

Statistical Thermodynamics of Nonuniform Fluids*

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We have developed a general formalism for obtaining the low-order distribution functions $n_q(\mathbf{r}_1, \dots, \mathbf{r}_q)$ and the thermodynamic parameters of nonuniform equilibrium systems where the nonuniformity is caused by a potential $U(\mathbf{r})$. Our method consists of transforming from an initial (uniform) density n_0 to the final desired density $n(\mathbf{r})$ via a functional Taylor expansion. When n_0 is chosen to be the density in the neighborhood of the \mathbf{r} 's we obtain n_q as an expansion in the gradients of the density. The expansion parameter is essentially the ratio of the microscopic correlation length to the scale of the inhomogeneities. Our analysis is most conveniently done in the grand ensemble formalism where the corresponding thermodynamic potential serves as the generating functional [with $U(\mathbf{r})$ as the variable] for the n_q . The transition from $U(\mathbf{r})$ to $n(\mathbf{r})$ as the relevant variable is accomplished via the direct correlation function which enters very naturally, relating the change in U at \mathbf{r}_2 due to a change in n at \mathbf{r}_1 . It is thus essentially the matrix inverse of the two-particle Ursell function. The recent results of Stillinger and Buff on the thermodynamic potentials for nonuniform systems follow as a special case of our analysis without any recourse to the virial expansion. Thus, they hold also in the liquid region. In a succeeding paper we apply our analysis to obtain the asymptotic behavior of the radial distribution function in a uniform system.

I. INTRODUCTION

IN a previous paper¹ we considered the form of the low-order distribution functions $n_q(\mathbf{r}_1, \dots, \mathbf{r}_q)$ in a nonuniform system represented by a canonical ensemble. We investigated there both the case of an equilibrium system, where the nonuniformity comes from the existence of an external force field, and the case where the system is in a quasi-stationary nonequilibrium state characterized by local thermodynamic variables. In the latter situation the local equilibrium canonical ensemble represents only the lowest-order approximation to the true state of affairs. In either case our principal aim was to show that the low-order distribution functions n_q obtained from the N -particle canonical ensemble by integration over $N - q$ variables were local quantities, i.e., depended only on the density and temperature in the vicinity of the region where $\mathbf{r}_1, \dots, \mathbf{r}_q$ are located. This is, of course, physically essential and intuitively "obvious."

We were able to prove this local property in reference 1 on the basis of a theorem (obtained rigorously only in the low-density limit) concerning the asymptotic form of the distribution n_{q+l} when the set of $q + l$ particles is separated into groups of q and l particles that are "far" apart,

$$n_{q+l} \rightarrow n_q n_l - \frac{1}{N^2} \frac{\partial N}{\partial \zeta} \left(\frac{N \partial n_q}{\partial N} \right) \left(\frac{N \partial n_l}{\partial N} \right), \quad (1.1)$$

where ζ is the characteristic parameter of the particle reservoir, chemical potential divided by kT , which when placed in contact with our system, would yield $N(\zeta) = N$. Using (1.1), we were able to develop some general expressions for the changes of the n_q with variations in the thermodynamic parameters which showed that they depended only on the values of these parameters within a correlation length of n_q , i.e., the asymptotic N^{-1} part disappeared in the end result. More precisely, this is the region in which the Ursell function \mathfrak{F}_q is different from zero for $N \rightarrow \infty$. We did not however carry out an explicit evaluation of these changes. This would indeed have been quite cumbersome within the canonical ensemble formalism, where N is fixed.

The purpose of this note is to carry out more explicitly, the evaluation of the n_q 's and that of the thermodynamic properties of nonuniform equilibrium systems. This will enable us to make contact with other recent work on such systems,^{2,3} and will also yield some new insights into the structure of fluids in general. For convenience, we shall use the

² F. H. Stillinger and F. P. Buff, *J. Chem. Phys.* **37**, 1 (1962).

³ E. W. Hart, *Phys. Rev.* **113**, 412 (1959); **114**, 27 (1959); T. Hill, *J. Chem. Phys.* **30**, 1521 (1959); F. P. Buff and F. H. Stillinger, *ibid.* **25**, 312 (1956). See also T. Morita and K. Hiroike, *Progr. Theoret. Phys. (Kyoto)*, **23**, 1003, (1960); C. De Dominicis, *J. Math. Phys.* **3**, 983 (1962).

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¹ J. L. Lebowitz and J. K. Percus, *Phys. Rev.* **122**, 1675 (1961).

grand ensemble formalism, where the existence of an infinite particle reservoir corresponds to making the N appearing in (1.1) effectively infinite and leads thus to true product distributions in the asymptotic region. The disappearance of the N^{-1} terms in (1.1) for an open system was proven rigorously in reference 1 in the region in which the virial expansion is valid.

II. GENERAL FORMALISM

The Hamiltonian of our system, when there are N particles present, will have the form

$$H_N = \sum_{i=1}^N p_i^2/2m + \sum_{i<j} \phi(\mathbf{r}_{ij}) + \sum_{i=1}^N U(\mathbf{r}_i), \quad (2.1)$$

where $U(\mathbf{r})$ is the external potential. We can consider either the case where U determines the spatial extent of the system or that where the system is in a periodic box of volume $\Omega = L^3$, in which case U also has to be periodic. The grand-canonical phase-space ensemble density is given by

$$\begin{aligned} \rho_N(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) &= (Z^{-1}/N!) e^{\beta\mu N - \beta H_N} \\ &= W(N) e^{-\beta H_N} / N! Q_N, \end{aligned}$$

where

$$\begin{aligned} W(N) &= e^{(\lambda + \beta\mu)N} Q_N / Z, \\ Z &= \sum_{N=0}^{\infty} Q_N e^{(\lambda + \beta\mu)N}, \end{aligned} \quad (2.2)$$

$$e^{(\lambda + \beta\mu)N} Q_N$$

$$= \frac{1}{N!} \int \exp \left[\sum_{i=1}^N \gamma(\mathbf{r}_i) - \beta \sum_{i<j} \phi(\mathbf{r}_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N$$

and

$$\begin{aligned} \beta &= (kT)^{-1}, \quad \lambda = \frac{3}{2} \ln (2\pi mkT/h^2) \\ \gamma(\mathbf{r}) &= \lambda + \beta\mu - \beta U(\mathbf{r}), \end{aligned}$$

with T the temperature, μ the chemical potential, and Z the grand canonical partition function. In a uniform system (periodic boundaries, $U = 0$), $\ln Z$ reduces to $\beta p \Omega$ where p is the pressure, differing⁴ from other definitions of the pressure (such as the average virial pressure $\beta \bar{p} = \partial \ln Z / \partial \Omega$) only by terms of order Ω^{-1} .

