. The method presented in Chapter III is likewise not applicable to two-phase systems. The reason for this fact is discussed in Part II.

APPENDIX B

THE FUNCTIONAL EXPANSION TECHNIQUE

Percus (Ref. 13, p. II-54) has derived a functional expansion for the change in density resulting from the application of an arbitrary external potential. We have that

$$n(\underset{\sim}{r}|u)e^{-\beta u(\underset{\sim}{r})} = n(\underset{\sim}{r}) + \int \mathcal{F}_2(\underset{\sim}{r}, \underset{\sim}{r}_1)(e^{-\beta u(\underset{\sim}{r}_1)} - 1)d\underset{\sim}{r}_1$$

$$+ \frac{1}{2} \iint \mathcal{F}_3(\underset{\sim}{r}, \underset{\sim}{r}_1, \underset{\sim}{r}_2)(e^{-\beta u(\underset{\sim}{r}_2)} - 1)(e^{-\beta u(\underset{\sim}{r}_1)} - 1)d\underset{\sim}{r}_1 d\underset{\sim}{r}_2 + \ldots \, , \tag{B-1}$$

where $\mathcal{F}$s are the Ursell distribution functions and $n(r)$ is the density before the potential is applied. $n(\underset{\sim}{r}|u)$ is the density function when the potential is acting on the system. We note that

$$\mathcal{F}_2(\underset{\sim}{r}_1, \underset{\sim}{r}_2) = n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2) - n^{(1)}(\underset{\sim}{r}_1)r^{(1)}(\underset{\sim}{r}_2)$$

and

$$\mathcal{F}_3(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3) = n^{(3)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3) - n^{(2)}(\underset{\sim}{r}_2, \underset{\sim}{r}_3)n^{(1)}(\underset{\sim}{r}_1) - n^{(2)}(\underset{\sim}{r}_3, \underset{\sim}{r}_1)n^{(1)}(\underset{\sim}{r}_2)$$

$$- n^{(2)}(\underset{\sim}{r}_1, \underset{\sim}{r}_2)n^{(1)}(\underset{\sim}{r}_3) + 2n^{(1)}(\underset{\sim}{r}_1)n^{(1)}(\underset{\sim}{r}_2)n^{(1)}(\underset{\sim}{r}_3) \; .$$

By considering the initial system to be uniform and letting $u(\underset{\sim}{r})$ represent an ideal wall at $z = 0$, one obtains

$$\rho(z_1) = n - n^2 \int\limits_{z_2<0} (g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - 1)\, d\mathbf{r}_2$$

$$+ \frac{n^3}{2} \int\limits_{z_2<0} \int\limits_{z_3<0} (g^{(3)}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - g^{(2)}(\mathbf{r}_2, \mathbf{r}_3) - g^{(2)}(\mathbf{r}_1, \mathbf{r}_3)$$

$$+2)\, d\mathbf{r}_2\, d\mathbf{r}_3 + O(n^4) \quad . \qquad \text{(B-2)}$$

We notice that Eq. (B-2) can be expanded as a density series and thus should duplicate Eq. (2.36). Using the fact that for a uniform fluid,

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = e^{-\beta\varphi(r_{12})} \left[1 + n \int d\mathbf{r}_3 f(r_{13}) f(r_{23}) + O(n^2) \right] \quad ,$$

where

$$f(r_{13}) = e^{-\beta\varphi(r_{13})} - 1 \quad ,$$

we can express Eq. (B-2) as

$$\rho(z_1) = n - n^2 \int\limits_{z_2<0} f(r_{12})\, d\mathbf{r}_2 + n^3 \left[\frac{1}{2} \int\limits_{z_2<0} \int\limits_{z_3<0} f(r_{12}) f(r_{23}) f(r_{13})\, d\mathbf{r}_2\, d\mathbf{r}_3 \; + \right.$$

$$\frac{1}{2} \int\limits_{z_2<0} \int\limits_{z_3<0} (f(r_{12}) f(r_{23}) + f(r_{13}) f(r_{23}) + f(r_{12}) f(r_{13}))\, d\mathbf{r}_2\, d\mathbf{r}_3$$

