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Equilibrium Statistical Mechanics of Inhomogeneous Fluids

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The excess thermodynamic and molecular properties induced in a classical single-component fluid by static external force fields are examined from several points of view. By utilizing the techniques of cluster theory, a local "pressure," $\bar{p}(\mathbf{r})$, is constructed whose spatial integral yields directly and precisely the logarithm of the grand partition function, including the result of interaction with container vessel walls as well as other external fields (present, for example, in gravitational or centrifugal equilibrium). In particular, it is remarked that the problem arising from cluster integral dependence upon vessel volume in the usual imperfect gas theory is solved. The density expansion for \bar{p} is transformed into an integral involving a modification (X_0) of the well-known "direct-correlation function," or non-nodal cluster function. Subsequent construction of local free energies provides a condi-

tion under which these quantities may be represented by uniform fluid values (evaluated at the local density), plus corrections involving just density gradients (or Laplacians). When the external force field is generated by a fixed set of particles, the formalism leads to new integral equations for molecular distribution functions. Comparison with similar previously known integral equations, in the pair distribution case, yields an explicit, formally exact, expression in terms of X_0 for the troublesome "elementary diagram cluster sum," which has prevented exact solution to the pair distribution problem. Finally, a new fluctuation theorem is derived, which relates the density derivative of surface tension for a fluid next to a planar wall of its vessel, to molecular distribution at this interface.

I.

THERE are several compelling reasons for interest in the theoretical study of inhomogeneous fluids. The entire field of gas adsorption studies on solid substrates alone provides a clear example of such a reason. The ultimate aim is understanding of the mechanisms of interaction, via adsorption forces, between an ambient fluid and various surfaces, and of the resulting inhomogeneous molecular distribution (typically displayed as an adsorption isotherm). Although several theories of adsorption processes exist,¹ they generally have relied on specific simplifying models. It is therefore desirable to examine the general phenomenon of adsorption (as a special kind of fluid inhomogeneity produced by externally applied forces) to extract ultimately as much information as possible of a general nature about surfaces from available experimental data, without worrisome interference of spurious model effects.

The general area of electrocapillarity likewise could profit from general investigations into inhomogeneous fluids. It still remains necessary, for example, to formulate in complete generality the quantitative theory of the static electrical double layer at colloid or electrode interfaces (which provides another class of stable composition inhomogeneities induced by external forces). Here, it has long been recognized that the traditional nonlinear Poisson-Boltzmann equation for charge density in the diffuse portion of a double layer suffers from lack of consistency.² In addition, the finite size of molecules constituting the electrolytic fluid is known at times to modify even qualitatively the double layer structure³ predicted on a Poisson-Boltzmann basis.

A third general inquiry still requiring detailed theoretical description is the problem of density

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¹ J. H. deBoer, *The Dynamical Character of Adsorption* (Clarendon Press, Oxford, England, 1953), Chap. V.

² R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (The MacMillan Company, New York, 1956), p. 409.

³ F. H. Stillinger, Jr., and J. G. Kirkwood, *J. Chem. Phys.* **33**, 1282 (1960).

variation through liquid-vapor interfaces,⁴ as well as prediction of related surface excess thermodynamic properties. In particular, one is especially interested in the variations of interfacial width and tension as the critical point is approached from below. Although these and related critical interfacial quantities have previously been predicted,^{5,6} our analysis below indicates that the local free energy estimates on which they are based do not apply in the critical region. The very large density fluctuations occurring at the critical point, which produce the familiar critical opalescence, are also traditionally an object of study for inhomogeneous fluid investigators. Recent indications of the complex character of molecular distributions at the critical point^{7,8} underline the desirability for exploiting a general theory of nonuniform fluids, especially since molecules themselves may be regarded as sources of an "external" force field (the intermolecular potential itself), and the resulting density fluctuations should find description in a comprehensive analysis of inhomogeneous fluids.

A fourth discipline, whose present lack of comprehensive and general statistical mechanical basis acts as a motivation, is the description of nucleation phenomena, both homogeneous and heterogeneous. Granted the validity of the critical nucleus concept as a means of estimating rates of the relevant kinetic process,⁹ there remains precisely the problem of computing the free energy of such a small inhomogeneity. In this connection it has been pointed out¹⁰ that the small size of typical critical nuclei and the resulting highly curved surfaces, gives rise to ambiguities in the usual application of macroscopic thermodynamic concepts to these entities. It is clear that only on a general statistical mechanical basis can one hope to find proper reformulation of these concepts.

Finally we mention only briefly other phenomena whose ultimate quantitative understanding will rest at least in part on general nonuniform fluid equilibrium theory:

(a) sorption of gases in polymers, of H₂ in Pd and Pt, and formation of clathrate compounds; in each case the host "lattice" provides effectively a rapidly varying force field, which may or may not be periodic;

(b) gravitational and centrifugal equilibrium in the strong field case;

(c) implications of equilibrium molecular distribution near container walls for formulation of proper

hydrodynamic boundary conditions for flow next to these walls, including the possibility of "slip."

It is obviously impossible to contribute significantly to each of the diverse areas cited by means only of an investigation such as the following, restricted to bare fundamentals. We therefore shall proceed with a less pretentious point of view, which limits us at the outset to purely classical fluids, for which the total interaction includes only single-particle external potentials, as well as pairwise additive (though not necessarily central) intermolecular potentials. The major purpose of this article is to investigate the excess properties of an imperfect fluid system which are induced by external forces; this investigation is implemented first by noting the generalization of the cluster theory of imperfect gases to include external forces, and second, by deriving a fluctuation theorem satisfied by certain of these external field excess quantities. With regard to the former, we remark that this paper presents the general formulation of ideas the authors have applied previously to description of the electrolyte interface under osmotic solution conditions,¹¹ for which the cluster approach is natural. More recently, Morita and Hiroike¹² have developed related ideas.

It is of course our hope that the formalism presented in this article eventually will have value in explaining details of the specific physical phenomena mentioned above.

The next section outlines the basis of the general cluster theory of imperfect gases in the presence of an external potential. By very simple topological arguments, it is possible to deduce a previously known relation between the activity and the local density $\rho^{(1)}(\mathbf{r})$ in terms of conceptually simple modifications of the usual imperfect gas irreducible cluster integrals. Simultaneously, there is exhibited in terms of these modified cluster integrals a local "pressure" $\bar{p}(\mathbf{r})$, whose integral over all space, divided by kT , yields rigorously the logarithm of the grand partition function, regardless of the extent of stable fluid inhomogeneity, or of the degree of curvature of the physical boundary surrounding the fluid. By virtue of the reduction of \bar{p} to the usual thermodynamic pressure within a region of homogeneity of the fluid, the $\rho^{(1)}(\mathbf{r})$ and $\bar{p}(\mathbf{r})$ expressions reduce to the usual major results of imperfect gas theory for the spatially uniform case.

A further importance of the quantity $\bar{p}(\mathbf{r})$ lies in recognition that its construction completely eliminates difficulty associated with the volume dependence of Mayer cluster integrals; its deviations from the usual thermodynamic pressure near the boundary of a fluid represents the entire effect of completely accounting for this dependence. On account of the simple nature of the \bar{p} result, we conjecture that its construction

⁴ *Proceedings of the Conference on Interfacial Phenomena and Nucleation*, edited by H. Reiss (AFCRC-TR-55-211A, Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C.), Vol. 2, pp. 39-51.

⁵ J. W. Cahn and J. E. Hilliard, *J. Chem. Phys.* **28**, 258 (1958).

⁶ E. W. Hart, *J. Chem. Phys.* **34**, 1471 (1961).

⁷ M. S. Green, *J. Chem. Phys.* **33**, 1403 (1960).

⁸ F. H. Stillinger, Jr., and H. L. Frisch, *Physica* **27**, 751 (1961).

⁹ J. Frenkel, *Kinetic Theory of Liquids* (Dover Publications, Inc., New York, 1955), Chap. VII.

¹⁰ F. P. Buff and J. G. Kirkwood, *J. Chem. Phys.* **18**, 991 (1950).

¹¹ F. P. Buff and F. H. Stillinger, Jr., *J. Chem. Phys.* **25**, 312 (1956).

