Long-Range Correlations in a Closed System with Applications to Nonuniform Fluids*

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We investigate the corrections to the representation of the joint distribution of $q+l$ particles, n_{q+l}, by the product $n_q n_l$ for large separation between the sets of q and l particles. For a system in which there exists a "finite correlation length," we find explicitly the $1/N$ correction term to the simple product, where N is the number of particles in our system. When $q+l$ is equal to two, this expression reduces to that familiar from the Ornstein-Zernike relations for scattering of light from a fluid. In a uniform gas, our derivation also yields the explicit $1/N$ dependence of equilibrium distributions. Our result on the asymptotic form is then used to determine the low-order distribution functions for an equilibrium system of varying density, as well as for a nonequilibrium system represented by a local-equilibrium ensemble. These distribution functions are shown to be governed by the temperature and density in the vicinity of the molecules considered. We find as expected that the two-body distribution function coincides, to within quadratic terms in the gradients, with its equilibrium value for a uniform system at the temperature and density of the midpoint. For the higher-order distributions, correction terms linear in the gradients are found.

1. INTRODUCTION

ONE of the fundamental concepts of macroscopic physics is that of a homogeneous system. The state of such a system is completely described by a set of intensive parameters which make no reference at all to the size or shape of the system, and by the total number of particles, N (unless otherwise specified, we deal with a one-component fluid). In actual systems, there are always inhomogeneities due to boundaries and to gravitational body forces. For sufficiently large systems, however, the boundary inhomogeneities, being confined to a region very close to the surface, i.e., involving distances comparable to the range of intermolecular forces, may be neglected when considering bulk properties of the system (or may be investigated explicitly by changing the boundaries). The inhomogeneities due to gravity (or other body forces) are usually very small over molecular distances and are treated by considering the fluid as made up of homogeneous parts with differing intensive parameters. One of the purposes of the present paper is to investigate and find from the point of view of statistical mechanics a justification of this procedure. We consider both the case of density variations alone, where we may have a true equilibrium system, and the case of temperature and velocity variations as well, where the system is to zero order in a state of local equilibrium.

In order to carry out this investigation, we first establish some results concerning the form of the joint distribution $n_{q+l}(\mathbf{r}_1,\cdots,\mathbf{r}_{q+l})$ of $q+l$ particles in equilibrium, when the set of q particles is "very far" from the set of l particles. The distribution n_{q+l} approaches the product of the distributions n_q and n_l plus a correction term. It is the form, Eq. (2.22), of this correction term which we find here under certain conditions. It turns out that this correction is related to the integral over all space for the Ursell functions in an infinite system. In the course of the derivation, we also find the explicit $1/N$ dependence of the low-order distributions for a completely uniform system, i.e., one confined to a box with periodic boundary conditions. This case was also studied by Oppenheim and Mazur[1] who, using a virial expansion and making essentially the same physical assumptions as we do, find a density expansion for the coefficients of the powers of $(1/N)$ in the distributions of a uniform system. It is possible to show that their density expansion may be summed to yield our result.

The general correction terms to the pair distribution function $n_2(\mathbf{r}_1,\mathbf{r}_2)$ when $|\mathbf{r}_1-\mathbf{r}_2| \rightarrow \infty$ have previously been investigated. When both $\mathbf{r}_1$ and $\mathbf{r}_2$ are in the interior of a fluid, the asymptotic form of n_2 is related indirectly (through normalization, see, e.g., Appendix B) to the scattering cross section of visible light (of wavelength long compared to the length of molecular correlations) by fluids found by Ornstein and Zernike.[2] When the dependence of the one-particle density $n(\mathbf{r})$ on $\mathbf{r}$ is neglected, and some further assumptions are made (implicitly) which will later become clear, then[2] through terms of relative order $1/N$,

$$n_2(r_{12}) \equiv n^2 g(r_{12}) \xrightarrow[r_{12}\to\infty]{} n^2[1-nkT\chi/N]. \quad (1.1)$$

[1] I. Oppenheim and P. Mazur, Physica 23, 197 (1957).
[2] L. S. Ornstein and F. Zernike, Proc. Amsterdam Acad. Sci. 17, 793 (1914). See also T. Hill, *Statistical Mechanics* (McGraw-Hill Book Company, Inc., New York, 1956), Appendix 7.

Here n is the average density N/V, χ is the isothermal compressibility

$$\chi \equiv \frac{1}{n}\frac{\partial n}{\partial p}\bigg|_T, \qquad (1.2)$$

and p is the pressure. Recently, one of us[3] also investigated by a very different method (based on a new virial theorem for total momentum fluctuations) the rather special case of the asymptotic form of $n_2(\mathbf{r}_1,\mathbf{r}_2)$ when $\mathbf{r}_1$ is adjacent to a rigid wall which forms the boundary of the fluid and $\mathbf{r}_2$ is far in the interior. It was found there that, again through order $1/N$,

$$n_2(\mathbf{r}_1,\mathbf{r}_2)\xrightarrow[r_{12}\to\infty]{}n_w n\left(1-\frac{1}{N}\frac{n}{n_w}\right), \qquad (1.3)$$

where

$$n_w = p/kT = n(\mathbf{r}_1) \qquad (1.4)$$

was shown to be the value of the density at a rigid wall. Equations (1.1) and (1.3) turn out to be special cases of Eq. (2.22) derived in this paper. Another consequence of Eq. (2.22) is the vanishing of $1/N$ correction terms to all distributions at $T=0$. This was conjectured by Feynman and Cohen.[4] It is here seen to rest upon our fundamental hypothesis of finite correlation length.

The basic assumption which is made implicitly in the derivation of (1.1) and in reference 1, and was explicitly made in reference 3, may be stated loosely as the absence of long-range correlations in a fluid. A rather stringent formulation of this assumption, which in one form or another is universally accepted in the theory of fluids, states[5,6] that if the fluid is disturbed somehow in a limited region of space of volume ω, then properties of parts of the fluid sufficiently far away from ω (the effective unit of length being the range of molecular forces) will be affected only to the extent of $O(\omega/V)$. Further, the effect of the disturbance is supposed to approach its asymptotic value exponentially fast. (The additional assumption of exponential approach is not necessary for many applications. It is usually sufficient that the approach go as some power of the inverse distance from the location of the disturbance. What does appear necessary to assume is the absence of fluctuating behavior extending over the whole container.) It is clear that the assumption of no long-range correlation can be made precise only in the limit of the volume V becoming infinite, the density remaining constant. It is also clear unfortunately that a proof of this central hypothesis would be extremely .difficult. Since this hypothesis is believed violated in the solid state, any proof of it would give a criterion for phase transitions. There is however an ample

experimental and intuitive basis for this characterization of the fluid state; we shall accept it here and use it in our proofs in this paper, leaving a more formal discussion to Appendix A.

We give two derivations of our general result, a thermodynamic one is in Sec. 2, and a statistical one based in part on the virial expansion, and thus presumably valid only for gases, in Sec. 3. The application of our result to nonuniform systems is presented in Sec. 4. In Appendix B, we extend the result on asymptotic expressions to mixtures, and also consider light scattering from mixtures. Appendix C contains a formulation of our main result in terms of Ursell functions, and Appendix D contains a further self-consistent confirmation of this result.

2. THERMODYNAMIC DERIVATION

In order to make our arguments concrete, we shall consider explicitly the asymptotic value of the pair density $n_2(\mathbf{r}_1,\mathbf{r}_2)$. Our argument, however, will be of such a form that extension of the results to the other distributions will be immediate. From its definition, n_2 is symmetric in $\mathbf{r}_1$ and $\mathbf{r}_2$. When $n_2(\mathbf{r}_1,\mathbf{r}_2)$ is integrated over the whole pair space, each pair is counted twice, thus yielding the normalization

$$\int\int n_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2 = N(N-1), \qquad (2.1)$$

where N is the number of particles and the integration is over the system volume V. [Since $n_2(\mathbf{r}_1,\mathbf{r}_2)$ is zero whenever $\mathbf{r}_1$ or $\mathbf{r}_2$ is outside V, the integration can be extended over all space, which is indeed necessary when there is no well-defined volume V.]