The lower order distribution functions f_q are defined as

$$\begin{aligned} f_q(\mathbf{r}_1, \dots, \mathbf{r}_q, \mathbf{p}_1, \dots, \mathbf{p}_q) &= \sum_{N=q}^{\infty} W(N) \frac{N!}{(N-q)!} \int \rho_N d\mathbf{r}_{q+1} \dots d\mathbf{r}_N d\mathbf{p}_{q+1} \dots d\mathbf{p}_N \\ &= \prod_{i=1}^q [(2\pi mkT)^{-3/2} e^{-\beta p_i^2/2m}] n_q(\mathbf{r}_1, \dots, \mathbf{r}_q), \end{aligned} \quad (2.3)$$

where

$$\begin{aligned} n_q &= \sum_N W(N) \frac{N!}{(N-q)!} \int \exp \left\{ -\beta \sum_{i=1}^N \left[\sum_{i<j} \phi(\mathbf{r}_{ij}) + U(\mathbf{r}_i) \right] \right\} / N! Q_N d\mathbf{r}_{q+1} \dots d\mathbf{r}_N \\ &= \sum_N W(N) n_q(\mathbf{r}_1, \dots, \mathbf{r}_q; N) \\ &= \frac{1}{Z} \sum_N \frac{1}{(N-q)!} \int \exp \left\{ \sum_{i=1}^N [\gamma(\mathbf{r}_i) - \beta \sum_{i<j} \phi(\mathbf{r}_{ij})] \right\} d\mathbf{r}_{q+1} \dots d\mathbf{r}_N. \end{aligned} \quad (2.4)$$

Here $n_q(N)$ is the q -particle configurational distribution in a canonical ensemble of systems containing N particles each.

It is seen from (2.2) and (2.4) that $\ln Z$ may be used as a generating functional for the n_q 's:

$$\delta \ln Z / \delta \gamma(\mathbf{r}_1) = n_1(\mathbf{r}_1) \equiv n(\mathbf{r}_1) \quad (2.5)$$

$$\begin{aligned} \delta n(\mathbf{r}_1) / \delta \gamma(\mathbf{r}_2) &= n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2) \\ &\quad + n(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \end{aligned} \quad (2.6)$$

$$\begin{aligned} \delta n_q(\mathbf{r}_1, \dots, \mathbf{r}_q) / \delta \gamma(\mathbf{r}) &= n_{q+1}(\mathbf{r}_1, \dots, \mathbf{r}_q, \mathbf{r}) \\ &\quad + n_q(\mathbf{r}_1, \dots, \mathbf{r}_q) \left[\sum_{i=1}^q \delta(\mathbf{r}_i - \mathbf{r}) - n(\mathbf{r}) \right]. \end{aligned} \quad (2.7)$$

Some simplification of notation is achieved if we introduce the distribution functions \hat{n}_q in which the various arguments are allowed to represent identical particles:

$$\begin{aligned} \hat{n}(\mathbf{r}) &= n(\mathbf{r}), \quad \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) + n(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2), \\ \hat{n}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= n_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + n_2(\mathbf{r}_1, \mathbf{r}_2) \delta(\mathbf{r}_2 - \mathbf{r}_3) \\ &\quad + n_2(\mathbf{r}_2, \mathbf{r}_3) \delta(\mathbf{r}_3 - \mathbf{r}_1) + n_2(\mathbf{r}_3, \mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &\quad + n(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) \delta(\mathbf{r}_2 - \mathbf{r}_3), \dots \end{aligned}$$

In terms of the \hat{n}_q 's, (2.7) assumes the form

$$\begin{aligned} \delta \hat{n}_q(\mathbf{r}_1, \dots, \mathbf{r}_q) / \delta \gamma(\mathbf{r}) &= \hat{n}_{q+1}(\mathbf{r}_1, \dots, \mathbf{r}_q, \mathbf{r}) \\ &\quad - \hat{n}_q(\mathbf{r}_1, \dots, \mathbf{r}_q) n(\mathbf{r}). \end{aligned} \quad (2.8)$$

If we define the corresponding Ursell distributions

⁴J. L. Lebowitz and J. K. Percus, Phys. Rev. 124, 1673 (1961).

$\hat{\mathcal{F}}_q$ to be the same functions of the \hat{n}_i as the \mathcal{F}_q are of the n_i :

$$\hat{\mathcal{F}}_1(\mathbf{r}_1) = \hat{n}_1(\mathbf{r}_1), \hat{\mathcal{F}}_2(\mathbf{r}_1, \mathbf{r}_2) = \hat{n}_2(\mathbf{r}_1, \mathbf{r}_2) - \hat{n}_1(\mathbf{r}_1)\hat{n}_1(\mathbf{r}_2), \dots,$$

the sequence (2.8) finally reduces to

$$\delta \hat{\mathcal{F}}_q(\mathbf{r}_1, \dots, \mathbf{r}_q) / \delta \gamma(\mathbf{r}) = \hat{\mathcal{F}}_{q+1}(\mathbf{r}_1, \dots, \mathbf{r}_q, \mathbf{r}). \quad (2.9)$$

The matrix inverse of (2.6) will play an important role in what follows. Writing it in the form

$$[n(\mathbf{r}_1)n(\mathbf{r}_2)]^{1/2} \delta \gamma(\mathbf{r}_2) / \delta n(\mathbf{r}_1) = \delta(\mathbf{r}_1 - \mathbf{r}_2) - C(\mathbf{r}_2, \mathbf{r}_1), \quad (2.10)$$

we find from the defining interrelation

$$\int (\delta n(\mathbf{r}_2) / \delta \gamma(\mathbf{r}), [\delta \gamma(\mathbf{r}) / \delta n(\mathbf{r}_1)]) d\mathbf{r} = \delta(\mathbf{r}_1 - \mathbf{r}_2) \quad (2.11)$$

that C satisfies the equation⁵

$$G(\mathbf{r}_2, \mathbf{r}_1) = C(\mathbf{r}_2, \mathbf{r}_1) + \int G(\mathbf{r}_2, \mathbf{r})C(\mathbf{r}, \mathbf{r}_1) d\mathbf{r}, \quad (2.12)$$

where

$$G(\mathbf{r}_2, \mathbf{r}_1) = [n(\mathbf{r}_1)n(\mathbf{r}_2)]^{-1/2} \mathcal{F}_2(\mathbf{r}_2, \mathbf{r}_1) = [n(\mathbf{r}_1)n(\mathbf{r}_2)]^{1/2} [g(\mathbf{r}_2, \mathbf{r}_1) - 1] \quad (2.13)$$

$$\mathcal{F}_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2).$$

The existence of the inverse (2.10) is a direct consequence of the use of a grand ensemble, for in a petit ensemble, $n(\mathbf{r})$ cannot be varied arbitrarily. It is clear from (2.12) that C is the generalization to nonuniform systems of the usual direct correlation function introduced by Ornstein and Zernike.⁶ Equations (2.10) and (2.12) may also be written in the form

$$C(\mathbf{r}_1, \mathbf{r}_2) = \left(\frac{n(\mathbf{r}_1)}{n(\mathbf{r}_2)} \right)^{1/2} \frac{\delta \ln [n(\mathbf{r}_1)e^{-\gamma(\mathbf{r}_1)}]}{\delta \ln n(\mathbf{r}_2)}, \quad (2.14)$$

$$(1 - C) = (1 + G)^{-1}, \quad (2.15)$$

the last being a matrix equation with $\mathbf{1}$ the unit matrix. The quantities G and C are always symmetric in their arguments; thus G and C are Hermitian.