¹² T. Morita and K. Hiroike, *Prog. Theoret. Phys. (Kyoto)* **25**, 537 (1961).

presented below may serve as basis for a complete theory of gas condensation based upon Mayer's earlier analysis,¹³ which has received considerable criticism.^{14,15}

Section III proceeds to examine the structure of the cluster series for $\rho^{(1)}(\mathbf{r})$ and $\bar{p}(\mathbf{r})$. In view of the formal simplifications that are possible by partial cluster summation in the homogeneous case, a generalization X_θ of the non-nodal cluster sum X occurring there¹⁶ is employed to re-express succinctly both $\rho^{(1)}(\mathbf{r})$ and $\bar{p}(\mathbf{r})$. Upon taking the external force field to be precisely that due to a fixed molecule identical to those comprising the fluid, a new integral equation for distribution of molecular pairs in a uniform fluid is deduced. Comparison with previous results for the same quantity¹⁶ yields immediately an expression in terms of X_θ and X for the intractable cluster sum corresponding to "elementary" diagrams, i.e., those which cannot be evaluated by repeated convolution.

The $\rho^{(1)}(\mathbf{r})$ and $\bar{p}(\mathbf{r})$ expressions also are used to construct local Helmholtz and Gibbs free energy densities. The extent of validity of local free energy expressions employing only local density gradients (or Laplacians) to correct for inhomogeneity can thereupon be related to the relative range of X_θ ; on this basis it is suggested that such asymptotic evaluations apply to weak gravitational and centrifugal field equilibria, but not to critical phenomena.

A fluctuation theorem is derived in Sec. IV, which represents the surface modification of a well-known bulk fluid relation between the isothermal compressibility and the radial distribution function.¹⁷ The analysis allows the bulk uniform fluid density derivative of the surface free energy (referred to an equimolar dividing surface) to be related to the same density variation of dividing surface position, and the distribution of excess particle pairs in the interfacial region.

II.

Let $U(\mathbf{r})$ represent the externally applied single-particle potential energy which induces under equilibrium conditions the inhomogeneous density distribution. We shall initially presume that $U(\mathbf{r})$ has risen to arbitrarily large values outside the region of space corresponding to the bounded fluid system of interest. Thus, the form of U suffices to provide a "container," confining the fluid assembly to the requisite finite region.

The entire statistical thermodynamics of such a system may in principle be derived from the grand

partition function

$$\exp(-\beta\Omega) = 1 + \sum_{N=1}^{\infty} \frac{y^N Z_N(\beta)}{N!}, \quad (1)$$

where we have set

$$\beta = (kT)^{-1}, \quad y = \lambda_T^{-3} \exp(\beta\mu).$$

The symbols k , T , μ , and λ_T stand respectively for Boltzmann's constant, absolute temperature, chemical potential per particle, and mean thermal de Broglie wavelength. The configuration integral for N identical particles interacting in pairs with a potential $v(ij)$, and subject to the external field $U(i)$, has been denoted

$$Z_N(\beta) = \int \exp\left\{-\beta\left[\sum_{i=1}^N U(i) + \sum_{i<j=1}^N v(ij)\right]\right\} d\mathbf{r}_1 \cdots d\mathbf{r}_N. \quad (2)$$

Here, the integrations may be extended over all space on account of the nature of U .

It will be recalled that the point of contact between the grand partition function and thermodynamic observables is provided by the relation^{18,19}

$$\Omega(\beta, y) = -\boldsymbol{\lambda} \cdot \mathbf{A}, \quad (3)$$

where the vector $\boldsymbol{\lambda}$ is constructed from generalized displacement parameters, and \mathbf{A} is its $\boldsymbol{\lambda}$ -independent conjugate force, defined by the first law of thermodynamics:

$$dE = TdS - \mathbf{A} \cdot d\boldsymbol{\lambda} + \mu d\bar{N}. \quad (4)$$

The only condition required of $\boldsymbol{\lambda}$ is that as its modulus decreases to zero (at constant T and μ), the mean number of particles in the system,

$$\bar{N} = [\partial(-\beta\Omega)/\partial \log y]_{\beta, \lambda}, \quad (5)$$

likewise must vanish. For homogeneous fluids the usual choices for $\boldsymbol{\lambda}$ and \mathbf{A} are of course the scalars: system volume V and pressure p , respectively. The derivation technique for the fluctuation theorem in Sec. IV will illustrate the variety of often more profitable alternative choices.

Beside the grand partition function itself, the other basic quantities of the theory are the molecular distribution functions $\rho^{(n)}$ for sets of n particles

$$\begin{aligned} \rho^{(n)}(\mathbf{r}_1 \cdots \mathbf{r}_n) \\ = \exp(\beta\Omega) \sum_{N=n}^{\infty} \frac{y^N}{(N-n)!} \int \exp\left\{-\beta\left[\sum_{i=1}^N U(i) + \sum_{i<j=1}^N v(ij)\right]\right\} \\ \cdot d\mathbf{r}_{n+1} \cdots d\mathbf{r}_N. \quad (6) \end{aligned}$$

Out of the entire set of such functions, the dominant interest lies in the singlet and pair ($n=1, 2$) functions.

¹³ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), Chap. 14.

¹⁴ S. Katsura and H. Fujita, *J. Chem. Phys.* **19**, 795 (1951).

¹⁵ N. Saito, *J. Chem. Phys.* **35**, 232 (1961).

¹⁶ J. M. J. van Leeuwen, J. Groeneveld, and J. deBoer, *Physica* **25**, 792 (1959).

¹⁷ T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), p. 236.

¹⁸ Reference 2, p. 234.

¹⁹ F. P. Buff and H. Saltsburg, *J. Chem. Phys.* **26**, 1526 (1957).

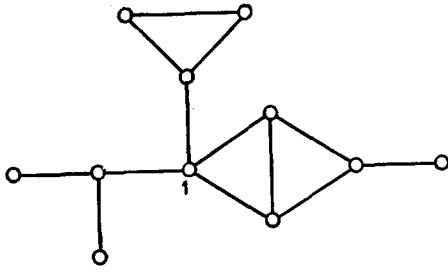


FIG. 1. An example of a cluster diagram occurring in the sum $S_{11}(1, \dots, 11)$ for which particle 1 splits the remaining ten particles into three subsets. These subsets are singly connected among themselves, i.e., by f -bond paths not including particle 1.

Following the usual cluster expansion approach,²⁰ we proceed to develop the integrands appearing in the grand partition function into f function expansions²¹

$$\exp(-\beta\Omega) = 1 + \sum_{N=1}^{\infty} \frac{y^N}{N!} \int \exp[-\beta \sum_{i=1}^N U(i)] \cdot \prod_{i < j=1}^N [1 + f(ij)] d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (7)$$

$$f(ij) = \exp[-\beta v(ij)] - 1.$$

If the products in (7) are expanded, and terms collected according to the connectedness of the associated cluster diagrams,²⁰ one obtains in the customary way a power series for the logarithm of the grand partition function

$$-\beta\Omega = \sum_{j=1}^{\infty} b_j y^j. \quad (8)$$

The coefficients b_j are modifications of the reducible cluster integrals encountered in the homogeneous imperfect gas theory,

$$b_j = (j!)^{-1} \int S_j(1 \cdots j) \exp[-\beta \sum_{i=1}^j U(i)] d\mathbf{r}_1 \cdots d\mathbf{r}_j, \quad (9)$$

and the $S_j(1 \cdots j)$ are the reducible cluster sums of f 's whose associated diagrams are at least singly connected. The first few S_j in explicit form are

$$\begin{aligned} S_1 &= 1, \\ S_2 &= f(12), \\ S_3 &= f(12)f(13) + f(12)f(23) + f(13)f(23) \\ &\quad + f(12)f(13)f(23). \end{aligned} \quad (10)$$

²⁰ Reference 13, Chap. 13.

²¹ It should be remarked that neither here nor in the following is it absolutely necessary to suppose that the pair potential is central. Even for monatomic particles there are important examples to the contrary. In the case of ions, there may exist pair image forces (see reference 11); in addition, computations have been made showing that the usual pair interaction between uncharged atoms is markedly changed by the proximity of a "wall" [O. Sinanoğlu and K. S. Pitzer, *J. Chem. Phys.* **32**, 1279 (1960)].