The assumption of a finite correlation length implies, for r_{12} very large, that

$$n_2(\mathbf{r}_1,\mathbf{r}_2)\to n(\mathbf{r}_1)n(\mathbf{r}_2)\left\{1-\frac{b}{N}[1+o(1)]\right\}, \qquad (2.2)$$

where we use the notation $A=B+o(1)$ to mean that $\lim_{N\to\infty}(A-B)=0$, and b is a number, independent of N, which will be determined later. To show this, we first write Eq. (2.2) in a form which exhibits more transparently its relation to the correlation length. Consider the conditional number density,

$$w(\mathbf{r}_2|\mathbf{r}_1)=n_2(\mathbf{r}_2,\mathbf{r}_1)/n(\mathbf{r}_1), \qquad (2.3)$$

for particles at $\mathbf{r}_2$ when it is known that there is a particle at $\mathbf{r}_1$. Equation (2.2) may then be written as

$$w(\mathbf{r}_2|\mathbf{r}_1)\to n(\mathbf{r}_2)[1-b/N+\cdots]. \qquad (2.4)$$

Now in a classical system in equilibrium, the presence of a particle at $\mathbf{r}_1$ does two things: (1) It leaves only $N-1$ particles with unspecified positions, and (2) it introduces an effective one-particle potential $\phi(\mathbf{r}_{j1})$ for the jth particle [here $\phi(\mathbf{r})$ is the assumed potential between any two molecules]. The conditional density

[3] J. L. Lebowitz, Phys. Fluids **3**, 64 (1960).
[4] R. P. Feynman and M. Cohen, Phys. Rev. **102**, 1189 (1956).
[5] O. Penrose and L. Onsager, Phys. Rev. **104**, 576 (1956).
[6] J. E. Mayer and E. Montroll, J. Chem. Phys. **9**, 2 (1941).

$w(\mathbf{r}_2|\mathbf{r}_1)$ is therefore identical with the ordinary density in a system of $N-1$ particles with this extra perturbing potential. Hence for distances large compared to λ, the range of ϕ, $w(\mathbf{r}_2|\mathbf{r}_1)$ should be equal to the density at $\mathbf{r}_2$ in a fluid consisting of $N-1$ particles, plus a term $O(\lambda^3/V)$. Since the difference in the density at $\mathbf{r}_2$ between a fluid consisting of N particles and one of $N-1$ particles is again $O(1/N)$, we are led to (2.4). For the special case of an ideal gas, $\phi=0$, and we find immediately that

$$w(\mathbf{r}_2|\mathbf{r}_1)=[(N-1)/N]n(\mathbf{r}_2)=n(\mathbf{r}_2)[1-1/N]. \quad (2.5)$$

From its definition, we of course always have

$$\int w(\mathbf{r}_2|\mathbf{r}_1)d\mathbf{r}_2=N-1. \quad (2.6)$$

For a real fluid, the added "external" potential $\phi(\mathbf{r}_{j1})$ produces a change in density in the vicinity of $\mathbf{r}_1$ with the result that the effective number of particles whose position is unspecified (which determines w_2 far away from $\mathbf{r}_1$) differs from $N-1$, and (2.5) is replaced by (2.4). We can express this idea more clearly in the following way. Let us divide the volume V into two macroscopic parts V_A and V_B, $V_A+V_B=V$. The part V_A contains the point $\mathbf{r}_1$, while all points $\mathbf{r}_2$ in V_B are sufficiently far from $\mathbf{r}_1$ that n_2 may be given its asymptotic value. The average number of particles normally in V_A and V_B will be designated by $\bar{N}_A$ and $\bar{N}_B$, where $\bar{N}_A$ and $\bar{N}_B$ are regarded here as both of order N. Now for any particular partition of the N particles into N_A in V_A and N_B in V_B, where

$$N_B \equiv N-N_A, \quad (2.7)$$

we may write

$$n_2(\mathbf{r}_1,\mathbf{r}_2|N_A,N_B)=n(\mathbf{r}_1|\mathbf{r}_2,N_A,N_B)n(\mathbf{r}_2|N_A,N_B). \quad (2.8)$$

Here $n(\mathbf{r}_1|\mathbf{r}_2,N_A,N_B)$ is the density at $\mathbf{r}_1$ when there are N_A particles in V_A and N_B particles in V_B, one of the latter being specified to be at $\mathbf{r}_2$; similarly, $n(\mathbf{r}_2|N_A,N_B)$ is the density at $\mathbf{r}_2$ when there are N_A particles in V_A and N_B in V_B. This situation corresponds to a model system in which V_A is separated from V_B by a surface S_A which is impenetrable for particles crossing between V_A and V_B, but which does not otherwise modify the Hamiltonian of the system.

We now have generally that

$$n_2(\mathbf{r}_1,\mathbf{r}_2)=\sum_{N_A} P(N_A)n_2(\mathbf{r}_1,\mathbf{r}_2|N_A,N-N_A), \quad (2.9)$$

where $P(N_A)$ is the probability of having N_A particles in V_A, and correspondingly $N-N_A$ in V_B. Thus, performing a Taylor expansion of n_2 about $N_A=\bar{N}_A$, we have

$$n_2(\mathbf{r}_1,\mathbf{r}_2)=n(\mathbf{r}_1|\mathbf{r}_2,\bar{N}_A,N-\bar{N}_A)n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A)$$
$$+\tfrac{1}{2}\langle(N_A-\bar{N}_A)^2\rangle(\partial^2/\partial\bar{N}_A^2)[n(\mathbf{r}_1|\mathbf{r}_2,\bar{N}_A,N-\bar{N}_A)$$
$$\times n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A)]+\cdots, \quad (2.10)$$

where

$$\langle(N_A-\bar{N}_A)^2\rangle=\sum_{N_A} P(N_A)(N_A-\bar{N}_A)^2.$$

We assert that (1) the Taylor expansion may be stopped at the term $\langle(N_A-\bar{N}_A)^2\rangle$, and (2) $n(\mathbf{r}_1|\mathbf{r}_2,\bar{N}_A,N-\bar{N}_A)$ in (2.10) may be replaced by $n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A)$. The first point follows from the fact that, judging from the prototype of an ideal gas, $\langle|N_A-\bar{N}_A|^s\rangle=O(\bar{N}_A^{\frac{1}{2}s})$; since the volume V_A is macroscopic, the remaining terms in the series are of order $\bar{N}_A^{-\frac{1}{2}}O(1/\bar{N}_A)$ and may be dropped. Secondly, the fixing of a particle at $\mathbf{r}_2$ in V_B for given values of N_A and N_B can affect the density at $\mathbf{r}_1$ in V_A only by modifying the distribution of particles in V_B close to the surface S_A; this in turn modifies the neighboring distribution in V_A close to S_A, which can then affect the density at $\mathbf{r}_1$. Since the potential change due to the positional perturbations of the particles near the surface in V_B extends only to the order of λ inside region V_A, the assumption of short-range correlation tells us that when $\mathbf{r}_1$ is far from the surface S_A,

$$n(\mathbf{r}_1|\mathbf{r}_2,\bar{N}_A,N-\bar{N}_A)=n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A)+(\lambda S_A/V_A)$$
$$\times[\text{order of deviation of } n(\mathbf{r}_S|\mathbf{r}_2,\bar{N}_A,N-\bar{N}_A)$$
$$\text{from } n(\mathbf{r}_S|\bar{N}_A,N-\bar{N}_A)], \quad (2.11)$$

where $\mathbf{r}_S$ denotes a surface particle in V_B. But again by the assumption of short-range correlation, the deviation in (2.11), elicited by a perturbation over a volume $\sim\lambda^3$, will be of order $O(\lambda^3/V_B)\sim O(1/N)=(N_A/N)O(1/N_A)$. The correction term in (2.11) for $\mathbf{r}_1$ and $\mathbf{r}_2$ far from S_A will then be $\sim n(\lambda S_A/N_A)O(1/N)$ and will vanish compared to $O(1/N)$ as V_A increases.