III. LOCAL NATURE OF DISTRIBUTION FUNCTIONS

We shall now use the results of the previous section to examine the degree of locality of the distribution functions in a nonuniform system, independently of any assumption as to existence and rapidity of convergence of virial expansions. Our approach will be to start with a suitable uniform system and then, by altering the external potential, create the density

⁵ J. Yvon, *Suppl. Nuovo cimento* **9**, 144 (1958); J. K. Percus, *Phys. Rev. Letters* **8**, 462 (1962).

⁶ L. S. Ornstein and F. Zernike, *Proc. Acad. Sci. Amsterdam* **17**, 793 (1914).

pattern desired. The process of "turning on" an inhomogeneity in density then enables one to express parameters of a nonuniform system in terms of analogous quantities of a "nearby" uniform system. In fact, as we shall see, the omnipresence of the direct correlation function of microscopic range makes it possible to deal with very large inhomogeneities on a macroscopic level.

The effect of a finite density change $\Delta n(\mathbf{r})$ on a quantity f specified initially for $n_0(\mathbf{r})$ may be determined by a functional Taylor expansion about $f[n_0]$.⁷ For this purpose, it is convenient to visualize the density change as due to a parameter α which varies from 0 to 1:

$$n(\mathbf{r}; \alpha) = \begin{cases} n_0(\mathbf{r}) & \text{at } \alpha = 0 \\ n(\mathbf{r}) & \text{at } \alpha = 1, \end{cases} \quad (3.1)$$

since an ordinary MacLaurin expansion, including remainder term, may then be used:

$$f[\alpha] = \sum_{j=0}^{s-1} \frac{1}{j!} \left. \frac{\partial^j f(\alpha)}{\partial \alpha^j} \right|_{\alpha=0} + \int_0^1 \frac{\partial^s f(\alpha)}{\partial \alpha^s} \frac{(1-\alpha)^{s-1}}{(s-1)!} d\alpha. \quad (3.2)$$

Now employing the chain rule

$$\frac{\partial}{\partial \alpha} = \int \frac{\partial n(\mathbf{r}; \alpha)}{\partial \alpha} \frac{\delta}{\delta n(\mathbf{r}; \alpha)} d\mathbf{r}, \quad (3.3)$$

we have the desired functional expansion

$$\begin{aligned} f[n] &= f[n_0] + \int \left. \frac{\partial n(\mathbf{r}_1; \alpha)}{\partial \alpha} \right|_0 \frac{\delta f[n_0]}{\delta n_0(\mathbf{r}_1)} d\mathbf{r}_1 \\ &+ \frac{1}{2} \left[\iint \left. \frac{\partial n(\mathbf{r}_1; \alpha)}{\partial \alpha} \frac{\partial n(\mathbf{r}_2; \alpha)}{\partial \alpha} \right|_0 \right. \\ &\times \left. \frac{\delta^2 f[n_0]}{\delta n_0(\mathbf{r}_1) \delta n_0(\mathbf{r}_2)} d\mathbf{r}_1 d\mathbf{r}_2 \right. \\ &+ \left. \int \left. \frac{\partial^2 n(\mathbf{r}_1; \alpha)}{\partial \alpha^2} \right|_0 \frac{\delta f[n_0]}{\delta n_0(\mathbf{r}_1)} d\mathbf{r}_1 \right] \\ &+ \dots + \int_0^1 \frac{(1-\alpha)^{s-1}}{(s-1)!} \left[\int \dots \int \frac{\partial n(\mathbf{r}_1; \alpha)}{\partial \alpha} \dots \right. \\ &\times \left. \frac{\partial n(\mathbf{r}_s; \alpha)}{\partial \alpha} \frac{\delta^s f[n(\alpha)]}{\delta n(\mathbf{r}_1; \alpha) \dots \delta n(\mathbf{r}_s; \alpha)} d\mathbf{r}_1 \dots d\mathbf{r}_s \right. \\ &+ \dots + \left. \int \left. \frac{\partial^s n(\mathbf{r}_1; \alpha)}{\partial \alpha^s} \frac{\delta f[n(\alpha)]}{\delta n(\mathbf{r}_1; \alpha)} d\mathbf{r}_1 \right] d\alpha. \quad (3.4) \end{aligned}$$

In the special case in which we choose, as we may,

$$\begin{aligned} n(\mathbf{r}; \alpha) &= (1-\alpha)n_0(\mathbf{r}) + \alpha n(\mathbf{r}) \\ &= n_0(\mathbf{r}) + \alpha \Delta n(\mathbf{r}), \end{aligned} \quad (3.5)$$

⁷ A systematic examination of the use of functional differentiation to obtain general results applicable to nonuniform systems has been made by G. Stell (to be published).

Eq. (3.4) reduces to

$$\begin{aligned}
 f[n] &= \sum_{j=0}^{s-1} \frac{1}{j!} \int \cdots \int \Delta n(\mathbf{r}_1) \cdots \Delta n(\mathbf{r}_j) \\
 &\times \frac{\delta^j f[n_0]}{\delta n_0(\mathbf{r}_1) \cdots \delta n(\mathbf{r}_j)} d\mathbf{r}_1 \cdots d\mathbf{r}_j \\
 &+ \int_0^1 \frac{(1-\alpha)^{s-1}}{(s-1)!} \int \cdots \int \Delta n(\mathbf{r}_1) \cdots n(\mathbf{r}_s) \\
 &\times \frac{\delta^s f[n(\alpha)]}{\delta n(\mathbf{r}_1; \alpha) \cdots \delta n(\mathbf{r}_s; \alpha)} d\mathbf{r}_1 \cdots d\mathbf{r}_s d\alpha. \quad (3.6)
 \end{aligned}$$