The analogous manipulations may be applied to the singlet density distribution $\rho^{(1)}(\mathbf{r}_1)$. Eq. (6) leads to

$$\rho^{(1)}(\mathbf{r}_1) = \exp(\beta\Omega) \sum_{N=1}^{\infty} \frac{y^N}{(N-1)!} \int \exp[-\beta \sum_{i=1}^N U(i)] \cdot \prod_{i < j=1}^N [1 + f(ij)] d\mathbf{r}_2 \cdots d\mathbf{r}_N. \quad (11)$$

After expansion of the integrands, the resulting products of f functions fall into connected sets either including, or not including, particle 1. In a given member of the expansion, let m denote the number of other particles connected by f -bond paths to particle 1. The number of distinct ways of grouping such that out of $N-1$ particles (numbered $2 \cdots N$), m are connected to 1, n_1 others are unconnected, n_2 sets of two are singly connected only to one another, \dots , n_j sets of j are singly connected only to each other, \dots , is precisely

$$(N-1)! / [m! \prod_{j=1}^{\infty} n_j! (j!)^{n_j}]. \quad (12)$$

We must have, of course,

$$m + n_1 \cdot 1 + n_2 \cdot 2 + \cdots + n_j \cdot j + \cdots = N-1.$$

By using the combinatorial factor (12), one concludes that the sum over N on the right-hand side of Eq. (11) may be written as a product of two factors. The first factor contains all contributions from connected f -function products not including particle 1, and may be identified as precisely the grand partition function. The remaining factor includes all possible connected f products including 1; the resulting transformation of Eq. (11) is

$$\rho^{(1)}(\mathbf{r}_1) = y \exp[-\beta U(\mathbf{r}_1)] \cdot \left\{ 1 + \sum_{m=1}^{\infty} \frac{y^m}{m!} \int S_{m+1}(1 \cdots m+1) \exp[-\beta \sum_{i=2}^{m+1} U(i)] \cdot d\mathbf{r}_2 \cdots d\mathbf{r}_{m+1} \right\}. \quad (13)$$

The integrals occurring here are essentially the same as the b_j of Eq. (9), with the exception that no integration over position \mathbf{r}_1 is performed.

By definition, the f products in each S_{m+1} appearing in (13) connect any pair of the particles $1 \cdots m+1$, if only indirectly. In many cases, however, removal of the particle 1 will not leave $2 \cdots m+1$ connected. Figure 1 illustrates by example a case in which particle 1 binds together three subsets of particles which are singly connected among themselves, but are connected to the other subsets only by f -bond paths passing through 1. Suppose that the m particles $2 \cdots m+1$ by this means form m_1 subsets of just one particle, m_2 subsets of two, \dots , for a given term in S_{m+1} , where obviously

$$m = \sum_{j=1}^{\infty} j m_j.$$

Then since there are exactly

$$m! / \left[\prod_{j=1}^{\infty} m_j! (j!)^{m_j} \right]$$

distinct ways of distributing particles $2 \cdots m+1$ into such subsets, one immediately sees that the sum in Eq. (13) represents the expansion of the exponential of a series including only integrals for diagrams having *all* particles exclusive of 1 connected among themselves:

$$\rho^{(1)}(\mathbf{r}_1) = y \exp\{-\beta U(\mathbf{r}_1) + \sum_{j=1}^{\infty} \frac{y^j}{j!} \int S_j(1 | 2 \cdots j+1) \exp[-\beta \sum_{i=2}^{j+1} U(i)] \cdot d\mathbf{r}_2 \cdots d\mathbf{r}_{j+1}\}. \quad (14)$$

The vertical bar in $S_j(1 | 2 \cdots j+1)$ indicates that the particles following it are connected among themselves, as well as to 1.

There is still another transformation which may be applied to (14). Figure 2 shows a typical cluster diagram in an $S_j(1 | 2 \cdots j+1)$. There exists a unique subset of $2 \cdots j+1$ which, together with 1, constitutes an irreducible (at least doubly connected) portion of the diagram. The remaining particles not in this irreducible part, are "hung unto" its vertices (exclusive of 1). For a given term in $S_j(1 | 2 \cdots j+1)$ let there be k particles from $2 \cdots j+1$ forming the irreducible subset with 1. These k could have been chosen from $2 \cdots j+1$ in

$$j! / k!(j-k)!$$

different ways. Of the remaining $j-k$ particles, suppose that s_1 are attached to a particular one of the vertices of the irreducible part, s_2 to a second, \cdots , s_k to the k th. This distribution could have been attained in

$$(j-k)! / \prod_{i=1}^k s_i!$$

ways.

When finally it is realized that the set of subdiagrams attached to any vertex of the irreducible subset is precisely that generated by the sum in Eq. (13), use of these last combinatorial factors leads to the result

$$\rho^{(1)}(\mathbf{r}_1) = y \exp\{-\beta U(\mathbf{r}_1) + \sum_{k=1}^{\infty} (k!)^{-1} \int S_k(1 \cdots k+1) \rho^{(1)}(\mathbf{r}_2) \cdots \rho^{(1)}(\mathbf{r}_{k+1}) \cdot d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1}\}. \quad (15)$$

$S_k(1 \cdots k+1)$ is the irreducible cluster sum of f 's connecting (at least doubly) $k+1$ particles. Thus, with the exception of its appearance as a single pre-exponential factor, y has been entirely eliminated from (15) in favor of local densities $\rho^{(1)}(\mathbf{r})$. The integrands occurring in (15) are generalizations of the customary irreducible Mayer integrals.²⁰ For the uniform fluid, the singlet densities may be removed from under the

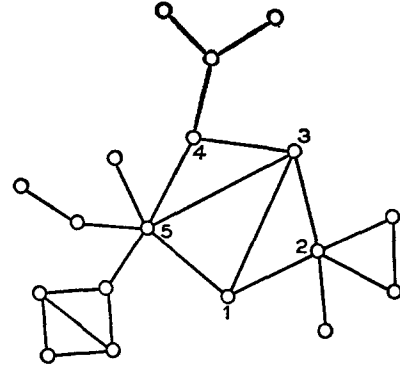


FIG. 2. A cluster diagram of the type occurring in the $S_j(1 | 2 \cdots j+1)$. Particles 2, 3, 4, and 5 constitute that portion of the diagram which, together with 1, form the unique irreducible portion "rooted" at 1.

integral to leave only irreducible products of f 's; this special case of Eq. (15) is well known.²⁰

Since the mean number of particles \bar{N} is precisely the spatial integral of $\rho^{(1)}(\mathbf{r}_1)$, Eq. (5) shows that

$$-\beta\Omega = \int d\mathbf{r}_1 \int_0^y (y')^{-1} \rho^{(1)}(\mathbf{r}_1, y') dy'. \quad (16)$$

For the completely homogeneous fluid, this quantity is βpV , i.e., the inner integral is βp . This suggests therefore that under our present more general circumstances it might be profitable to seek a local "pressure" $\bar{p}(\mathbf{r}_1)$ whose integral over \mathbf{r}_1 yields $-\Omega$ rigorously, and which reduces to the usual hydrostatic pressure p under conditions of homogeneity.

Define for conciseness $d_k(\mathbf{r}_1)$ to be the generalized irreducible integrals appearing in (15); that is,

$$\rho^{(1)}(\mathbf{r}_1) = y \exp[-\beta U(\mathbf{r}_1) + \sum_{k=1}^{\infty} d_k(\mathbf{r}_1, y)]. \quad (17)$$

Then use of this identity to eliminate the explicit appearance of y from the integrand of (16) leads to

$$\begin{aligned} -\beta\Omega &= \int d\mathbf{r}_1 \int_0^y \exp[-\beta U(\mathbf{r}_1) + \sum_{k=1}^{\infty} d_k(\mathbf{r}_1, y')] \\ &\quad \cdot d\{\rho^{(1)}(\mathbf{r}_1, y') \exp[\beta U(\mathbf{r}_1) - \sum_{k=1}^{\infty} d_k(\mathbf{r}_1, y')]\} \\ &= \int d\mathbf{r}_1 \int_0^y \left\{ \frac{\partial \rho^{(1)}(\mathbf{r}_1, y')}{\partial y'} - \rho^{(1)}(\mathbf{r}_1, y') \right. \\ &\quad \left. \cdot \sum_{k=1}^{\infty} \frac{\partial d_k(\mathbf{r}_1, y')}{\partial y'} \right\} dy' \\ &= \int d\mathbf{r}_1 \left\{ \rho^{(1)}(\mathbf{r}_1, y) \right. \\ &\quad \left. - \sum_{k=1}^{\infty} \int_0^y \rho^{(1)}(\mathbf{r}_1, y') \frac{\partial d_k(\mathbf{r}_1, y')}{\partial y'} dy' \right\}. \quad (18) \end{aligned}$$