$$\left. - \int\limits_{z_2<0} \int\limits_{\text{all } z_3} (f(r_{12}) + 1) f(r_{13}) f(r_{23})\, d\mathbf{r}_2\, d\mathbf{r}_3 \right] + O(n^4) \quad ,$$

or

$$\rho(z_1) = n - n^2 \int\limits_{z_2<0} f(r_{12}) d\underset{\sim}{r}_2 + n^3\Bigg[-\frac{1}{2} \int\limits_{z_2<0} \int\limits_{z_3<0} f(r_{12}) f(r_{23}) f(r_{13}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3$$

$$- \int\limits_{z_2<0} \int\limits_{z_3>0} f(r_{12}) f(r_{23}) f(r_{13}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 + \frac{1}{2} \int\limits_{z_2<0} \int\limits_{z_3<0} f(r_{12}) f(r_{13}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3$$

$$- \int\limits_{z_2<0} \int\limits_{z_3>0} f(r_{13}) f(r_{23}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 \Bigg] + O(n^4) \quad . \qquad \text{(B-3)}$$

We shall now show that Eq. (2. 36),

$$\rho(z_1) = n + n^2\Bigg[\int\limits_{z_2>0} f(r_{12}) d\underset{\sim}{r}_2 - \beta_1 \Bigg] + n^3\Bigg[\frac{1}{2}\Bigg(\int\limits_{z_2>0} f(r_{12}) d\underset{\sim}{r}_2 - \beta_1 \Bigg)^2$$

$$+ \int\limits_{z_2>0} \int\limits_{z_3>0} f(r_{12}) f(r_{23}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 - \beta_1 \int\limits_{z_2>0} f(r_{12}) d\underset{\sim}{r}_2$$

$$+ \frac{1}{2} \int\limits_{z_2>0} \int\limits_{z_3>0} f(r_{12}) f(r_{23}) f(r_{13}) d\underset{\sim}{r}_2 \, d\underset{\sim}{r}_3 - \beta_2 \Bigg] + O(n^4) \quad ,$$

is equivalent to Eq. (B-3).

Since

$$\beta_1 = \int f(r_{12}) d\underset{\sim}{r}_2 = \int f(r_{23}) d\underset{\sim}{r}_3$$

and

$$\beta_2 = \iint f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \quad ,$$

Eq. (2.36) can be written as

$$\rho(z_1)=n-n^2 \int\limits_{z_2<0} f(r_{12})d\underset{\sim}{r}_2 +n^3\left[\frac{1}{2}\int\limits_{z_2<0}\int\limits_{z_3<0} f(r_{12})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3\right.$$

$$-\int\limits_{z_2>0}\int\limits_{z_3<0} f(r_{12})f(r_{23})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 + \frac{1}{2}\int\limits_{z_2>0}\int\limits_{z_3>0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3$$

$$\left.-\frac{1}{2}\iint f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3\right] + O(n^4) \quad ,$$

or

$$\rho(z_1) = n-n^2 \int\limits_{z_2<0} f(r_{12})d\underset{\sim}{r}_2 +n^3\left[\frac{1}{2}\int\limits_{z_2<0}\int\limits_{z_3<0} f(r_{12})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3\right.$$

$$-\int\limits_{z_2>0}\int\limits_{z_3<0} f(r_{12})f(r_{23})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 - \int\limits_{z_2<0}\int\limits_{z_3>0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3$$

$$\left.-\frac{1}{2}\int\limits_{z_2<0}\int\limits_{z_3<0} f(r_{12})f(r_{23})f(r_{13})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3\right] +O(n^4) \quad .$$

Because

$$\int\limits_{z_2>0}\int\limits_{z_3<0} f(r_{12})f(r_{23})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 = \int\limits_{z_2<0}\int\limits_{z_3>0} f(r_{13})f(r_{23})d\underset{\sim}{r}_2\, d\underset{\sim}{r}_3 \quad ,$$

this last expression is the same as Eq. (B-3).

We should remark that the above functional expansion technique is closely related to the method presented in Chapter III and, for the purposes of obtaining a density series solution to the problem, appears simpler to implement.

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