It is to be noted that the variational derivatives which have direct significance are [see (2.5)–(2.7)] with respect to $\gamma(\mathbf{r})$, not $n(\mathbf{r})$. We must then transform appropriately:

$$\begin{aligned}
 \frac{\delta f[n]}{\delta n(\mathbf{r})} &= \int \frac{\delta f[n]}{\delta \gamma(\mathbf{r}')} \frac{\delta \gamma(\mathbf{r}')}{\delta n(\mathbf{r})} d\mathbf{r}', \\
 \frac{\delta^2 f[n]}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} &= \iint \frac{\delta^2 f[n]}{\delta \gamma(\mathbf{r}'_1) \delta \gamma(\mathbf{r}'_2)} \frac{\delta \gamma(\mathbf{r}'_1)}{\delta n(\mathbf{r}_1)} \frac{\delta \gamma(\mathbf{r}'_2)}{\delta n(\mathbf{r}_2)} d\mathbf{r}'_1 d\mathbf{r}'_2 \\
 &+ \int \frac{\delta f[n]}{\delta \gamma(\mathbf{r}')} \frac{\delta^2 \gamma(\mathbf{r}')}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} d\mathbf{r}', \cdots \quad (3.7)
 \end{aligned}$$

The successive derivatives of γ are obtained from the general matrix relation

$$D(A^{-1})_{ii} = - \sum (A^{-1})_{ik} D(A_{ki})(A^{-1})_{ii} \quad (3.8)$$

for an arbitrary first-order differential operator D . Thus,

$$\begin{aligned}
 \frac{\delta^2 \gamma(\mathbf{r}')}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} &= \int \left(\frac{\delta \gamma(\mathbf{r}'')}{\delta n(\mathbf{r}_2)} \right) \frac{\delta}{\delta \gamma(\mathbf{r}'')} \left(\frac{\delta n}{\delta \gamma} \right)^{-1}(\mathbf{r}', \mathbf{r}_1) d\mathbf{r}'' \quad (3.9)
 \end{aligned}$$

becomes

$$\begin{aligned}
 \frac{\delta^2 \gamma(\mathbf{r}')}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} &= - \int \frac{\delta \gamma(\mathbf{r}'')}{\delta n(\mathbf{r}_2)} \frac{\delta \gamma(\mathbf{r}')}{\delta n(\mathbf{r}_1)} \\
 &\times \frac{\delta^2 n(\mathbf{r}')}{\delta \gamma(\mathbf{r}'') \delta \gamma(\mathbf{r}''')} \frac{\delta \gamma(\mathbf{r}''')}{\delta n(\mathbf{r}_1)} d\mathbf{r}'_1 d\mathbf{r}'' d\mathbf{r}''', \quad (3.10)
 \end{aligned}$$

and higher derivatives are similarly found.

We may term a distribution function $n_s(\mathbf{x}_1 \cdots \mathbf{x}_s)$ in an inhomogeneous system local in character if its deviation from the value it would have in a uniform system, of density $n(\mathbf{x})$ with \mathbf{x} in the region $\mathbf{x}_1, \cdots, \mathbf{x}_s$, is of the order of a molecular dimension divided by the scale of the inhomogeneity. Let us suppose for definiteness that, having fixed the point \mathbf{x} , then throughout the system

$$|n(\mathbf{r}) - n(\mathbf{x})| \leq [|\mathbf{r} - \mathbf{x}|/L(\mathbf{x})]n(\mathbf{x}). \quad (3.11)$$

If $f[n] = n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n)$, then Eq. (3.6), by virtue of (2.7), (3.7), and (2.8), reduces for the case when (3.6) is truncated after one term,

$$\begin{aligned}
 n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n) &= n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\mathbf{x})) \\
 &+ \int_0^1 \iint \Delta n(\mathbf{r}) \left\{ n_{s+1}(\mathbf{x}_1, \cdots, \mathbf{x}_s, \mathbf{r}'; n(\alpha)) \right. \\
 &+ n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\alpha)) \left[\sum_1^s \delta(\mathbf{x}_i - \mathbf{r}') - n(\mathbf{r}') \right] \Big\} \\
 &\times [n(\mathbf{r})n(\mathbf{r}')]^{-1/2} [\delta(\mathbf{r} - \mathbf{r}')] \\
 &- C(\mathbf{r}, \mathbf{r}'; n(\alpha))] d\mathbf{r}' d\mathbf{r} d\alpha. \quad (3.12)
 \end{aligned}$$

Assuming that

$$\begin{aligned}
 \int [n(\mathbf{r})n(\mathbf{r}')]^{-1/2} |C(\mathbf{r}, \mathbf{r}'; n(\alpha))| d\mathbf{r} &\leq (K_1 - 1)/n(\mathbf{r}', \alpha), \\
 \int [n(\mathbf{r})n(\mathbf{r}')]^{-1/2} |\mathbf{r} - \mathbf{r}'| |C(\mathbf{r}, \mathbf{r}'; n(\alpha))| d\mathbf{r}/K_1 &\leq \lambda_1/n(\mathbf{r}', \alpha), \\
 \int \left| \frac{n_{s+1}(\mathbf{x}_1, \cdots, \mathbf{x}_s, \mathbf{r}'; n(\alpha))}{n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\alpha))n(\mathbf{r}'; \alpha)} - 1 \right| d\mathbf{r}' &\leq (K_2 - s)/n(\mathbf{x}), \\
 \int |\mathbf{r}' - \mathbf{x}| \left| \frac{n_{s+1}(\mathbf{x}_1, \cdots, \mathbf{x}_s, \mathbf{r}'; n(\alpha))}{n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\alpha))n(\mathbf{r}'; \alpha)} - 1 \right| d\mathbf{r}'/K_2 &\leq \lambda_2 n(\mathbf{x}) \quad (3.13)
 \end{aligned}$$

exist over the full integration range, it follows from $|\Delta n(\mathbf{r})| \leq [n(\mathbf{x})/L(\mathbf{x})](|\mathbf{r}' - \mathbf{x}| + |\mathbf{r} - \mathbf{r}'|)$ and (3.13) that

$$\begin{aligned}
 |n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n) - n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\mathbf{x}))| & \\
 &\leq \left(K_1 K_2 \frac{\lambda_1 + \lambda_2}{L(\mathbf{x})} + s K_1 \frac{R}{L(\mathbf{x})} \right) \\
 &\times \int n_s(\mathbf{x}_1, \cdots, \mathbf{x}_s; n(\alpha)) d\alpha, \quad (3.14)
 \end{aligned}$$

where \mathbf{x} is the point of smallest density in the set $\mathbf{x}_1, \cdots, \mathbf{x}_s$ and R is the diameter of the set.