The foregoing argument can be improved by further dividing V_B into V_B', surrounding $\mathbf{r}_2$, and V_B'' separating V_B' from V_A. We shall however not attempt this here. Accepting then the above argument, we now rewrite Eq. (2.10) asymptotically as

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \to n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A)n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A)$$
$$+\tfrac{1}{2}\langle(N_A-\bar{N}_A)^2\rangle\frac{\partial^2}{\partial\bar{N}_A^2}[n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A)$$
$$\times n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A)]. \quad (2.10')$$

The steps which led to (2.10) may also be utilized to write

$$n(\mathbf{r}_1)=\sum P(N_A)n_1(\mathbf{r}_1|N_A,N-N_A)$$
$$=n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A)$$
$$+\tfrac{1}{2}\langle(N_A-\bar{N}_A)^2\rangle\frac{\partial^2}{\partial\bar{N}_A^2}n(\mathbf{r}_1|\bar{N}_A,N-\bar{N}_A),$$
$$n(\mathbf{r}_2)=n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A)$$
$$+\tfrac{1}{2}\langle(N_A-\bar{N}_A)^2\rangle\frac{\partial^2}{\partial\bar{N}_A^2}n(\mathbf{r}_2|\bar{N}_A,N-\bar{N}_A). \quad (2.12)$$

In (2.12), we have neglected terms of smaller order than $1/\bar{N}_A$, but this is consistent with V_A being of macroscopic size. Combining Eqs. (2.11) and (2.12) then yields in the asymptotic region

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \rightarrow n(\mathbf{r}_1)n(\mathbf{r}_2)$$

$$+\langle(\delta N_A)^2\rangle\left[\frac{\partial}{\partial\bar{N}_A}n(\mathbf{r}_1|\bar{N}_A, N-\bar{N}_A)\right]$$

$$\times\left[\frac{\partial}{\partial\bar{N}_A}n(\mathbf{r}_2|\bar{N}_A, N-\bar{N}_A)\right], \quad (2.13)$$

where $\delta N_A = N_A - \bar{N}_A$.

Since the second term in (2.13) is already of order $1/N$, any parts of it which are of further order $o(1)$ can be omitted. This permits (since $\mathbf{r}_1$ and $\mathbf{r}_2$ are far from the surface) the replacement to order S/V,

$$n(\mathbf{r}_1|\bar{N}_A, N-\bar{N}_A)=n(\mathbf{r}_1|\bar{N}_A, 0),$$
$$n(\mathbf{r}_2|\bar{N}_A, N-\bar{N}_A)=n(\mathbf{r}_2|0, N-\bar{N}_A). \quad (2.14)$$

Both $\bar{N}_A$ and $\bar{N}_B$ are functions of N. We may therefore express (2.13) in terms of derivatives with respect to N. Thus

$$\frac{\partial n(\mathbf{r}_2|0, N-\bar{N}_A)}{\partial\bar{N}_A}=-\frac{dn(\mathbf{r}_2|0, \bar{N}_B)}{d\bar{N}_B}$$

$$=-\frac{dn(\mathbf{r}_2|0, \bar{N}_B(N))}{dN}\left(\frac{d\bar{N}_B}{dN}\right)^{-1}$$

$$=-\frac{\partial n(\mathbf{r}_2)}{\partial N}\frac{dN}{d\bar{N}_B}, \quad (2.15a)$$

and similarly

$$\frac{\partial n(\mathbf{r}_1|\bar{N}_A, 0)}{\partial\bar{N}_A}=\frac{\partial n(\mathbf{r}_1)}{\partial N}\frac{dN}{d\bar{N}_A}, \quad (2.15b)$$

again neglecting terms of order S/V. Setting $n=N/V$ and leaving the n dependence implicit, Eq. (2.13) thus reduces to

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \rightarrow n(\mathbf{r}_1)n(\mathbf{r}_2)-\frac{1}{N}n\frac{\partial n(\mathbf{r}_1)}{\partial n}n\frac{\partial n(\mathbf{r}_2)}{\partial n}$$

$$\times\langle(\delta N_A)^2\rangle\frac{1}{N}\left(\frac{dN}{d\bar{N}_A}+\frac{dN}{d\bar{N}_B}\right), \quad (2.16)$$

where we have used the identity $(dN/d\bar{N}_A)(dN/d\bar{N}_B) = dN/d\bar{N}_A + dN/d\bar{N}_B$.

We now show that the expression (2.16) is independent of the division into volumes V_A and V_B, and find its explicit form. It follows from the general principles of statistical mechanics that

$$P(N_A)=\exp\{-[F_A(T,V_A,N_A)+F_B(T,V_B,N_B)$$

$$-F(T,V,N)]/kT\}\sim\exp\left\{-\frac{1}{2}\frac{(\delta N_A)^2}{kT}\right.$$

$$\times\left[\frac{\partial^2 F_A(T,V_A,\bar{N}_A)}{\partial\bar{N}_A^2}+\frac{\partial^2 F_B(T,V_B,\bar{N}_B)}{\partial\bar{N}_B^2}\right]\right\}, \quad (2.17)$$

F being the Helmholtz free energy, and we have again consistently neglected terms of order $o(1)$. Here the most probable value of N_A, which for our purpose may be set equal to $\bar{N}_A$, is determined from the condition

$$\mu_A=\frac{\partial F_A(T,V_A,\bar{N}_A)}{\partial\bar{N}_A}=\mu_B=\frac{\partial F_B(T, V_B, N-\bar{N}_A)}{\partial N}=\mu,$$

and $\mu=\mu_A(\bar{N}_A(N))=\mu(N)$ is the chemical potential of the full system. This readily yields the expression

$$\langle(\delta N_A)^2\rangle=kT\left[\frac{\partial\mu}{\partial N}\left(\frac{\partial N}{\partial\bar{N}_A}+\frac{\partial N}{\partial\bar{N}_B}\right)\right]^{-1}, \quad (2.18)$$

or, combining with Eq. (2.16),

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \rightarrow n(\mathbf{r}_1)n(\mathbf{r}_2)$$

$$-\frac{kT}{N}\left[n\frac{\partial n(\mathbf{r}_1)}{\partial n}\right]\left[n\frac{\partial n(\mathbf{r}_2)}{\partial n}\right]\left(\frac{1}{N}\frac{\partial N}{\partial\mu}\right). \quad (2.19)$$

For a uniform system with no body forces, the quantity $(1/N)\partial N/\partial\mu$ is equal to n times the isothermal compressibility χ. For a general nonuniform system, we may still write

$$\frac{1}{N}\frac{\partial N}{\partial\mu}=n\bar{\chi}, \quad (2.20)$$

where $\bar{\chi}$ is now some average compressibility. This leads us finally to the asymptotic expression,

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \rightarrow n(\mathbf{r}_1)n(\mathbf{r}_2)$$

$$-\frac{nkT\bar{\chi}}{N}\left[n\frac{\partial}{\partial n}n(\mathbf{r}_1)\right]\left[n\frac{\partial}{\partial n}n(\mathbf{r}_2)\right]. \quad (2.21)$$

When $\mathbf{r}_1$ and $\mathbf{r}_2$ are both in the interior of a uniform fluid, (2.21) becomes the Ornstein-Zernike relation

$$g(r) \rightarrow 1-nkT\bar{\chi}/N, \quad (1.1')$$

while if $\mathbf{r}_1$ is at a rigid wall, then, as shown in reference 3,

$$n_w=n(\mathbf{r}_1 \text{ at wall})=p/kT, \quad \partial n(\mathbf{r}_1)/\partial n=1/(nkT\bar{\chi}),$$

and

$$n_2(\mathbf{r}_1,\mathbf{r}_2) \rightarrow n_w n\left(1-\frac{n}{n_w}\frac{1}{N}\right), \quad (1.3')$$

a result derived in reference 3.

The extension of the above analysis to the distribu-

tion of $q+l$ particles is straightforward and yields

$$n_{q+l} \rightarrow n_q n_l - \frac{nkT\bar{\chi}}{N}\left(n\frac{\partial n_q}{\partial n}\right)\left(n\frac{\partial n_l}{\partial n}\right). \quad (2.22)$$

3. STATISTICAL MECHANICS DERIVATION

We shall now investigate the asymptotic behavior of n_{q+l} from a statistical mechanical viewpoint. To do this involves two steps: (1) a decomposition of quite general validity of thermodynamic quantities and distribution functions into a dominant part and an $O(1/N)$ correction term expressed in terms of the dominant part, and (2) a computation of the spatial asymptotic form of the dominant part of a distribution and consequently of the $O(1/N)$ term, in which the explicit form of the canonical partition function plays a crucial role. Since the dominant part in fact represents a grand canonical average from which the fixed-N components are then extracted, there is a family relation with the "box within a box" thermodynamic argument of the previous section.