In the remaining double integrals we may interchange the order of \mathbf{r}_1 and y' integrations. Noting furthermore that

$$S_k(1 \cdots k+1) \rho^{(1)}(\mathbf{r}_1, y') \cdots \rho^{(1)}(\mathbf{r}_{k+1}, y')$$

is completely symmetric with respect to interchange of any two particle positions, Eq. (18) may be rewritten

$$\begin{aligned} -\beta\Omega &= \int \rho^{(1)}(\mathbf{r}_1, y) d\mathbf{r}_1 - \sum_{k=1}^{\infty} (k!)^{-1} \\ &\quad \cdot \int_0^y dy' \int S_k(1 \cdots k+1) \rho^{(1)}(\mathbf{r}_1, y') (\partial/\partial y') \\ &\quad \cdot [\rho^{(1)}(\mathbf{r}_2, y') \cdots \rho^{(1)}(\mathbf{r}_{k+1}, y')] d\mathbf{r}_1 \cdots d\mathbf{r}_{k+1} \\ &= \int \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \cdot \frac{1}{k!} \int_0^y dy' \int S_k(1 \cdots k+1) \\ &\quad \cdot (\partial/\partial y') [\rho^{(1)}(\mathbf{r}_1, y') \cdots \rho^{(1)}(\mathbf{r}_{k+1}, y')] d\mathbf{r}_1 \cdots d\mathbf{r}_{k+1} \\ &= \int \rho^{(1)}(\mathbf{r}_1) d\mathbf{r}_1 - \sum_{k=1}^{\infty} \frac{k}{k+1} \cdot \frac{1}{k!} \int S_k(1 \cdots k+1) \\ &\quad \cdot \rho^{(1)}(\mathbf{r}_1) \cdots \rho^{(1)}(\mathbf{r}_{k+1}) d\mathbf{r}_1 \cdots d\mathbf{r}_{k+1}. \quad (19) \end{aligned}$$

Therefore, if we define

$$\beta\bar{p}(\mathbf{r}_1) = \rho^{(1)}(\mathbf{r}_1) \left[1 - \sum_{k=1}^{\infty} \frac{k}{k+1} d_k(\mathbf{r}_1) \right], \quad (20)$$

the requisite conditions on our local pressure are satisfied. In particular, Eq. (20) reproduces the usual virial expansion for the pressure of a uniform imperfect gas.²⁰

Equation (20) constitutes the major result of this section, for it demonstrates the existence of a local quantity \bar{p} which can represent not only the equation of state of a homogeneous imperfect gas, but in the presence of possibly very complicated and rapidly varying (over atomic dimensions) externally applied potentials, can also completely characterize the resulting modified thermodynamics. If these external forces are produced at the surface of an adsorbing substrate for the fluid considered, the resulting deviation of \bar{p} near the interface from its bulk pressure value in principle yields the entire surface free energy, regardless of the degree of curvature of the surface, or its heterogeneity.

The local density expression (17), on the other hand, has previously been derived by Yvon,²² and Morita and Hiroike.¹² The only joint application of the ideas behind both Eqs. (17) and (20) appears to be an investigation of the surface tension of dilute electrolytes by the authors¹¹; the attractive feature of that example was the sufficiency of just the simple ring clusters in each S_k , suitably generalized to the multi-

²² J. Yvon, *Actualités Scientifique et Industrielles*, (Hermann & Cie, Paris, France, 1935), No. 203, p. 28, where the result is suggested by a successive approximation technique. The more general result appears in: D. Massignon, *Mechanique Statistique des Fluides* (Dunod, Paris, France, 1957), p. 143.

component case, rigorously to account for the low concentration limiting surface tension increment.

The expression displayed in Eq. (20) for the local pressure has been obtained without approximation. A particular type of wall force $U(\mathbf{r})$ would be one which rigorously vanishes inside some well-defined geometric volume V , but is positively infinite everywhere outside V . In effect, of course, this simply confines the integrations in the original configuration integrals (2) to the interior of V . However this is precisely the situation in which volume dependence of cluster integrals has been stressed in criticism of the Mayer condensation theory.^{14,15} Equation (20) therefore represents the result of completely accounting for the effect of finite system volume. If no external forces act on the fluid beside this ideal type of wall force, then certainly the local density $\rho^{(1)}(\mathbf{r})$ near the wall will fluctuate from its uniform value in the interior of V , but these fluctuations will die away within a few molecular diameters from the surface, since fluids neither possess nor can propagate long-range order. By virtue of Eq. (20), $\bar{p}(\mathbf{r})$ will also exhibit fluctuations from the bulk pressure, which are likewise confined to the immediate vicinity of the wall. This evidently is the only effect of cluster integral volume dependence, at least within the region of convergence of the resulting modified cluster series equation of state.

III.

The irreducible cluster sums S_k occur in the integrands of both fundamental relations (15) and (20). Since by definition the graphs of the individual terms of each $S_k(1, 2 \cdots k+1)$ are at least doubly connected we know that there are always at least two *independent* f -bond paths connecting particles 1 and 2. Stated differently, this amounts to the condition that no nodal point exists between 1 and 2; that is, no point at which if the diagram were cut, separation into two disjoint subdiagrams would occur, one containing 1 and the other containing 2. This is exactly the topological condition on graphs which constitute the "non-nodal" cluster function $X(12)$, which arises in the cluster theory of the radial distribution function in uniform fluids.¹⁶

But (15) and (20) cannot immediately be rewritten in terms of $X(12)$ for two reasons:

(a) The numerical factor preceding each cluster integral in these equations would have to be $[(k-1)!]^{-1}$, rather than $(k!)^{-1}$;

(b) The integrands contain position-dependent singlet densities $\rho^{(1)}(\mathbf{r}_i)$, whereas $X(12)$ is defined with the uniform fluid densities appearing outside the integrals

$$X(12, \rho) = \sum_{k=1}^{\infty} \frac{\rho^{k-1}}{(k-1)!} \int S_k(12 \cdots k+1) d\mathbf{r}_3 \cdots d\mathbf{r}_{k+1}. \quad (21)$$

These difficulties can formally be rectified, however. If

the inhomogeneous system includes a large region within which $U(\mathbf{r})$ vanishes identically, $\rho^{(l)}(\mathbf{r})$ will in its interior equal precisely ρ , the ordinary uniform fluid density at temperature T and chemical potential μ . For all \mathbf{r} , set

$$g(\mathbf{r}) = \rho^{(l)}(\mathbf{r})/\rho. \quad (22)$$

Then for a given $g(\mathbf{r})$ we may define a modification $X_\theta(12, \rho')$ of the non-nodal function in Eq. (21), to be essentially the latter, but with extra factors g in each integrand

$$X_\theta(12, \rho') = \sum_{k=1}^{\infty} \frac{(\rho')^{k-1}}{(k-1)!} \int \mathfrak{S}_k(1, 2 \cdots k+1) \cdot g(\mathbf{r}_3, \rho) \cdots g(\mathbf{r}_{k+1}, \rho) d\mathbf{r}_3 \cdots d\mathbf{r}_{k+1}. \quad (23)$$

Unlike the precursor X in Eq. (21), this is no longer generally a function only of the distance r_{12} for central $v(12)$, which interaction form we shall now assume for simplicity in the remainder of this, and the following section.