Thus n_s will certainly exhibit local character in the sense described above if $C(\mathbf{r}, \mathbf{r}')$ and $n_{s+1}(\mathbf{r}, \mathbf{r}')/n_s(\mathbf{r}, \mathbf{r}') - 1$ fall off faster than $1/r^4$ as $r \rightarrow \infty$. By including further terms in (3.6), one can similarly produce a remainder term which is bounded by a higher power of a microscopic to macroscopic length. Disregarding the remainder, let us investigate the form of these terms, which are expressible in terms of parameters of a uniform system. If we apply (3.7) and (3.10) to (3.6), and

make use of (2.9), the full Taylor expansion of $f[n]$ becomes

$$\begin{aligned}
 f[n] &= f[n_0] + \int \frac{\delta f(n_0)}{\delta \gamma(\mathbf{r}')} [n_0(\mathbf{x})n_0(\mathbf{r}')]^{-1/2} \\
 &\times [\delta(\mathbf{r} - \mathbf{r}') - C_0(\mathbf{r}, \mathbf{r}')] \Delta n(\mathbf{x}) \, d\mathbf{x} \, d\mathbf{r}' \\
 &+ \frac{1}{2} \int \frac{\delta^2 f(n_0)}{\delta \gamma(\mathbf{r}'_1) \delta \gamma(\mathbf{r}'_2)} [n_0(\mathbf{x}_1)n_0(\mathbf{x}'_2)] \\
 &\times n_0(\mathbf{x}_2)n_0(\mathbf{x}'_2)]^{-1/2} [\delta(\mathbf{x}_1 - \mathbf{r}'_1) - C_0(\mathbf{x}_1, \mathbf{r}'_1)] \\
 &\times [\delta(\mathbf{x}_2 - \mathbf{r}'_2) - C_0(\mathbf{x}_2, \mathbf{r}'_2)] \\
 &\times \Delta n(\mathbf{x}_1) \Delta n(\mathbf{x}_2) \, d\mathbf{r}'_1 \, d\mathbf{r}'_2 \, d\mathbf{x}_1 \, d\mathbf{x}_2 \\
 &- \frac{1}{2} \int \frac{\delta f(n_0)}{\delta \gamma(\mathbf{r}')} \hat{\mathfrak{F}}_{30}(\mathbf{r}'_1 \mathbf{r}'' \mathbf{r}''') [n_0(\mathbf{x}_2)n_0(\mathbf{r}'')] \\
 &\times n_0(\mathbf{r}'_1)n_0(\mathbf{r}')n_0(\mathbf{x}_1)n_0(\mathbf{r}''')]^{-1/2} \\
 &\times [\delta(\mathbf{x}_2 - \mathbf{r}''') - C_0(\mathbf{x}_2, \mathbf{r}''')] [\delta(\mathbf{r}'_1 - \mathbf{r}') \\
 &- C_0(\mathbf{r}'_1, \mathbf{r}')] [\delta(\mathbf{x}_1 - \mathbf{r}''') - C_0(\mathbf{x}_1, \mathbf{r}''')] \\
 &\times \Delta n(\mathbf{x}_1) \Delta n(\mathbf{x}_2) \, d\mathbf{r}'_1 \, d\mathbf{r}'' \, d\mathbf{r}'' \, d\mathbf{r}'''' \, d\mathbf{x}_1 \, d\mathbf{x}_2 + \dots \quad (3.15)
 \end{aligned}$$

This is in essence a local decomposition. That is, $\delta^s f / \delta \gamma(\mathbf{r}_1) \dots \delta \gamma(\mathbf{r}_s)$ will, in general, vanish unless $\mathbf{r}_1, \dots, \mathbf{r}_s$ are within a microscopic correlation range of each other, and of any space points associated with f itself. The $\hat{\mathfrak{F}}$, likewise vanish asymptotically with respect to all arguments. The connecting links are always direct correlation factors $C_0(r, r')$, and since these are similarly short range (indeed the range of the internal potential, according to the P.Y. approximation⁸), the various Δn are thereby restricted to the same region. In fact, since each Δn is restricted to a predetermined region, one can absorb large spacial inhomogeneities and still utilize a Taylor expansion

$$\begin{aligned}
 \Delta n(\mathbf{r}) &= \Delta n(\mathbf{x}) + (\mathbf{r} - \mathbf{x}) \cdot \nabla (\Delta n(\mathbf{x})) \\
 &+ \frac{1}{2} (\mathbf{r} - \mathbf{x})(\mathbf{r} - \mathbf{x}) : \nabla \nabla (\Delta n(\mathbf{x})) + \dots \quad (3.16)
 \end{aligned}$$

Consider once more the distribution functions and in particular the s -body Ursell distribution $\hat{\mathfrak{F}}_s(\mathbf{x}_1, \dots, \mathbf{x}_s)$, in an inhomogeneous system. We shall again compare this to the corresponding distribution for a uniform system at constant density $n_0(\mathbf{x}) = n(\mathbf{x})$ for some point \mathbf{x} in the vicinity of $\mathbf{x}_1, \dots, \mathbf{x}_s$, which we will later choose more carefully. Now $\Delta n(\mathbf{r}) = n(\mathbf{r}) - n(\mathbf{x})$ and (3.16) becomes

$$\begin{aligned}
 \Delta n(\mathbf{r}) &= (\mathbf{r} - \mathbf{x}) \cdot \nabla n(\mathbf{x}) \\
 &+ \frac{1}{2} (\mathbf{r} - \mathbf{x})(\mathbf{r} - \mathbf{x}) : \nabla \nabla n(\mathbf{x}) + \dots \quad (3.17)
 \end{aligned}$$

Furthermore, for isotropic potentials, the "unperturbed" distributions are functions of interparticle distance alone. Hence

$$\begin{aligned}
 &\int [\delta(\mathbf{r} - \mathbf{r}') - C_0(\mathbf{r}, \mathbf{r}')] (\mathbf{r} - \mathbf{x}) \, d\mathbf{r} \\
 &= \int [\delta(\mathbf{r}) - C_0(\mathbf{r})] (\mathbf{r} + \mathbf{r}' - \mathbf{x}) \, d\mathbf{r} \\
 &= (\mathbf{r}' - \mathbf{x}) \int [\delta(\mathbf{r}) - C_0(\mathbf{r})] \, d\mathbf{r} \\
 &= -(\mathbf{x} - \mathbf{r}') \beta / n_0 \chi_0 \quad (3.18)
 \end{aligned}$$

where χ is the isothermal compressibility [see Eq. (4.17)]. In a similar fashion

$$\begin{aligned}
 &\int [\delta(\mathbf{r} - \mathbf{r}') - C_0(\mathbf{r}, \mathbf{r}')] (\mathbf{r} - \mathbf{x})(\mathbf{r} - \mathbf{x}) \, d\mathbf{r} \\
 &= (\mathbf{x} - \mathbf{r}')(\mathbf{x} - \mathbf{r}') \beta / n_0 \chi_0 - \frac{1}{3} (\Lambda^2 \beta / n_0 \chi_0) \mathbf{1}
 \end{aligned}$$

where

$$\begin{aligned}
 \Lambda^2 &= \int r^2 C_0(\mathbf{r}) \, d\mathbf{r} / \int [\delta(\mathbf{r}) - C_0(\mathbf{r})] \, d\mathbf{r} \\
 &= \frac{\int r^2 G_0(\mathbf{r}) \, d\mathbf{r}}{\int [\delta(\mathbf{r}) + G_0(\mathbf{r})] \, d\mathbf{r}} \quad (3.19)
 \end{aligned}$$