The equilibrium statistical mechanics of an interacting N-particle system in a volume V may be obtained from the partition function Q_N, or from its physical counterpart, the free energy

$$F_N = -(1/\beta)\ln Q_N, \quad (3.1)$$

where $k\beta$ is the uniform reciprocal temperature. Q_N is given explicitly by

$$Q_N = (1/N!)\int \exp(-\beta H_N)(d\mathbf{r}d\mathbf{p}/h^3)^N, \quad \text{classical}$$

$$= \text{Tr}\exp(-\beta H_N), \quad \text{quantum mechanical}, \quad (3.2)$$

H_N being the system Hamiltonian. However, the precise form of Q_N is unimportant at this stage. What is vital is the smallness of density fluctuations, to the extent that the grand partition function,

$$Q(z) = \sum_0^\infty Q_M z^M, \quad (3.3)$$

at fixed V and z has contributions from only a very small range of particle number M. If this is so, we may contemplate a Darwin-Fowler or steepest descent extraction of Q_N from $Q(z)$.

Let us define

$$L(z) = \ln Q(z). \quad (3.4)$$

For an open system or grand canonical ensemble, L is related to the pressure by $L = pV/kT$ and z to the chemical potential by $\beta\mu = \ln z$. Here, the quantity L is but a means to an end, for we may express Q_N in

terms of it through the contour integral

$$Q_N = (1/2\pi i)\oint \exp[L(\zeta)]\zeta^{-N}d\zeta/\zeta$$

$$= (1/2\pi)\int_{-\pi}^{\pi}\exp[L(re^{i\theta}) - Ni\theta - N\ln r]d\theta. \quad (3.5)$$

The large-N asymptotic form of (3.5) appears from a steepest descent evaluation as[7]

$$Q_N \cong z^{-N}e^{L(z)}\left\{2\pi z\frac{\partial}{\partial z}\left[z\frac{\partial}{\partial z}L(z)\right]\right\}^{-\frac{1}{2}}, \quad (3.6)$$

where

$$z\partial L(z)/\partial z = N \quad (3.7)$$

determines z. If the method is valid, corrections to (3.6) for derived quantities such as F_N may be shown to be of order $O(1/N^2)$ compared to the principal term, and this is strictly negligible for most applications, including ours. Such a statement is as always fully meaningful only for a uniform fluid, where one can take the limit $N \rightarrow \infty$ at constant density, but the same numerical order of magnitude should hold for a non-uniform system. From (3.1), we have as well

$$-\beta F_N \cong L(z) - N\ln z - \frac{1}{2}\ln 2\pi$$

$$-\frac{1}{2}\ln\left\{z\frac{\partial}{\partial z}\left[z\frac{\partial}{\partial z}L(z)\right]\right\}. \quad (3.8)$$

On the basis of (3.8), we may introduce the "dominant part" of F_N,

$$-\beta F_N^{(0)} \equiv L(z) - N\ln z - \frac{1}{2}\ln 2\pi. \quad (3.9)$$

$F_N^{(0)}$, which coincides with the result of the usual Mayer-Ursell virial expansion,[8] is of course just the grand canonical average, and would yield the correct free energy per particle in an infinitely large uniform system. In a general system, the principal property of $F_N^{(0)}$ which will be utilized is the following. Consider any variation of the system which does not affect total particle number. Then according to (3.9),

$$-\delta(\beta F_N^{(0)}) = \delta L(z) - (N/z)\delta z,$$

or, inserting (3.7),

$$-\delta(\beta F_N^{(0)}) = \delta L(z) - [\partial L(z)/\partial z]\delta z.$$

Hence we may write

$$-\delta(\beta F_N^{(0)}) = \delta L(z)|_{z=\text{const}}. \quad (3.10)$$

Equation (3.10) permits us to compute a variation of $F_N^{(0)}$ explicitly in terms of L without being required

[7] See, e.g., J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 142.

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

to solve for z. Finally, F_N is to be expressed in terms of $F_N^{(0)}$. Since

$$-\beta\frac{\partial F_N^{(0)}}{\partial N}=\left(\frac{\partial z}{\partial N}\right)\left(\frac{\partial L}{\partial z}-\frac{N}{z}\right)-\ln z=-\ln z,$$

i.e., the thermodynamic relation $\mu=\partial F/\partial N$, then

$$\beta\frac{\partial^2 F_N^{(0)}}{\partial N^2}=\left(\frac{1}{z}\right)\frac{\partial z}{\partial N}=\left(z\frac{\partial N}{\partial z}\right)^{-1}=\left[\frac{\partial}{\partial z}\left(z\frac{\partial}{\partial z}L\right)\right]^{-1}.$$

Inserting into Eqs. (3.8) and (3.9), we have

$$\beta F_N\cong\beta F_N^{(0)}-\tfrac{1}{2}\ln\left(\beta\frac{\partial^2 F_N^{(0)}}{\partial N^2}\right). \qquad (3.11)$$

Equation (3.11) may be rewritten in terms of the compressibility. For a very large uniform system, F_N/N is a function of $n\equiv N/V$ alone. Hence the isothermal compressibility may be written as

$$\chi=\left(n\frac{\partial p}{\partial n}\right)^{-1}=\left(-N\frac{\partial}{\partial N}\frac{\partial F}{\partial V}\right)^{-1}$$

$$=\left[-N\frac{\partial}{\partial N}\left(N\frac{\partial}{\partial V}\frac{F}{N}\right)\right]^{-1}$$

$$=\left[n\frac{\partial}{\partial N}\left(N^2\frac{\partial}{\partial N}\frac{F}{N}\right)\right]^{-1}=\left(nN\frac{\partial^2 F}{\partial N^2}\right)^{-1}.$$

For an arbitrary system, we may correspondingly define an average compressibility,

$$\bar{\chi}\equiv\left(\frac{n}{N}n^2\frac{\partial^2}{\partial n^2}F_N^{(0)}\right)^{-1}, \qquad (3.12)$$

where differentiation is at constant volume (or constant external potential). Equation (3.12) is seen to be equivalent to the expression (2.20). Further, applying a variation δ, commuting with N, to (3.11) yields by virtue of (3.12)

$$\delta F_N=\delta F_N^{(0)}-\frac{1}{N}\frac{n\bar{\chi}}{2\beta}n^2\frac{\partial^2}{\partial n^2}(\delta F_N^{(0)}), \qquad (3.13)$$

our fundamental relation. The second term on the right-hand side of (3.13) is a correction, containing the factor $1/N$. For a large uniform system, the relative correction (F_N itself goes as N) is literally a $1/N$ term, while for a nonuniform system, this is still a reasonable assessment of its numerical value.

Relation (3.13) is readily applied to determining the N dependence and asymptotic form of the configuration space distribution functions. For the N dependence, it suffices to express the distributions in terms of the free energy. Suppose that the system Hamiltonian contains

an s-body potential,

$$H=\cdots+\frac{1}{s!}\sum_{i_1\neq\cdots\neq i_s}\phi^{(s)}(\mathbf{r}_{i_1},\cdots,\mathbf{r}_{i_s})+\cdots, \qquad (3.14)$$

which in the final evaluation is to be given its actual value, perhaps zero, but not until then. Then it is easily shown that the s-body distribution function n_s, normalized so that

$$\int n_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)d\mathbf{r}_1,\cdots,d\mathbf{r}_s=N!/(N-s)!, \qquad (3.15)$$

may be written as

$$n_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)=-\frac{s!}{\beta}\frac{1}{Q_N}\frac{\delta Q_N}{\delta\phi^{(s)}(\mathbf{r}_1,\cdots,\mathbf{r}_s)},$$

or

$$n_s=s!\,\delta F_N/\delta\phi^{(s)}. \qquad (3.16)$$

By making $\phi^{(s)}$ other than a pure configuration-space potential, this result extends at once to phase-space distributions and density matrices. Now applying (3.13) to (3.16) results in the relation

$$n_s=n_s^{(0)}-\frac{1}{N}\frac{n\chi}{2\beta}n^2\frac{\partial^2}{\partial n^2}n_s^{(0)}, \qquad (3.17)$$

where $n_s^{(0)}$, arising via (3.16) from $F_N^{(0)}$, actually represents a grand canonical average distribution. When $n_s^{(0)}$ depends only on $n=N/V$, then it coincides with n_s in an infinite system, and (3.17) expresses the $1/N$ corrections. For example, with $s=2$ and large separation r_{12}, then in a uniform system, (3.17) reduces to the previously discussed $n_2=n^2(1-n\chi/\beta N)$. For a nonuniform system, the utility of (3.17) derives from the special properties which $n_s^{(0)}$ possesses, and in particular its simple asymptotic form.