In the strict sense, $g(\mathbf{r}, \rho)$ is a unique function (in the absence of phase transitions) of the uniform system density ρ . As indicated in (23), though, X_θ is defined more generally to include a variable density parameter ρ' , for any given function $g(\mathbf{r}, \rho)$, which may only incidentally happen to refer to a different uniform system density $\rho \neq \rho'$. With this interpretation, Eq. (17) may be divided by its limit for a $U(\mathbf{r})=0$ region to yield

$$\begin{aligned} \log g(\mathbf{r}_1, \rho) &= -\beta U(\mathbf{r}_1) + \sum_{k=1}^{\infty} \int_0^\rho d\rho' \frac{(\rho')^{k-1}}{(k-1)!} \\ &\cdot \int \mathfrak{S}_k(1, 2 \cdots k+1) [g(\mathbf{r}_2, \rho) \cdots g(\mathbf{r}_{k+1}, \rho) - 1] d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1} \\ &= -\beta U(\mathbf{r}_1) + \int_0^\rho d\rho' \int d\mathbf{r}_2 [g(\mathbf{r}_2, \rho) \\ &\cdot X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho') - X(r_{12}, \rho')]. \quad (24) \end{aligned}$$

A similar transformation may be applied to the local pressure definition (20)

$$\begin{aligned} \beta \bar{p}(\mathbf{r}_1) &= \rho^{(l)}(\mathbf{r}_1) - \sum_{k=1}^{\infty} \frac{1}{(k-1)!} \int_0^\rho (\rho')^k d\rho' \\ &\cdot \int \mathfrak{S}_k(1, 2 \cdots k+1) g(\mathbf{r}_1, \rho) \cdots g(\mathbf{r}_{k+1}, \rho) d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1} \\ &= \rho^{(l)}(\mathbf{r}_1) - g(\mathbf{r}_1, \rho) \int_0^\rho \rho'^2 d\rho' \int X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho') \\ &\cdot g(\mathbf{r}_2, \rho) d\mathbf{r}_2. \quad (25) \end{aligned}$$

It is now possible to exhibit local Gibbs and Helmholtz free energies, which we denote by $G(\mathbf{r}_1)$ and $A(\mathbf{r}_1)$ respectively, whose spatial integrals yield the

corresponding exact total values of the system free energy. Using (24) and (25), along with the logarithm of (17)

$$\begin{aligned} \beta G(\mathbf{r}_1) &= \beta \rho^{(l)}(\mathbf{r}_1) \mu \\ &= \rho^{(l)}(\mathbf{r}_1) \{ \log[\lambda_T^3 \rho^{(l)}(\mathbf{r}_1)] + \beta U(\mathbf{r}_1) \\ &\quad - \int d\mathbf{r}_2 g(\mathbf{r}_2, \rho) \int_0^\rho X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho') d\rho' \}; \quad (26) \end{aligned}$$

$$\begin{aligned} \beta A(\mathbf{r}_1) &= \beta \rho^{(l)}(\mathbf{r}_1) \mu - \beta \bar{p}(\mathbf{r}_1) \\ &= \rho^{(l)}(\mathbf{r}_1) \{ \log[\lambda_T^3 / e] \rho^{(l)}(\mathbf{r}_1) + \beta U(\mathbf{r}_1) \\ &\quad + \int d\mathbf{r}_2 g(\mathbf{r}_2, \rho) \int_0^\rho [(\rho'/\rho) - 1] X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho') d\rho' \}. \quad (27) \end{aligned}$$

The individual terms in these two expressions have a clear meaning. In each case the leading contributions are local ideal gas contributions, and to this is added the local energy change of the fluid due to its presence in the nonvanishing external force field $U(\mathbf{r}_1)$. The remaining integrals, with density-averaged X_θ 's as kernels, yield the appropriate free energy of interaction between neighboring elements of the fluid.

We see therefore that X_θ plays a fundamental role in the theory of inhomogeneous fluids. The most crucial point at this juncture concerns the range of applicability of the expressions containing this quantity. For applications involving fluids in the gas phase, there can be no question that the cluster integral manipulations leading to the major results of this and the previous section are justified. Furthermore, the general structure of solution theory^{23,24} assures that under osmotic conditions, essentially the same manipulations (after replacement of the bare interaction potentials by pure solvent potentials of mean force) are equally applicable to selected properties of liquids. In particular, the condensed phase analog of our local pressure $\bar{p}(\mathbf{r})$ is a local osmotic pressure $\pi(\mathbf{r})$.¹¹

The status of the central quantity X_θ , in the case a condensed liquid phase resides in the system, is much less clear. There appear roughly to be two convergence possibilities under which representation of local thermodynamic parameters in terms of this function may be useful. This paper however cannot provide a rigorous answer to the difficult questions whether either, or neither, of these hypotheses are true:

(A) From the conservative viewpoint, one would not require even conditional convergence of the several cluster sums in the liquid phase. Instead, attention may be focused entirely on the interfacial region, and by a suitable subtractive procedure, the possibly divergent cluster series may be entirely eliminated from the bulk liquid to leave a series which vanishes

²³ W. G. McMillan and J. E. Mayer, J. Chem. Phys. **13**, 276 (1945).

²⁴ J. G. Kirkwood and F. P. Buff, J. Chem. Phys. **19**, 774 (1951).

everywhere except in the interfacial region. Thus, in the case of a simple liquid-vapor coexistence with a planar interface, we may write for $\Delta\bar{p}(x_1)$, defined as the difference between \bar{p} at a given distance x_1 from a suitable dividing surface placed in the interface, and the common value of the pressure within the interior of either phase

$$\Delta\bar{p}(x_1) = \rho^{(1)}(x_1) - \rho_\alpha - \sum_{k=1}^{\infty} \frac{k}{k+1} \cdot \frac{1}{k!} \int \mathfrak{S}_k(1 \cdots k+1) \cdot [\rho^{(1)}(x_1) \cdots \rho^{(1)}(x_{k+1}) - \rho_\alpha^{k+1}] d\mathbf{r}_2 \cdots d\mathbf{r}_{k+1},$$

when x_1 is on the α -phase side of the dividing surface. Here, ρ_α is the uniform density within the bulk of the α phase. A similar expression would hold if x_1 were on the β -phase side of the dividing surface. One would anticipate improved convergence for the new series, since the integrand now effectively vanishes unless each $\mathbf{r}_2 \cdots \mathbf{r}_{k+1}$ is on the *same* side of the dividing surface; roughly speaking, this amounts to a reduction in the previously available configuration space by a factor 2^{-k} .

(B) Alternatively, it would be assumed that a rearrangement and resummation of the original cluster sums yield the properties of the condensed phase, *both* in the interfacial region and in the bulk liquid. Such a hope, apparently, has been the motivation recently behind analysis of the cluster sums according to topological character of the associated graphs.¹⁶ In our own case, this procedure leads to an integral relation between the quantity X_θ on the one hand, and the singlet and pair distribution functions in an inhomogeneous fluid on the other hand:

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \rho) - 1 = X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho) + \int X_\theta(\mathbf{r}_1, \mathbf{r}_3, \rho) \rho^{(1)}(\mathbf{r}_3) \cdot [g^{(2)}(\mathbf{r}_3, \mathbf{r}_2, \rho) - 1] d\mathbf{r}_3,$$

$$g^{(2)}(\mathbf{r}_1, \mathbf{r}_2, \rho) = \rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) / \rho^{(1)}(\mathbf{r}_1) \rho^{(1)}(\mathbf{r}_2). \quad (28)$$

For the uniform fluid, this reduces to the familiar relation between the spherically symmetric pair correlation and direct (non-nodal) correlation functions, $g^{(2)}(r_{12}, \rho)$ and $X(r_{12}, \rho)$,¹⁶

$$g^{(2)}(r_{12}, \rho) - 1 = X(r_{12}, \rho) + \rho \int X(r_{13}, \rho) [g^{(2)}(r_{32}, \rho) - 1] d\mathbf{r}_3. \quad (28')$$

In liquids, the fact that $g^{(2)}(r)$ exhibits only moderate order at molecular distances, and none at long range, allows unique solution of (28') for X in terms of $g^{(2)}$. Therefore by utilizing a Fourier integral transform on experimentally determined $g^{(2)}$'s, we see that at least in liquid bulk, an unambiguous quantity X exists, which is identical with the convergent sum of the cluster series (21), when in the gas phase this latter certainly has meaning. For inhomogeneous liquids, $g^{(2)}$ will have lost its isotropy, but the extent and type of

correlation it reflects is still qualitatively the same. Accordingly, Eq. (28) ought likewise to possess a unique inverse, and viewpoint (B) above would seek to provide a means of reordering cluster sum (23) to converge to the same function.

We propose tentatively to proceed under the assumption that a unique computational procedure for X_θ will eventually be demonstrated in condensed phases. For the present it is sufficient to bear in mind that for some purposes $X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho')$ can probably be approximated by $X(r_{12}, \rho')$, where the appropriate density for comparison, say, is the local density in the inhomogeneous system midway between positions \mathbf{r}_1 and \mathbf{r}_2

$$\rho'' = \rho' g[\frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)].$$

This assignment obviously reduces to the required limit for spatial uniformity.