Combining (3.15)–(3.19), we obtain in general

$$\begin{aligned}
 f[n(\mathbf{r})] &= f_0[n(\mathbf{x})] \\
 &+ \frac{\beta}{n_0^2 \chi_0} \int \frac{\delta f_0}{\delta \gamma(\mathbf{r}')} \{ [-(\mathbf{x} - \mathbf{r}') \cdot \nabla n(\mathbf{x})] \\
 &+ \frac{1}{2} [(\mathbf{x} - \mathbf{r}')(\mathbf{x} - \mathbf{r}') - \frac{1}{3} \Lambda^2 \mathbf{1}] \cdot \nabla \nabla n(\mathbf{x}) \} \, d\mathbf{r}' \\
 &+ \frac{1}{2} \left(\frac{\beta}{n_0^2 \chi_0} \right)^2 \iint \frac{\delta^2 f_0}{\delta \gamma(\mathbf{r}'_1) \delta \gamma(\mathbf{r}'_2)} \\
 &\times (\mathbf{x} - \mathbf{r}'_1)(\mathbf{x} - \mathbf{r}'_2) \, d\mathbf{r}'_1 \, d\mathbf{r}'_2 : \nabla n(\mathbf{x}) \nabla n(\mathbf{x}) \\
 &- \frac{1}{2} \frac{\beta^2}{n_0^3 \chi_0^2} \iint \frac{\delta f_0}{\delta \gamma(\mathbf{r}')} \hat{\mathfrak{F}}_{30}(\mathbf{r}'_1 \mathbf{r}'_2 \mathbf{r}'_3) \\
 &\times [\delta(\mathbf{r}'_1) - C_0(\mathbf{r}'_1)] (\mathbf{x} - \mathbf{r}' - \mathbf{r}'_2) \\
 &\times (\mathbf{x} - \mathbf{r}' - \mathbf{r}'_3) \, d\mathbf{r}' \dots d\mathbf{r}'_3 : \nabla n(\mathbf{x}) \nabla n(\mathbf{x}) + \dots, \quad (3.20)
 \end{aligned}$$

where throughout subscript zero indicates that the quantities are those for a uniform system at density $n(\mathbf{x})$. According to (2.9), the modified Ursell distributions are readily amenable to expansion in locally uniform parameters. We have from (3.20),

⁸ J. K. Percus and J. G. Yeivick, Phys. Rev. **110**, 1 (1958); referred to as P. Y.; J. Lebowitz, J. Percus and I. Zucker have shown recently that for a one dimensional gas of hard spheres $C(r)$ vanishes outside the hard sphere diameter (to be published). G. Stell has shown that $C(r) = 0$ outside the hard sphere diameter implies the P. Y. equation for any dimension (to be published).

choosing $\mathbf{x} = \sum_i \mathbf{x}_i/s$ and observing the structure of the "unperturbed" distributions

$$\begin{aligned} \hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2) &= \hat{\mathfrak{F}}_{20}(\mathbf{x}_1, \mathbf{x}_2) \\ &+ \left\{ \frac{1}{2} \left(\frac{\beta}{n_0 \chi_0} \right) \int \hat{\mathfrak{F}}_{30}(\mathbf{x}_1 \mathbf{x}_2, \mathbf{r}') \right. \\ &\times [(\mathbf{x} - \mathbf{r}')(\mathbf{x} - \mathbf{r}') + \frac{1}{3} \Lambda^2 \mathbf{1}] d\mathbf{r}' : \nabla \nabla n(\mathbf{x}) \\ &+ \frac{1}{2} \left(\frac{\beta}{n_0 \chi_0} \right)^2 \int \hat{\mathfrak{F}}_{40}(\mathbf{x}_1 \mathbf{x}_2 \mathbf{r}_1 \mathbf{r}_2)(\mathbf{x} - \mathbf{r}_1) \\ &\times (\mathbf{x} - \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 : \nabla n(\mathbf{x}) \nabla n(\mathbf{x}) \\ &- \frac{1}{2} \left(\frac{\beta}{n_0 \chi_0} \right)^2 \int \hat{\mathfrak{F}}_{30}(\mathbf{x}_1 \mathbf{x}_2 \mathbf{r}) \\ &\times \hat{\mathfrak{F}}_{30}(\mathbf{r}_1 \mathbf{r}_2 \mathbf{r}_3) [\delta(\mathbf{r}_1) - C_0(\mathbf{r}_1)] (\mathbf{x} - \mathbf{r}_1)(\mathbf{x} - \mathbf{r}) \\ &\left. \times d\mathbf{r} \cdots d\mathbf{r}_3 : \nabla n(\mathbf{x}) \nabla n(\mathbf{x}) + \cdots \right\}, n_0 \end{aligned} \quad (3.21)$$

while $\hat{\mathfrak{F}}_s$, for $s > 2$, contains a first-order term as well.

IV. THERMODYNAMIC POTENTIALS

We can also use the results of Sec. II to obtain explicit expressions for the various thermodynamic potentials in nonuniform systems. The expressions are generalizations of those found by Stillinger and Buff.² For comparison of notation, the quantity

$$X(\mathbf{r}_1, \mathbf{r}_2) \equiv C(\mathbf{r}_1, \mathbf{r}_2)/[n(\mathbf{r}_1)n(\mathbf{r}_2)]^{1/2}, \quad (4.1)$$

of Stillinger and Buff, will be employed.

Let us recall the interrelations between the commonly used potentials in a grand canonical ensemble. By virtue of its role as generating function, the grand canonical potential

$$\Xi = \frac{1}{\beta} \ln Z \quad (4.2)$$

is basic to our considerations. A generalized Legendre transformation with respect to $\gamma(\mathbf{r})$ suffices to introduce the remaining potentials. From (2.5), coupled with the expression $G = N\mu = \int \mu n(\mathbf{r}) d\mathbf{r}$ for the Gibbs free energy, we have

$$\begin{aligned} \int \gamma(\mathbf{r}) \delta \Xi / \delta \gamma(\mathbf{r}) d\mathbf{r} \\ = G - \int U(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \lambda N / \beta. \end{aligned} \quad (4.3)$$

The Helmholtz free energy $F = G - \Xi$ then results from

$$\begin{aligned} \int \gamma(\mathbf{r}) \delta \Xi / \delta \gamma(\mathbf{r}) d\mathbf{r} - \Xi \\ = F - \int U(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \lambda N / \beta. \end{aligned} \quad (4.4)$$

It is of course a consequence of (4.4) that

$$[\delta / \delta n(\mathbf{r})] \left[F - \int U(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \lambda N / \beta \right] = \gamma(\mathbf{r}) / \beta \quad (4.5)$$

so that F too serves as a generating function.