Our major objective is to find the asymptotic form of n_{q+l} when the coordinates separate into two distinct bunches,

$$q=(\mathbf{r}_1,\cdots,\mathbf{r}_q) \quad \text{and} \quad l=(\mathbf{r}_{q+1},\cdots,\mathbf{r}_{q+l}).$$

For this purpose, the corresponding asymptotic form of $n_{q+l}^{(0)}$ is required, and it may be obtained by assuming sufficiently rapid convergence of the standard cluster expansion for $L(z)$, a stronger condition than the previously employed finite correlation length. The point is this. First consider classical equilibrium statistical mechanics. If the factor

$$f^{(s)}(\mathbf{r}_1,\cdots,\mathbf{r}_s)=\exp[-\beta\phi^{(s)}(\mathbf{r}_1,\cdots,\mathbf{r}_s)]-1 \qquad (3.18)$$

is regarded as a "star" connecting vertices $\mathbf{r}_1,\cdots,\mathbf{r}_s$, and if we further introduce the Ursell factor

$$U_t(\mathbf{r}_1,\cdots,\mathbf{r}_t)=\sum D_t(\mathbf{r}_1,\cdots,\mathbf{r}_t), \qquad (3.19)$$

where the D_t run over all (nonrepeated) products of $f^{(s)}$ represented by diagrams in which the $\mathbf{r}_1,\cdots,\mathbf{r}_t$ are

connected, then it is known (see Hill[9]) that $Q(z)$ of (3.2) and (3.3) achieves the form

$$Q(z) = \exp\left\{\sum\left[\int U_t(\mathbf{r}_1, \cdots, \mathbf{r}_t)d^t\mathbf{r}\, z^t C^t/t!\right]\right\}, \quad (3.20)$$

where

$$d^t\mathbf{r} \equiv d\mathbf{r}_1 d\mathbf{r}_2 \cdots d\mathbf{r}_t.$$

Here C is a factor resulting from momentum integrations. From (3.16) and (3.10), then

$$n_s{}^{(0)} = \sum z^t C^t\left(\frac{-s!}{\beta}\right)\frac{\delta}{\delta\phi^{(s)}}\left(\int U_t\frac{d^t\mathbf{r}}{t!}\right), \quad (3.21)$$

whose simplicity is due to the fact that explicit z dependence is untouched by the variation.

Suppose now that (3.21) converges rapidly enough that only terms up to some finite t need be considered. For finite-range forces, this then requires only clusters up to some finite spatial diameter, related of course to the correlation length but conceivably depending on s. Sets q and l in $s = q + l$ are then to be regarded as asymptotically separated if q and l are separated, member from member, by more than this finite diameter. If under these conditions $\delta\int D_t d^t\mathbf{r}/\delta\phi^{(q+l)}$ did not disconnect set q from set l in D_t, the cluster would have an impermissibly large diameter. Thus a separation must occur. We note that $U_t/t!$ lists all distinct diagrams (with undesignated vertices, but weighted by the number of repetitions under vertex permutation), while $(-s!/\beta)\delta/\delta\phi^{(s)}$ for separated q and l removes a "star" $f^{(s)}$ in any order in which it may be presented. It follows that, including both possibilities $f^{(q)}$ and 1 for the q connection, and similarly for the l, the separation is into

$$\left(\frac{-q!}{\beta}\right)\left(\frac{\delta}{\delta\phi^{(q)}}\right)\int D_m\frac{d^m\mathbf{r}}{m!}\left(\frac{-l!}{\beta}\right)\frac{\delta}{\delta\phi^{(l)}}\left(\int D_n\frac{d^n\mathbf{r}}{n!}\right).$$

Here $m + n = t$, and all distinct combinations D_m, D_n are obtained in this fashion. Inserting into (3.21), we at once conclude that

$$n_{q+l}{}^{(0)} \longrightarrow n_q{}^{(0)} n_l{}^{(0)} \quad (3.22)$$

for asymptotic separation of sets q and l. This may be regarded as the characteristic property of $n_s{}^{(0)}$: The grand canonical distributions, for asymptotic decomposition into particle subsets, separate through order $1/N$ into their component distributions. [It might appear that a corresponding statement could be made for the diagrammatic density expansion of a canonical ensemble with periodic boundary conditions and translation-invariant potential, but since the generating function for the irreducible clusters is no longer the free energy, and since more diagrams may be decomposed by the variational differentiation, the form (3.22)

is not obtained. Instead, one finds (3.23) directly, but more laboriously.]

Applying the correction formula (3.17) to the combination $n_{q+l} - n_q n_l$, we have

$$n_{q+l} - n_q n_l = n_{q+l}{}^{(0)} - \left(\frac{n^3\bar{\chi}}{2\beta N}\right)\frac{\partial^2 n_{q+l}{}^{(0)}}{\partial n^2}$$

$$- \left[n_q{}^{(0)} - \left(\frac{n^3\bar{\chi}}{2\beta N}\right)\frac{\partial^2 n_q{}^{(0)}}{\partial n^2}\right]\left[n_l{}^{(0)} - \left(\frac{n^3\bar{\chi}}{2\beta N}\right)\frac{\partial^2 n^{(0)}}{\partial n^2}\right].$$

Employing (3.22), and dropping the final $O(1/N^2)$ term as well as the deviation of n_q from $n_q{}^{(0)}$ within a correction term, then

$$n_{q+l} \rightarrow n_q n_l - \frac{1}{N}\frac{n\bar{\chi}}{\beta}\left(n\frac{\partial n_q}{\partial n}\right)\left(n\frac{\partial n_l}{\partial n}\right), \quad (3.23)$$

the desired asymptotic relation. The foregoing is classical. For quantum mechanical distributions, the explicit form of the Ursell factor is altered,[10] but similar comments are appropriate. The noncommutativity of coordinates and momenta however introduces additional effective coupling in the form of propagation factors of range of the order of the thermal de Broglie wavelength, $(\beta\hbar^2/2m)^{\frac{1}{2}}$, thereby contributing to the maximum effective cluster diameter. At very low temperature, $\beta \rightarrow \infty$, greater care is required, as it is when infinite range, e.g., Coulomb forces, are present.

We remark here further on the relation of Eq. (3.17) to the general N dependence of the low-order distribution functions. This may be of some direct relevance in dealing with systems in which N is actually a small number, such as those used in machine calculations by Alder[11] and others. When our assumption concerning the convergence of the virial expansion is valid, then for a uniform system, $n_s{}^{(0)}$ depends only upon the density,[11a] in which case as indicated following (3.17), $n_s{}^{(0)}$ coincides with the leading term in a $1/N$ development of n_s. Equation (3.17) then states a verifiable relation between the N-independent term and the first correction to it, which is proportional to $1/N$.

The relation (3.23) may also be extended to the intrinsic correlations or Ursell distribution functions. This is carried out in Appendix C.

4. THE LOCAL NATURE OF DISTRIBUTION FUNCTIONS

We shall now apply the results of the previous sections to a one-component fluid whose intensive

[10] See, e.g., C. Bloch and C. de Dominicis, Nuclear Phys. **7**, 459 (1958).