In case the function $X_\theta(\mathbf{r}_1, \mathbf{r}_2, \rho')$ has a range which is short compared with distances over which $\rho^{(1)}(\mathbf{r}_1)$ changes appreciably (as in many gravitational or centrifugal density distribution problems), the X_θ 's appearing in Eqs. (25), (26), and (27) may with negligible error be replaced by $X[r_{12}, \rho(\mathbf{r}_1)]$, and these expressions then have locally uniform fluid forms. Thereupon, one sees that the local pressure and free energies are precisely equal to the corresponding quantities in a hypothetical uniform fluid whose density everywhere is just equal to $\rho^{(1)}(\mathbf{r}_1)$ at the position considered in the real inhomogeneous system. This simplification is of course the basis of the usual thermodynamics in external force fields.²⁵ When the local density changes more rapidly, though, the finite extent of X_θ can become important. In particular, one can readily compute the leading corrections to the local homogeneity values. One obtains contributions to each of $\bar{p}(\mathbf{r}_1)$, $F(\mathbf{r}_1)$, and $A(\mathbf{r}_1)$ depending on the local values of $\nabla^2 \rho^{(1)}(\mathbf{r}_1)$ and $[\nabla \rho^{(1)}(\mathbf{r}_1)]^2$,²⁶ with coefficients that may be written in terms of $X[r_{12}, \rho^{(1)}(\mathbf{r}_1)]$, and the lowest order perturbations of X_θ from X caused by nonconstancy of $g(\mathbf{r})$. These corrections are strictly valid only in the asymptotic limit of slow variations in $\rho^{(1)}(\mathbf{r})$, as measured by the ratio of $|\nabla \log \rho^{(1)}(\mathbf{r})|$ to the range of both $X[r_{12}, \rho(\mathbf{r}_1)]$ and the perturbations.

It is often claimed that certain critical phenomena may adequately be explained by use of local free energy densities, which are equal precisely to local homogeneity values, supplemented by these lowest order asymptotic corrections in spatial variations of $\rho^{(1)}(\mathbf{r}_1)$. In particular, the liquid-vapor interface becomes wide just below the critical temperature T_c , while the bulk liquid and vapor densities approach equality, so that the interfacial density profile varies very slowly from the interior of one phase to the

²⁵ E. A. Guggenheim, *Thermodynamics* (North-Holland Publishing Company, Amsterdam, 1957), Chap. 10.

²⁶ As is well known, in computation of the entire grand partition function, or total Gibbs and Helmholtz free energies, these two types of terms are interconvertible by partial integration.

other. Unfortunately, however, it is now well established that even $X(r_{12}, \rho)$ does not remain short-ranged at the critical point,^{7,8} and probably similar behavior should be expected for the more complicated X_ρ . Consequently, the asymptotic reduction of integrals (25), (26), and (27) is not possible. A convincing piece of evidence for inaccuracy of the asymptotic free energy densities for computation of critical point molecular distribution stems from the incorrect predictions they imply for pair correlation functions.⁸

Therefore, in the case of critical density distributions, along with more obvious examples such as calculation of liquid-vapor interfacial properties well below T_c , the full integral expressions (24)–(27) are required for accurate description.

In concluding this section, we point out that Eq. (24) leads to an interesting formal identity for the “elementary diagram cluster sum” $E(r_{12})$, familiar from the usual partial cluster summation techniques of the pair distribution problem.¹⁶ The complex topological character of diagrams for terms in E , it will be recalled, makes their analytic evaluation impossible in virtually all cases. To obtain the identity, Eq. (24) may be applied to a special case in which the “external” potential U is the potential set up by a particle of the fluid held fixed at some point \mathbf{r}_0 ²⁷

$$U(\mathbf{r}_1) = v(r_{01}). \quad (29)$$

Under this circumstance $\rho^{(1)}(\mathbf{r}_1)$ is equal to

$$\rho^{(2)}(r_{01})/\rho = \rho g^{(2)}(r_{01}),$$

where $g^{(2)}$ is the previously mentioned spherically symmetric pair correlation function in the uniform fluid with density ρ . Equation (24) states for this case

$$\log g^{(2)}(r_{01}, \rho) = -\beta v(r_{01}) + \int_0^\rho d\rho' \int d\mathbf{r}_2 [g^{(2)}(r_{02}, \rho) X_\rho(\mathbf{r}_1, \mathbf{r}_2, \rho') - X(r_{12}, \rho')]. \quad (30)$$

The extra g factors in the integrands of definition (23) are now pair correlation functions $g^{(2)}(r_{0j})$. The integral Eq. (30) may be compared with a similar result derived by the usual cluster summation analysis¹⁶

$$\log g^{(2)}(r_{01}, \rho) = -\beta v(r_{01}) + E(r_{01}, \rho) + \rho \int [g^{(2)}(r_{02}, \rho) - 1] X(r_{21}, \rho) d\mathbf{r}_2, \quad (31)$$

in which E appears explicitly. Subtraction of (30) from (31) yields the desired result

$$E(r_{01}, \rho) = \int_0^\rho d\rho' \int d\mathbf{r}_2 \{ g^{(2)}(r_{02}, \rho) \cdot [X_\rho(\mathbf{r}_1, \mathbf{r}_2, \rho') - X(r_{12}, \rho)] - [X(r_{12}, \rho') - X(r_{12}, \rho)] \}. \quad (32)$$

²⁷ We suppose for the moment that the system is “contained” either by supplementary wall forces sufficiently far from \mathbf{r}_0 not to disturb the density distribution near this point, or by use of periodic boundary conditions.

Convergence of the \mathbf{r}_2 integral is ensured for fluids by the fact that both square-bracketed differences in the integrand of (32) become equal when r_{02} is large [so $g^{(2)}(r_{02})$ is unity].

Since the behavior of E near the critical point affects markedly the behavior of the system predicted on the basis of a cluster-theoretic approach,⁸ it is very desirable to know if Eq. (32), or some similar relation, is capable of giving a proper critical point theory. We shall not pursue this very difficult inquiry in this preliminary report. Equation (32) does, however, indicate the close relation of the fundamental quantity X_ρ to the highly connected clusters which undoubtedly are important in dense fluids. If the exact results derived or quoted in this section are supplemented in the regime of hypothesis B by a closure relation for X_ρ (such as the previously noted midpoint-density estimate in terms of X), there should result a powerful method for treating dense fluids, which implicitly acknowledges the relevance of high cluster connectivity. We wish therefore to suggest that a numerically practicable distribution function theory of dense fluids might more profitably rest on reasonable approximation to the ubiquitous quantity X_ρ , rather than to distribution functions themselves (as in the Kirkwood superposition approach²⁸).

Generalization of identification (29) to U 's equal to the sum of pair potentials for more than just a single fixed fluid particle obviously leads to integral equations analogous to (30) for higher order distribution functions.

IV.

We turn attention next to a relation between excess external field quantities that are the subject of this article, which may be deduced from consideration of the fluctuation in number of particles in the open system. Specifically, we shall suppose that the external field amounts only to the forces exerted on the molecules comprising the fluid by the container walls, and that the fluid is entirely homogeneous except in the vicinity of this boundary. The resulting fluctuation theorem, Eq. (51) below, is valid for both gas and liquid systems, independent of any cluster-sum convergence question which arose in the preceding sections.

This particular fluctuation theorem represents only one of several that might be exhibited. We have elected specifically to examine the case corresponding to a single-phase homogeneous fluid in contact with the vessel walls to form the relevant interface, rather than to examine the liquid-vapor interface in a gravitational field, where fluctuations at constant chemical potential (selected to maintain phase coexistence) would be of primary concern. We note in this connection that a relation between liquid-vapor interfacial density fluctuations and a generalized virial has already been

²⁸ J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).