Now we would like to demonstrate the local nature of the thermodynamic potentials, i.e., the extent to which local energy densities can be defined in an inhomogeneous system. Let us first consider Ξ , and integrate the infinitesimal change under a density variation, $\delta \Xi = \int [\delta \Xi / \delta n(\mathbf{r})] \delta n(\mathbf{r}) d\mathbf{r}$, to obtain the $s = 1$ case of (3.4), with (3.7) applied,

$$\begin{aligned} \Xi[n] &= \Xi[n_0] \\ &+ \int_0^1 \iint \frac{\partial n(\mathbf{r}; \alpha)}{\partial \alpha} \frac{\delta \Xi[n(\alpha)]}{\delta \gamma(\mathbf{r}'; \alpha)} \frac{\delta \gamma(\mathbf{r}'; \alpha)}{\delta n(\mathbf{r}; \alpha)} d\mathbf{r} d\mathbf{r}' d\alpha. \end{aligned} \quad (4.6)$$

From (2.5) and (2.10) with (4.1), it follows that

$$\begin{aligned} \beta \Xi[n] &= \beta \Xi[n_0] + (N - N_0) \\ &- \int_0^1 \iint n(\mathbf{r}'; \alpha) \frac{\partial n(\mathbf{r}; \alpha)}{\partial \alpha} X(\mathbf{r}\mathbf{r}'; \alpha) d\mathbf{r} d\mathbf{r}' d\alpha. \end{aligned} \quad (4.7)$$

In particular, if the density is turned on from $n_0 = 0$, in which case $\beta \Xi[n_0] = N_0$, we may write

$$\begin{aligned} \beta \Xi &= \int \left[n(\mathbf{r}) - \int_0^1 \int n(\mathbf{r}; \alpha) \frac{\partial n(\mathbf{r}'; \alpha)}{\partial \alpha} \right. \\ &\quad \left. \times X(\mathbf{r}\mathbf{r}'; \alpha) d\mathbf{r}' d\alpha \right] d\mathbf{r} \\ &= \int \hat{p}(\mathbf{r}) d\mathbf{r}. \end{aligned} \quad (4.8)$$

Here $\hat{p}(\mathbf{r})$ is a fictitious pressure which coincides with the thermodynamic pressure in a uniform system (which has been turned on uniformly). Clearly however, $\hat{p}(\mathbf{r})$ as here defined depends upon the exact process, represented by α , which has been used to get from $n_0 = 0$ to $n(\mathbf{r})$. In the special case $n(\mathbf{r}; \alpha) = \alpha n(\mathbf{r})$, Eq. (4.8) becomes identical with Eq. (25) of Stillinger and Buff. If $X(\mathbf{r}\mathbf{r}'; \alpha)$ remains short range throughout the transformation from n_0 to $n(\mathbf{r})$, then $\hat{p}(\mathbf{r})$ depends only upon $n(\mathbf{r}')$ in the vicinity of $\mathbf{r}' = \mathbf{r}$ and thus $\hat{p}(\mathbf{r})$ is a valid energy density; this may prohibit thermodynamic transitions during the "turning on" and hence restrict the locality property to gases.

Equations (26) and (27) of Stillinger and Buff, which express the Gibbs and Helmholtz free energies as volume integrals involving X , may be derived in a similar fashion. In Eq. (4.3), we have already made use of the fact that, from $\beta G = \int n(\mathbf{r}) \beta \mu d\mathbf{r}$, one has

$$\beta G = \int n(\mathbf{r}) \gamma(\mathbf{r}) d\mathbf{r} + \int [\beta U(\mathbf{r}) - \lambda] n(\mathbf{r}) d\mathbf{r}. \quad (4.9)$$

To obtain the form of (4.8), $\gamma(\mathbf{r})$ is then expanded as well. It is only necessary to observe that $n_0 = 0$ may be achieved by increasing the external potential without bound so that all particles are squeezed back into the reservoir. Then, it is easy to see, from (2.4), that $\gamma(\mathbf{r}) - \ln n(\mathbf{r})$ approaches zero. Hence, precisely in the fashion of (4.6) to (4.8), we find

$$\gamma(\mathbf{r}) - \ln n(\mathbf{r}) = - \int_0^1 \int \frac{\partial n(\mathbf{r}'; \alpha)}{\partial \alpha} X(\mathbf{r}\mathbf{r}', \alpha) d\mathbf{r}' d\alpha \quad (4.10)$$

or

$$\beta G = \int n(\mathbf{r})[\beta U(\mathbf{r}) + \ln n(\mathbf{r}) - \lambda] - \int_0^1 \int n(\mathbf{r}) \frac{\partial n(\mathbf{r}'; \alpha)}{\partial \alpha} X(\mathbf{r}\mathbf{r}'; \alpha) d\mathbf{r}' d\alpha d\mathbf{r}. \quad (4.11)$$

From $F = G - \Xi$, then

$$\beta F = \int \left\{ n(\mathbf{r})[\beta U(\mathbf{r}) + \ln n(\mathbf{r}) - \lambda] - \int_0^1 \int (n(\mathbf{r}) - n(\mathbf{r}; \alpha)) \frac{\partial n(\mathbf{r}'; \alpha)}{\partial \alpha} \times X(\mathbf{r}\mathbf{r}'; \alpha) d\mathbf{r}' d\alpha \right\} d\mathbf{r}. \quad (4.12)$$

The specialization $n(\mathbf{r}; \alpha) = \alpha n(\mathbf{r})$ again recovers the results of Stillinger and Buff.