[11] See, e.g., B. J. Alder and T. E. Wainwright, J. Chem. Phys. **27**, 1208 (1957).

[11a] *Note added in proof.* This is true up to the kth power in the density, where $k = (L/a)$, L being the length of the periodic container. The coefficients of the higher powers in the virial expansion will contain implicit nonanalytic dependence on V. We are presently studying this dependence.

parameters such as density, temperature, and local velocity vary slowly with position. The Gibbs ensemble describing such a system has been considered by many authors.[12] The classical ensemble density $\mu(X)$, where $X = \{\cdots r_i, \cdots, p_i \cdots\}$ is a point in the Γ space of the system, is generally written as a local equilibrium part $\tilde{\mu}(X)$ and a correction term $\mu'(X)$. The part $\tilde{\mu}(X)$ is a superposition of canonical (or grand canonical) ensembles for each small region of the fluid at its own temperature $T(x)$, velocity $v(x)$, and density $n(x)$:

$$\mu(X) = \tilde{\mu}(X) + \mu'(X), \tag{4.1}$$

$$\tilde{\mu}(X) = \frac{1}{N!Q} \exp\left\{ -\int dx\, \beta(x)[E(X,x) \right.$$
$$\left. - v(x) \cdot P(X,x) - \nu(x)n(X,x)] \right\}. \tag{4.2}$$

Here x is a point in physical space, $\beta(x) = [kT(x)]^{-1}$, and $\nu(x)$ is chosen to give the correct density $n(x)$. $E(X,x)$, $P(X,x)$ and $n(X,x)$ are the microscopic energy, momentum, and particle density at x when the state of the system is represented by the phase point X[13]:

$$E(X,x) = \sum_1^N \delta(x - r_i)[p_i^2/2m + \tfrac{1}{2}\sum_j \phi(r_{ij}) + U(r_i)],$$

$$P(X,x) = \sum_1^N \delta(x - r_i)p_i, \tag{4.3}$$

$$n(X,x) = \sum_1^N \delta(x - r_i).$$

$\phi(r_{ij})$ and $U(r_i)$ are the internal and external potentials, respectively; $\tilde{Q}$ is a normalization constant, reducing to the canonical partition function Q_N for an equilibrium ensemble. Thus

$$\tilde{\mu}(X) = \tilde{\mu}_{\text{un.}}(X)/N!\tilde{Q},$$
where

$$\tilde{\mu}_{\text{un.}}(X) = \exp\left\{ -\sum_1^N \left[-\gamma(r_i) + \beta(r_i) \right. \right.$$
$$\left. \left. \times \left(\frac{[p_i - mv(r_i)]^2}{2m} + \tfrac{1}{2}\sum_j \phi(r_{ij}) \right) \right] \right\}, \tag{4.4}$$

$$\tilde{Q} = (1/N!)\int \tilde{\mu}_{\text{un.}}(X)dr_1 \cdots dp_N,$$
and

$$\gamma(r_i) = [-U(r_i) + \tfrac{1}{2}mv(r_i)^2 + \nu(r_i)]\beta(r_i). \tag{4.5}$$

The term $\mu'(X)$ in (4.1) is of first order in the gradients of the hydrodynamical variables in the sense of vanishing in the case of uniformity, and has a vanishing integral. It is μ' which is supposed responsible

for the dissipative behavior, while $\tilde{\mu}$ should yield the equilibrium form, at the local value of the intensive variables, for such quantities as energy density $E(x)$, pressure $p(x)$, etc. This will be true if the low-order distributions f_s, and in particular the two-body distribution function $f_2(r_1, r_2, p_1, p_2)$, computed from $\tilde{\mu}$ have their equilibrium form at the local value of the intensive variables. We shall investigate the validity of this hypothesis.

Now the distribution f_s for the position and momentum of s particles factors readily into a position distribution $\tilde{n}_s(r_1, \cdots, r_s)$ and a momentum distribution (with positional dependence in the large). We have

$$\tilde{f}_s(r_1, \cdots, r_s, p_1, \cdots, p_s)$$
$$= \frac{N!}{(N-s)!} \int \tilde{\mu}\, dr_{s+1} \cdots dr_N dp_{s+1} \cdots dp_N$$
$$= \tilde{n}_s(r_1, \cdots, r_s)\prod_1^s \left\{ [2\pi mkT(r_i)]^{\frac{3}{2}} \right.$$
$$\left. \times \exp\left(-\beta(r_i)\frac{[p_i - mv(r)_i]^2}{2m} \right) \right\}. \tag{4.6}$$

The momentum distribution is thus locally Maxwellian and we need consider only $\tilde{n}_s(r_1, \cdots, r_s)$. The position distribution $\tilde{n}_s$ is a functional of the temperature $T(r)$ and (through γ) of the density $n(r)$ in the whole container. It is our aim to show that, for slow variation of $\beta(r)$ and $n(r)$, the n_s depend only on the values of these quantities in the region containing $r_1, \cdots, r_s$. In fact, it will develop that, for $s = 1, 2,$

$$\tilde{n}_s(r_1, \cdots, r_s) = n_s(r_1, \cdots, r_s; \bar{\beta}, \bar{n}), \tag{4.7}$$

to second order in the gradients. Here n_s is the equilibrium distribution for a system at uniform temperature $(k\bar{\beta})^{-1}$ and density $\bar{n}$; $\bar{\beta} = \beta(R)$ and $n = n(R)$, where $R = (1/s)\sum_1^s r_i$ is the s-particle centroid. For $s > 2$, gradients at R will also be required. However, there will be no contributions from outlying elements of the fluid, so that even for $s > 2$ the distribution function is truly local, as expected.

We shall consider first the change in $\tilde{n}_s$ due to a change in the function $\gamma(r)$. It readily follows from Eqs. (4.4) and (4.6) that

$$\frac{\delta\tilde{n}_s(r_1, \cdots, r_s)}{\delta\gamma(r)} = \tilde{n}_s(r_1, \cdots, r_s)\sum_1^s \delta(r_i - r)$$
$$+ \tilde{n}_{s+1}(r_1, \cdots, r_s, r) - \tilde{n}_s(r_1, \cdots, r_s)n_1(r). \tag{4.8}$$

($\tilde{n}_1 = n_1$ is the density which determines γ.) Hence under the infinitesimal alteration $\delta\gamma(r)$,

$$\delta\tilde{n}_s(r_1, \cdots, r_s) = \tilde{n}_s(r_1, \cdots, r_s)\sum_1^s \delta\gamma(r_i)$$
$$+ \int [n_{s+1}(r_1, \cdots, r_s, r) - \tilde{n}_s(r_1, \cdots, r_s)n_1(r)]\delta\gamma(r)dr,$$

[12] H. Mori, Phys. Rev. **112**, 1829 (1958); J. L. Lebowitz, Phys. Rev. **114**, 1192 (1957).
[13] J. Lebowitz, H. Frisch, and E. Helfand, Phys. Fluids **3**, 325 (1960).

which, since

$$\int [\bar{n}_{s+1}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{r}) - \bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)n_1(\mathbf{r})]d\mathbf{r}$$
$$= -s\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s), \quad (4.9)$$

may be written in the more convenient form:

$$\delta\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s) = \int [\bar{n}_{s+1}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{r})$$

$$- \bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)n_1(\mathbf{r})][\delta\gamma(\mathbf{r}) - (1/s)\sum\delta\gamma(\mathbf{r}_i)]d\mathbf{r}. \quad (4.10)$$

To take advantage of the asymptotic expression (2.22) or (3.23), (4.10) is further decomposed as

$$\delta\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s) + \frac{n\bar{\chi}}{N\beta}n^2\frac{\partial\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)}{\partial n}\int\frac{\partial n_1(r)}{\partial n}$$

$$\times\left[\delta\gamma(\mathbf{r}) - \frac{1}{s}\sum\delta\gamma(\mathbf{r}_i)\right]d\mathbf{r} = \int\left[\bar{n}_{s+1}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{r})\right.$$

$$\left. - \bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)n_1(\mathbf{r}) + \frac{n\bar{\chi}}{N\beta}n^2\frac{\partial\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)}{\partial n}\frac{\partial n_1(\mathbf{r})}{\partial n}\right]$$

$$\times\left[\delta\gamma(\mathbf{r}) - \frac{1}{s}\sum\delta\gamma(\mathbf{r}_i)\right]d\mathbf{r}. \quad (4.11)$$

According to (3.1) and (3.12), the mean compressibility $\bar{\chi}$ and reciprocal energy β need not be specified more precisely, for the combination

$$n\bar{\chi}/\beta = N(-n^2\partial^2\ln\tilde{Q}/\partial n^2)^{-1}, \quad n=N/V, \quad (4.12)$$

is directly determined by $\tilde{Q}$.