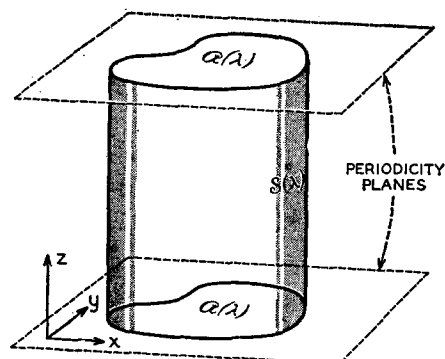


FIG. 3. The cylindrical system utilized for deduction of the fluctuation theorem in Sec. IV. The distance between the planes is λ , and the area defined by each of their intersections with the equimolar dividing surface $S(\lambda)$ is $A(\lambda)$.

exhibited in the statistical mechanical verification of the Gibbs adsorption equation.²⁹

It is possible to show by standard arguments³⁰ that even in the presence of inhomogeneities induced by external forces

$$\begin{aligned} \int [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 \\ = kT(\partial\bar{N}/\partial\mu)_T - \bar{N} \\ = \bar{N}^2 - \bar{N}^2 - \bar{N}, \end{aligned} \quad (33)$$

which represents generalization, to present circumstances, of the usual grand ensemble number fluctuation formula. In terms of a scalar displacement parameter λ and its conjugate thermodynamic force Λ , the Gibbs-Duhem equation reads

$$Nd\mu = -SdT + \lambda d\Lambda. \quad (34)$$

Consequently,

$$\bar{N} \left[\frac{\partial\mu}{\partial(\lambda/\bar{N})} \right]_T = \lambda \left[\frac{\partial\Lambda}{\partial(\lambda/\bar{N})} \right]_T,$$

or

$$(\partial\mu/\partial\bar{N})_{\lambda,T} = -(\lambda^2/\bar{N}^2)(\partial\Lambda/\partial\lambda)_{\bar{N},T}, \quad (35)$$

so that Eq. (33) becomes

$$\begin{aligned} \int [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 \\ = -kT(\bar{N}^2/\lambda^2)(\partial\Lambda/\partial\lambda)_{\bar{N},T} - \bar{N}. \end{aligned} \quad (36)$$

We next specify a useful type of system and its displacement parameter. Figure 3 illustrates schematically a nonuniform system which is presumed to be bounded laterally by short-range wall forces $U(\mathbf{r})$, and in the vertical direction (along the z axis) it is supposed that periodic boundary conditions apply. One may for

²⁹ F. P. Buff, *Advances in Chem. Ser.* No. 33 (American Chemical Society, Washington, D. C., 1961), p. 340.

³⁰ J. G. Kirkwood and F. P. Buff, *J. Chem. Phys.* **19**, 774 (1951).

the moment regard $U(\mathbf{r})$ as uniform in the z direction, so the over-all appearance of the system is a right cylinder. For typical adsorbing walls, $U(\mathbf{r})$ will have a one-dimensionally localized attractive part which, for successive positions farther into the wall, gives way to a steeply rising repulsive behavior (Fig. 4), with $U(\mathbf{r}) = +\infty$ everywhere outside the cylinder. The attractive well typically has a diameter comparable to molecular dimensions, so in virtually the entire interior of the system, $U(\mathbf{r}) = 0$. It will furthermore be supposed that the curvature of the walls is everywhere sufficiently small that the considerations below may be interpreted as applying to a planar interface, with adsorbing wall potential dependent only on normal distance to the locally flat and parallel equipotential surfaces. In particular λ will be the vertical distance between the periodicity planes. The effect of variation in λ is change in both the available volume for the molecules comprising the system, as well as the wall area on which they may be adsorbed.³¹

On account of the local pressure result in Sec. II, we may write

$$\Omega = -\lambda \cdot (\lambda^{-1}) \int \bar{p}(\mathbf{r}, \lambda) d\mathbf{r}; \quad (37)$$

the integrations are unbounded in the x and y directions,

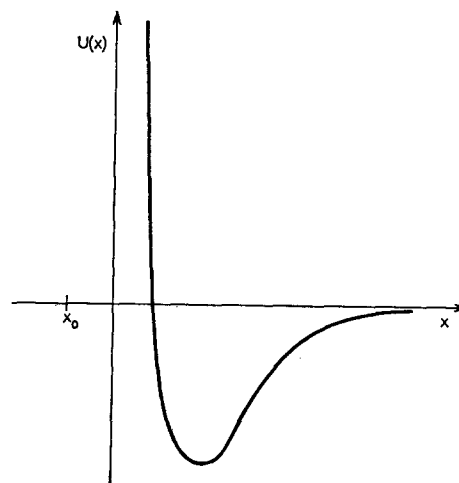


FIG. 4. Variation of the adsorbing wall potential with normal distance x measured toward the system interior. The position x_0 of the equimolar dividing surface depends both on temperature and the bulk fluid density.

³¹ Of course this choice of λ represents only one of an infinite variety of nontrivially related possibilities. The conditions on λ stated in Sec. II allow any sort of geometric distortion of the system, which will "squeeze" all particles out of the system (at constant μ and T) by the time λ goes to zero. This can be accomplished by moving periodicity boundaries inward, as has been the choice here, or by scaling the component of \mathbf{r} in $U(\mathbf{r})$ so as effectively to move the repulsive portion of this external potential inward. Another type of choice would be addition of a term (U_0 is a constant)

$$[(1-\lambda)/\lambda]U_0$$

to the original $U(\mathbf{r})$, which has the same effect as λ varies between 0 and 1.

but cover only a periodicity interval λ along the z axis. Comparison with Eq. (3) thus identifies the conjugate force Λ in a trivial manner for any choice of λ

$$\Lambda = (\lambda^{-1}) \int \bar{p}(\mathbf{r}, \lambda) d\mathbf{r}. \quad (38)$$

In order to discuss excess surface properties of this system, it is necessary to select a specific dividing surface \mathcal{S} . Surface properties may then be identified as usual by computing the difference between the actual system properties and those of a hypothetical system occupying the interior of \mathcal{S} , which has local properties everywhere in this interior equal to the bulk homogeneous fluid values. Specifically, \mathcal{S} may be taken as an equipotential surface of $U(\mathbf{r})$, and will presently be identified as the equimolar dividing surface.

The particular value of choosing the previously specified type of system arises from the fact that the grand partition function may then properly be written:

$$\exp[\beta p V(\lambda) - \beta \gamma \mathcal{S}(\lambda)], \quad (39)$$

in the asymptotic zero-curvature wall limit, as indicated by comparison of Eqs. (3) and (4), after the latter has been put in the usual form of the thermodynamic first law:

$$dE = TdS - pdV + \gamma d\mathcal{S} + \mu dN,$$

including planar surface tension work. Here, p is the pressure of the uniform hypothetical system, $V(\lambda)$ is the volume of the interior of $\mathcal{S}(\lambda)$ [which equals $\lambda \mathcal{Q}(\lambda)$, if $\mathcal{Q}(\lambda)$ is the cross-sectional area of $\mathcal{S}(\lambda)$ in any periodicity plane], and γ is the surface tension at the planar fluid-wall interface, referred to dividing surface $\mathcal{S}(\lambda)$. By subtracting an identity of type (33) for the hypothetical system from that for the actual one, we shall thus obtain a new relation involving γ .

If the x axis is normally and inwardly oriented to \mathcal{S} at some point of intersection x_0 , then this planar surface tension may be expressed in terms of the local pressure by

$$\gamma = - \int_{-\infty}^{x_0} \bar{p}(x) dx + \int_{x_0}^{+\infty} [p - \bar{p}(x)] dx. \quad (40)$$

The upper limit in the second integral has been allowed to become infinite, assuming sufficiently rapid convergence of its integrand to zero with increasing x , upon passage first to infinite system size.

We examine the derivative $(\partial \Lambda / \partial \lambda)_{\bar{N}, T}$, whose inverse occurs in Eq. (36). Comparing (37), (38), and (39), one has

$$\begin{aligned} (\partial \Lambda / \partial \lambda)_{\bar{N}, T} &= [V(\lambda) / \lambda] (\partial p / \partial \lambda)_{\bar{N}, T} - [\mathcal{S}(\lambda) / \lambda] \\ &\cdot (\partial \gamma / \partial \lambda)_{\bar{N}, T} + p \left\{ \frac{\partial [V(\lambda) / \lambda]}{\partial \lambda} \right\}_{\bar{N}, T} - \gamma \left\{ \frac{\partial [\mathcal{S}(\lambda) / \lambda]}{\partial \lambda} \right\}_{\bar{N}, T}. \end{aligned} \quad (41)$$

Varying λ at constant \bar{N} changes the bulk density, and

possibly also the number of adsorbed molecules per unit surface area. Accordingly, both $V(\lambda) / \lambda$ and $\mathcal{S}(\lambda) / \lambda$ can change slightly with λ as a result of change in position of the equimolar dividing surface \mathcal{S} . But since we shall be concerned solely with the planar interface limit, the last term in (41) may be disregarded; it provides correction only when finite wall curvature is considered important.