One would now like to expand the presumably local energy densities in terms of the local particle density and its derivatives, as in (3.21). The lack of uniqueness suggests conceptual difficulties, and this is reinforced by the fact that in expanding a total energy, there is no "neighborhood" uniform density from which one can develop the actual density. However, the expression (4.9) is itself a unique decomposition of the Gibbs free energy, with energy density

$$n(\mathbf{r})\mu = \beta^{-1}[n(\mathbf{r})\gamma(\mathbf{r}) + n(\mathbf{r})(\beta U(\mathbf{r}) - \lambda)]. \quad (4.13)$$

If $\gamma(\mathbf{r})$ is then expanded according to (3.20) about its value at uniform density $n(\mathbf{r})$, we readily obtain

$$\beta\mu = \beta U(\mathbf{r}) + \beta\mu_0[n(\mathbf{r})] - \frac{1}{6}(\Lambda^2\beta/n^2\chi_0)\nabla^2 n(\mathbf{r}) - \frac{1}{6}l^2(\beta/n^2\chi_0)^2[\nabla \cdot n(\mathbf{r})^2] + \dots, \quad (4.14)$$

where Λ^2 has been defined in Eq. (3.19) and

$$l^2 = n \int \hat{\mathcal{F}}_{30}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)[\delta(\mathbf{r}_1) - C_0(\mathbf{r}_1)]_{\mathbf{r}_2 \cdot \mathbf{r}_3} d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (4.15)$$

The quantities with subscript zero refer, as in Sec.

III, to uniform systems at density $n(\mathbf{r})$, and thus Λ^2 and l^2 are also functions of $n(\mathbf{r})$. Equation (4.15), which defines the Gibbs free energy per particle in a nonuniform system as a "local functional" of the particle density, differs from the other free energy density expressions of this section in that it does not depend explicitly on the "path" along which $n(\mathbf{r})$ has been built up. We have tried to find similar path independent expressions for the other free energy densities but have not succeeded so far.

Equation (4.15) may also be thought of as determining the density $n(\mathbf{r})$ for a system with a chemical potential μ , which is a constant independent of \mathbf{r} , subject to an external field $U(\mathbf{r})$. When the external field causes only slight inhomogeneities in the fluid, the gradient terms may be neglected to obtain

$$\mu \approx U(\mathbf{r}) + \mu_0(n(\mathbf{r})). \quad (4.16)$$

This equation will have a unique solution for $\mu(\mathbf{r})$, which may be but slightly inhomogeneous, only when one is not near a phase transition. Equation (4.16) will also be valid generally for a dilute gas where $\mu_0(n) \propto \ln n$, since the remaining terms in (4.14) vanish as $n \rightarrow 0$.

Finally, we shall make some remarks concerning another thermodynamic parameter, the isothermal compressibility. For a uniform system, with a constant change δn due to a constant change $\delta\gamma$, we have

$$\delta\Xi = \delta n \int [\delta\Xi/\delta\gamma(\mathbf{r})][\delta\gamma(\mathbf{r})/\delta n(\mathbf{r}')] d\mathbf{r} d\mathbf{r}',$$

yielding, as in (4.7),

$$\partial(\beta p\Omega)/\partial n = \Omega - n \int X(\mathbf{r} - \mathbf{r}') d\mathbf{r} d\mathbf{r}',$$

so that

$$\chi_0^{-1} = n \partial p/\partial n = nkT \left[1 - n \int X(\mathbf{r}) d\mathbf{r} \right]. \quad (4.17)$$

By virtue of the relation

$$\int [g(\mathbf{r}) - 1] d\mathbf{r} = \left[\int X(\mathbf{r}) d\mathbf{r} \right] \left\{ 1 + n \int [g(\mathbf{r}) - 1] d\mathbf{r} \right\}, \quad (4.18)$$

where

$$g(\mathbf{r}_1 - \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2)/n^2,$$

obtained by integrating Eq. (2.13), (4.17) is identical with the well-known Ornstein-Zernike compressibility expression. Equation (4.18) is a special case of a simple important relationship in uniform systems. Since G and C then depend only upon the difference of their arguments, they are diagonal in

Fourier transform space k , so that (2.12) implies

$$C(\mathbf{k}) = G(\mathbf{k})/[1 + G(\mathbf{k})]. \quad (4.19)$$

Analogous relations for nonuniform systems may be obtained by multiplying (2.12) by $[n(\mathbf{r}_1)n(\mathbf{r}_2)]^{1/2}$ and integrating with respect to \mathbf{r}_2 :

$$\begin{aligned} \int \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 &= \int C(\mathbf{r}_1, \mathbf{r}_2)[n(\mathbf{r}_1)n(\mathbf{r}_2)]^{1/2} \\ &\times \left[1 + n^{-1}(\mathbf{r}_2) \int \mathfrak{F}_2(\mathbf{r}_2, \mathbf{r}) d\mathbf{r} \right] d\mathbf{r}_2 \\ &= n(\mathbf{r}_1) \int X(\mathbf{r}_1, \mathbf{r}_2) \left[n(\mathbf{r}_2) \right. \\ &\left. + \int \mathfrak{F}_2(\mathbf{r}_2, \mathbf{r}) d\mathbf{r} \right] d\mathbf{r}_2. \end{aligned} \quad (4.20)$$

Now it follows from the definition of n_a , (2.4), that

$$\begin{aligned} \int [n_{a+1}(\mathbf{r}_1, \dots, \mathbf{r}_{a+1}) - n_a(\mathbf{r}_1, \dots, \mathbf{r}_a)n(\mathbf{r}_{a+1})] d\mathbf{r}_{a+1} \\ = \sum W(N)[Nn_a(N) - \langle N \rangle n_a(N)] - qn_a \\ = kT \partial n_a / \partial \mu - qn_a. \end{aligned} \quad (4.21)$$

In particular, therefore,

$$\int \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 = kT \partial n(\mathbf{r}_1) / \partial \mu - n(\mathbf{r}_1). \quad (4.22)$$

Combining (4.22) and (4.20) yields

$$\frac{\partial n(\mathbf{r}_1)}{\partial \beta \mu} = n(\mathbf{r}_1) \left\{ 1 + \int X(\mathbf{r}_1, \mathbf{r}_2) \frac{\partial n(\mathbf{r}_2)}{\partial \beta \mu} d\mathbf{r}_2 \right\}. \quad (4.23)$$

Equation (4.23) reduces to (4.17) for a uniform system when use is made of the relation

$$dp/dn = n d\mu/dn. \quad (4.24)$$

V. CONCLUSION

The general formalism developed here, which is summarized in Eq. (3.15), is suitable for application to many specific problems. We have used (3.15)⁹ with $f[n] = \gamma(\mathbf{r})$ and an external potential $U(\mathbf{r})$ caused by keeping one of the fluid molecules fixed at the origin to investigate the asymptotic form of $g(r)$ in a uniform system. This is compared with the Ornstein-Zernike results obtainable from a truncation of (4.14). We also plan to apply our formalism to obtain an expression for the surface tension. This will be related to finding 'path independent' expressions for the other free energy densities (besides the Gibbs). The latter would also yield an expression for the entropy density which might be of use also for nonequilibrium systems.

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⁹ J. L. Lebowitz and J. K. Percus "Asymptotic Behavior of the Radial Distribution Function" (to be published in J. Math. Phys., February 1963).