By virtue of the relation (3.23), the integral on the right-hand side of (4.11) has contributions only from $\mathbf{r}$ within some conservative multiple of the correlation length from at least one of $\mathbf{r}_1, \cdots, \mathbf{r}_s$, certainly a finite region R independent of V when all $\mathbf{r}_i$ are far from the walls. Hence (4.11) is seen at once to be a local expression for the change of $\bar{n}_s$. Further simplification may be achieved. Assume that the spatial rate of change of $\delta\gamma(\mathbf{r})$ may be regarded as uniform in region R. Then $\delta\gamma(\mathbf{r}) - (1/s)\sum\delta\gamma(\mathbf{r}_i)$ may be replaced by $[\mathbf{r} - (1/s)\sum\mathbf{r}_i]$ $\cdot\nabla\delta\gamma(\mathbf{R})$, where $\mathbf{R}$ is the center of mass of $\mathbf{r}_1, \cdots, \mathbf{r}_s$. Similarly, assume that $n_1(\mathbf{r})$ and $\partial n_1(\mathbf{r})/\partial n$ are essentially constant *in this region*, for we are concerned with large scale inhomogeneities, while $\bar{n}_{s+1}$ is also uniform in that it depends only upon interparticle distances. Under these conditions, if one makes the center-of-mass reflection $\mathbf{r} \to (2/s)\sum\mathbf{r}_i - \mathbf{r}$, the second bracket in the integral reverses sign. On the other hand, for $s=1$ or 2, a center-of-mass reflection of $\mathbf{r}$ leaves the distances of $\bar{n}_{s+1}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{r})$ unaltered, so that the first bracket is unchanged. Hence the right-hand side of (4.11) vanishes, and we are left with

$$\delta\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s) = \left\{-\frac{n\bar{\chi}}{N\beta}n^2\int\frac{\partial n_1(\mathbf{r})}{\partial n}\left[\delta\gamma(\mathbf{r})\right.\right.$$

$$\left.\left. - \frac{1}{s}\sum\delta\gamma(\mathbf{r}_i)\right]d\mathbf{r}\right\}\frac{\partial\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)}{\partial n}, \quad (4.13)$$

for $s=1$ or 2. This is of $O(1)$ with respect to N.

Consider first the case $s=1$. Equation (4.13) then reduces to

$$\delta n_1(\mathbf{r}_1) = \frac{n\bar{\chi}}{N\beta}n^2\int\frac{\partial n_1(\mathbf{r})}{\partial n}[\delta\gamma(\mathbf{r}_1) - \delta\gamma(\mathbf{r})]d\mathbf{r}\frac{\partial n_1(\mathbf{r}_1)}{\partial n}, \quad (4.14)$$

which, noting that $(\partial/\partial n)\int n_1(\mathbf{r})d\mathbf{r} = \partial N/\partial n = V$ and inserting (2.20), may be solved for $\delta\gamma(\mathbf{r}_1)$ in the form

$$\delta\gamma(\mathbf{r}_1) = \frac{\beta}{n^2\bar{\chi}}\frac{\delta n_1(\mathbf{r}_1)}{\partial n_1(\mathbf{r}_1)/\partial n} + \frac{1}{V}\int\frac{\partial n_1(\mathbf{r})}{\partial n}\delta\gamma(\mathbf{r})d\mathbf{r}$$

$$= \left(\frac{\partial\beta\mu}{\partial n}\bigg/\frac{\partial n_1(\mathbf{r}_1)}{\partial n}\right)\delta n_1(\mathbf{r}_1) + \text{const.} \quad (4.15)$$

Thus, the change in $\gamma(\mathbf{r}_1)$ required to produce a given change in $n_1(\mathbf{r}_1)$ is, except for a constant, identical with that which would be obtained by changing $\beta\mu$ by means of a change in total particle number (or over-all density n) adjusted to yield the actual local density $n_1(\mathbf{r}_1)$. This shows that a slowly varying density can be interpreted by representing each fluid element as an open system exchanging particles with neighboring fluid elements (total particle number being maintained), and gives meaning to $(1/\beta)\gamma(\mathbf{r})$ as a local chemical potential, up to a constant independent of $\mathbf{r}$ (but which may depend on the function γ).

Let us illustrate this by considering the variation of density of an ideal gas in a uniform gravitational field in the z direction (a potential of mgz) due to a change in the gravitational force constant g. According to (4.5), this will result from $\delta\gamma(\mathbf{r}) = -\beta m\delta gz$. Further, since $n(\mathbf{r}) = N\beta mg\exp(-\beta mgz)$ for a unit area of gas between $z=0$ and $z=\infty$, then $\delta n(\mathbf{r}_1) = (1/g - \beta mz_1)$ $\times n(\mathbf{r}_1)\delta g$, which would equivalently be produced by a δN of $(1/g - \beta mz_1)n\delta g$. Now the chemical potential is given here by

$$\mu = \partial F/\partial N = (\partial/\partial N)(-1/\beta)\left[\tfrac{3}{2}N\ln(2\pi m/\beta h^2)\right.$$

$$\left. - \ln N! + N\ln\int\exp(-\beta mgz)dz\right]$$

$$\cong \text{const} - (1/\beta)\ln N + (1/\beta^2 mg),$$

so that $\delta(\beta\mu) = \delta N/N - \delta g/\beta^2 mg^2$. Under the above changes, this becomes $\delta(\beta\mu) = -\beta m\delta gz_1$, which is indeed identical with $\delta\gamma(\mathbf{r}_1)$.

To complete the picture, consider next the case $s=2$,

in which our principal interest lies. Observing that $\sum \delta\gamma(r_i) = s\delta\gamma(R)$ through first order gradient terms, we find that Eq. (4.13) takes on precisely the same form as Eq. (4.14) for $n_1(R)$. It follows then that

$$\delta\bar{n}_2(r_1,r_2) = \left(\frac{\partial\bar{n}_2(r_1,r_2)}{\partial n} \middle/ \frac{\partial n_1(R)}{\partial n}\right)\delta n_1(R). \quad (4.16)$$

In other words, the change in $\bar{n}_2(r_1,r_2)$ produced by $\delta\gamma$ is equal to that which would be obtained by only altering the number of particles in the system so that the local density $n_1(R)$ at the center of mass $R = \frac{1}{2}(r_1 + r_2)$ attains its actual value. Thus we reach the desired conclusion that a variation of $n_1(r)$ also has the same local effect on n_2 as an equivalent change in local density achieved by changing the total particle number.

The infinitesimal process leading to (4.14) can be iterated as long as neither the gradient of the effective external potential $\gamma(r)$ nor the form of the two-body distribution vary significantly within a correlation length. Starting with a uniform motionless fluid [of small (surface×correlation length/volume) ratio], we can further conclude in this fashion that with the sole condition that the external force and local velocity (and hence local density) be slowly varying in space, the 2-body distribution will be precisely that of a uniform fluid of density equal to the local density at the center of the two particles.