The major advantage of choosing \mathcal{S} to be the equimolar dividing surface is that the density ρ in the uniform hypothetical system is by definition simply

$$\rho(\lambda) = \bar{N} / V(\lambda) = \bar{N} / \lambda \mathcal{Q}(\lambda).$$

This is also the density at the center of the real system, where wall forces are unimportant. If this expression is differentiated with respect to λ at constant \bar{N} and T , one finds

$$\begin{aligned} (\partial \rho / \partial \lambda)_{\bar{N}, T} &= -\rho \{ \lambda^{-1} + [\mathcal{Q}(\lambda)]^{-1} [\partial \mathcal{Q}(\lambda) / \partial \lambda] \}_{\bar{N}, T} \\ &= -\rho \{ \lambda^{-1} + [\mathcal{Q}(\lambda)]^{-1} [\partial \mathcal{Q}(\lambda) / \partial \rho] \}_{\bar{N}, T} \\ &\quad \cdot (\partial \rho / \partial \lambda)_{\bar{N}, T}. \end{aligned} \quad (42)$$

Assuming once again the possibility of passing to infinite integral limits as in Eq. (40), the position x_0 of the equimolar dividing surface is uniquely defined by

$$0 = \int_{-\infty}^{x_0(\rho)} g(x, \rho) dx + \int_{x_0(\rho)}^{+\infty} [g(x, \rho) - 1] dx. \quad (43)$$

Taking derivatives, one obtains a length parameter l ,

$$\begin{aligned} l &= \left[\frac{\partial x_0(\rho)}{\partial \log \rho} \right]_T \\ &= \int_{-\infty}^{+\infty} \left[\frac{\partial g(x, \rho)}{\partial \log \rho} \right]_T dx, \end{aligned} \quad (44)$$

equal to the outward movement of the dividing surface for fractional changes in the homogeneous fluid bulk density. On account of the fact that the density derivative of $\mathcal{Q}(\lambda)$ occurring in (42) is trivially related to l , and to $\mathcal{S}(\lambda) / \lambda$ [the length of the perimeter of $\mathcal{Q}(\lambda)$], Eq. (42) may be transformed into the result

$$(\partial \rho / \partial \lambda)_{\bar{N}, T} = -(\rho / \lambda) \{ 1 + [l \mathcal{S}(\lambda) / V(\lambda)] \}^{-1}. \quad (45)$$

The volume $l \mathcal{S}(\lambda)$ for our system is very much smaller than the entire volume $V(\lambda)$, so that the dimensionless ratio of these quantities amounts only to a small correction in Eq. (45), which may be identified as a (planar) surface effect.

Expression (45) may next be used to rewrite Eq. (41), where the last term has been disregarded

$$\begin{aligned} (\partial \Lambda / \partial \lambda)_{\bar{N}, T} &= -(\rho / \lambda) \{ 1 + [l \mathcal{S}(\lambda) / V(\lambda)] \}^{-1} \\ &\cdot \left\{ \frac{V(\lambda)}{\lambda} \left(\frac{\partial p}{\partial \rho} \right)_T - \frac{\mathcal{S}(\lambda)}{\lambda} \left(\frac{\partial \gamma}{\partial \rho} \right)_T + p \left[\frac{\partial [V(\lambda) / \lambda]}{\partial \rho} \right]_{\bar{N}, T} \right\}. \end{aligned} \quad (46)$$

The last partial derivative is just $l\mathcal{S}(\lambda)/\lambda\rho$. Therefore,

$$\begin{aligned} (\partial\Delta/\partial\lambda)_{\bar{N},T} = & -[\rho V(\lambda)/\lambda^2](\partial p/\partial\rho)_T \\ & \cdot \{1 + [l\mathcal{S}(\lambda)/V(\lambda)]\}^{-1} \\ & \cdot \{1 + [(p/\rho) - l^{-1}(\partial\gamma/\partial\rho)_T](\partial\rho/\partial p)_T [l\mathcal{S}(\lambda)/V(\lambda)]\}. \end{aligned} \quad (47)$$

Finally, Eq. (47) permits elimination of that partial derivative from Eq. (36); retaining terms only through first order in $l\mathcal{S}(\lambda)/V(\lambda)$, one finds

$$\begin{aligned} & \int [\rho^{(2)}(\mathbf{r}_1, \mathbf{r}_2) - \rho^{(1)}(\mathbf{r}_1)\rho^{(1)}(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 \\ & = [kT\bar{N}(\partial\rho/\partial p)_T - \bar{N}] + kT\bar{N}(\partial\rho/\partial p)_T \\ & \cdot \{1 + [l^{-1}(\partial\gamma/\partial\rho)_T - (p/\rho)](\partial\rho/\partial p)_T\} [l\mathcal{S}(\lambda)/V(\lambda)]. \end{aligned} \quad (48)$$

The first bracketed difference on the right-hand side of Eq. (48) may be identified as the usual fluctuation integral over the hypothetical uniform system:

$$kT\bar{N}(\partial\rho/\partial p)_T - \bar{N} = \int_V d\mathbf{r}_1 \int d\mathbf{r}_2 [\rho^{(2)}(\mathbf{r}_{12}) - \rho^2]. \quad (49)$$

The \mathbf{r}_1 integration in (49) spans only the interior of \mathcal{S} (between the periodicity planes), whereas the \mathbf{r}_2 integration covers all space.

The isothermal compressibility of the uniform fluid is defined

$$\kappa = (1/\rho)(\partial\rho/\partial p)_T. \quad (50)$$

Therefore, if (49) is subtracted from (48), we obtain the surface fluctuation theorem in its final form, after appealing to invariance of distribution functions under translation parallel to \mathcal{S}

$$[\partial\gamma/(\partial \log\rho)]_T = (p - \kappa^{-1})l + (2\Delta^{(2)}/kT\kappa^2\rho^2). \quad (51)$$

$\Delta^{(2)}$ is the excess number of particle pairs in the system, per unit area of equimolar dividing surface, due to the inhomogeneity of the surface region:

$$\begin{aligned} 2\Delta^{(2)} = & \int_{-\infty}^{x_0} dx_1 \int d\mathbf{r}_{12} [\rho^{(2)}(x_1, \mathbf{r}_{12}) - \rho^{(1)}(x_1)\rho^{(1)}(x_2)] \\ & + \int_{x_0}^{+\infty} dx_1 \int d\mathbf{r}_{12} [\rho^{(2)}(x_1, \mathbf{r}_{12}) - \rho^{(2)}(r_{12}) \\ & - \rho^{(1)}(x_1)\rho^{(1)}(x_2) + \rho^2]. \end{aligned} \quad (52)$$

Either theorem (51) or the integral formula (40) may be regarded as alternates, for computing γ , to the usual stress tensor technique for planar interfaces with the inclusion of external forces.^{11,32} As in the stress tensor method, Eq. (51) would have to be supplemented by an interfacial superposition principle before numerical evaluation. It appears from (51) that very rapid changes in γ with respect to ρ variations can be expected both at the critical point of the uniform fluid (since $\kappa \rightarrow 0$), and at the critical points for the two-dimensional layers which may successively form at the adsorbing wall in a condensed state (since then l probably diverges).³³

In a typical measurement of gas adsorption on a suitable solid adsorbent, the length l can be estimated from the measured isotherm, and knowledge of the adsorbing surface area. If this result is combined with careful measurements of adsorption heats, γ (and hence its ρ derivative), is then measurable, at least in principle. Therefore, the only nonoperational quantity in (51) is the surface excess density of molecular pairs, $\Delta^{(2)}$. It should be emphasized, however, that the various theories of multilayer adsorption^{1,34} provide definite modelistic predictions about surface distribution of molecules, so that $\Delta^{(2)}$ is not inaccessible. Since these theories typically divide the interfacial region into a three-dimensional lattice of sites available for molecular occupation, the integral (52) would be replaced by a lattice sum. The rigorous fluctuation theorem might therefore provide a useful test for various multilayer adsorption theories.

We finally remark that although (51) was derived under the assumption of uniformity of $U(\mathbf{r})$ along the z direction, this restriction may easily be relaxed. If the lateral adsorbing wall is itself represented by an ensemble of different U 's which are macroscopically similar, but which possess microscopic inhomogeneities of molecular extent, then (51) is still valid if the molecular distribution functions defining l and $\Delta^{(2)}$ are regarded as *averages* over members of the wall ensemble, and where \mathcal{S} is an equipotential surface of the average U .

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³³ T. L. Hill, J. Phys. Chem. **59**, 1065 (1955).

³⁴ G. Delmas and D. Patterson, J. Phys. Chem. **64**, 1827 (1960).