The simple expression (4.14) is not valid for $\bar{n}_s$ with $s > 2$. Indeed, the vanishing of the short-range contribution to the right-hand side of (4.11) was established by an elaboration of the familiar argument[14] that for $\bar{n}_2(r_1,r_2)$ there exists no vector of local character, symmetric in r_1, r_2 which can combine with $\nabla\gamma(R)$ to give a first order correction. This argument fails for $s > 2$. Instead, a density gradient can provoke an anisotropy in the local s-body distribution. Replacing (4.13) by (4.11) in (4.16), and representing $\bar{n}_{s+1}/\bar{n}_s$ by the superposition approximation,[15] results in a relatively simple correction to (4.16) which we cite for the sake of completeness: If

$$\bar{n}_s(r_1,\cdots,r_s) \sim \prod n_1(r_i)\prod_{i>j}[\bar{n}_2(r_i,r_j)/n_1(r_i)n_1(r_j)],$$

then

$$\delta\bar{n}_s(r_1,\cdots,r_s) - \left(\frac{\partial\bar{n}_s(r_1,\cdots,r_s)}{\partial n} \middle/ \frac{\partial n_1(R)}{\partial n}\right)\delta n_1(R)$$

$$= \bar{n}_s(r_1,\cdots,r_s)\int\left[\prod\left(\frac{\bar{n}_2(r_i,r)}{n_1(r_i)n_1(r)}\right)\right.$$

$$\left. - \prod\left(\frac{\bar{n}_{2\,as.}(r_i,r)}{n_1(r_i)n_1(r)}\right)\right]n_1(r)(r-R)dr\cdot\nabla\delta\gamma(R). \quad (4.17)$$

Here $\bar{n}_{2\,as.}$ is the asymptotic form of $\bar{n}_2$.

[14] H. S. Green, *Molecular Theory of Fluids* (Interscience Publishers, New York, 1952), Chap. 5, Sec. 5.
[15] J. G. Kirkwood and E. M. Boggs, J. Chem. Phys. **10**, 394 (1942).

We proceed next to the case of a slowly varying local temperature, anticipating that low order distributions will again maintain their equilibrium form. Changing the function $\beta(r)$ in (4.4) has two effects on $\bar{n}_s$ of (4.6). First, there are one-body terms which will alter, namely $\gamma(r)$ and the $\exp\{-\frac{3}{2}\ln[2\pi mkT(r)]\}$ arising from normalization of the momentum distribution. We have just seen that a slow alteration of a one-body term leads to an $\bar{n}_2$ in which this term may be taken as literally constant. There remains then the effect upon the two-body potential terms, that is, upon

$$\beta(q,r)\phi(q,r) \equiv \frac{1}{2}[\beta(q) + \beta(r)]\phi(q,r).$$

Clearly

$$\delta(\beta\phi) = \frac{1}{2}[\delta\beta(q) + \delta\beta(r)]\phi(q,r).$$

It is now only necessary to extend Eqs. (4.8)–(4.10) to two-body variations. Doing so, we have

$$2\frac{\delta\bar{n}_s(r_1,\cdots,r_s)}{\delta\beta\phi(q,r)} = \bar{n}_s(r_1,\cdots,r_s)\sum_{i\neq j}\delta(r_i-q)\delta(r_j-r)$$

$$+ \bar{n}_{s+1}(r_1,\cdots,r_s,q)\sum\delta(r_i-r)$$

$$- \bar{n}_{s+1}(r_1\cdots r_s,r)\sum\delta(r_j-r)$$

$$+ \bar{n}_{s+2}(r_1,\cdots,r_s,q,r)$$

$$- \bar{n}_s(r_1,\cdots,r_s)\bar{n}_2(q,r), \quad (4.18)$$

from which

$$2\delta\bar{n}_s(r_1,\cdots,r_s) = \int\delta\beta\phi(q,r)[\bar{n}_{s+2}(r_1,\cdots,r_s,q,r)$$

$$- \bar{n}_s(r_1,\cdots,r_s)\bar{n}_2(q,r)]dqdr$$

$$+ 2\int\sum\delta\beta\phi(r_i,q)[\bar{n}_{s+1}(r_1,\cdots,r_s,q)$$

$$- \bar{n}_s(r_1,\cdots,r_s)n_1(q)]dq + 2\bar{n}_s(r_1,\cdots,r_s)$$

$$\times\int\sum\delta\beta\phi(r_i,q)n_1(q)dq$$

$$+ \bar{n}_s(r_1,\cdots,r_s)\sum'\delta\beta\phi(r_i,r_j), \quad (4.19)$$

where $\sum'$ denotes the omission of $i = j$.

Our inquiry now concerns the extent to which the change in $\bar{n}_s(r_1,\cdots,r_s)$ differs from that which would occur due to a uniform change in temperature corresponding to that at the midpoint $R = (1/s)\sum r_i$ of $r_1,\cdots,r_s$. Thus, being more explicit, we wish to consider

$$\bar{n}_s(r_1,\cdots,r_s;\beta(r)+\delta\beta(r)) - \bar{n}_s(r_1,\cdots,r_s;\beta(r)+\delta\bar{\beta}),$$

the difference of two types of variation, where $\delta\bar{\beta}$ is the uniform variation $\delta\beta(R)$, and $\gamma(r)$ is the same for both distributions. Again, this difference may be divided into an asymptotic and a residual part:

$$2[\bar{n}_s(r_1,\cdots,r_s;\beta(r)+\delta\bar{\beta}) - \bar{n}_s(r_1,\cdots,r_s;\beta(r)+\delta\beta(r))]$$

$$= (n^3\bar{\chi}/N\beta)\partial\bar{n}_s(r_1,\cdots,r_s)/\partial n\left[\int\Delta(q,r,\bar{r})\bar{n}_2(q,r)dqdr\right.$$

$$\left. + 2\int\sum\Delta(q,r_i,R)n_1(q)dq\right] + T_1 + T_2 + T_3 + T_4,$$

where

$$T_1 = \int \Delta(\mathbf{q},\mathbf{r},\mathbf{R})[\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)\bar{n}_2(\mathbf{q},\mathbf{r})$$

$$- \bar{n}_{s+2}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{q},\mathbf{r}) + (n^3\bar{\chi}/N\beta)\partial\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)/$$

$$\partial n \partial \bar{n}_2(\mathbf{q},\mathbf{r})/\partial n]d\mathbf{q}d\mathbf{r},$$

$$T_2 = \int \sum \Delta(\mathbf{q},\mathbf{r}_i,\mathbf{R})[\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)n_1(\mathbf{q})$$

$$(4.20)$$

$$- \bar{n}_{s+1}(\mathbf{r}_1,\cdots,\mathbf{r}_s,\mathbf{q}) + (n^3\bar{\chi}/N\beta)\partial\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)/$$

$$\partial n \partial n_1(\mathbf{q})/\partial n]d\mathbf{q},$$

$$T_3 = -2\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)\int \sum \Delta(\mathbf{q},\mathbf{r}_i,\mathbf{R})n_1(\mathbf{q})d\mathbf{q},$$

$$T_4 = -\bar{n}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)\sum{}'\Delta(\mathbf{r}_i,\mathbf{r}_j,\mathbf{R}),$$

and

$$\Delta(\mathbf{q},\mathbf{r},\mathbf{R}) \equiv [\tfrac{1}{2}\delta\beta(\mathbf{q})+\tfrac{1}{2}\delta\beta(\mathbf{r})-\delta\beta(\mathbf{R})]\phi(\mathbf{q},\mathbf{r}).$$

The "unperturbed" distributions all have temperature dependence $\beta(\mathbf{r})$, although this is not explicitly indicated. The elimination of correction terms T_1-T_4 in (4.20) is possible once more only if $s=1$ or 2, which we henceforth assume.

In order to reduce (4.20), let us more carefully define the slow variation of $\delta\beta$, in the sense that if L is a macroscopic length, l a microscopic one, then $L\nabla\delta\beta$ is of order $\delta\beta$, but $l\nabla\delta\beta$ and $l^2\nabla\nabla\delta\beta$ may be taken as zero. Consider first the term T_1. Again assuming local dependence of $\bar{n}_{s+2}$, $\bar{n}_2$, ϕ on interparticle distance alone, both $\phi(\mathbf{q},\mathbf{r})$ and $[\bar{n}_s\bar{n}_2-\bar{n}_{s+2}\cdots]$ are unchanged by an inversion through the center of mass: $\mathbf{x}\to 2\mathbf{R}-\mathbf{x}$. But $\phi(\mathbf{q},\mathbf{r})$ insists that $\mathbf{q}$ be close to $\mathbf{r}$ and the asymptotic deviation $[\bar{n}_s\bar{n}_2-\bar{n}_{s+2}\cdots]$ then requires that $\mathbf{q}$ and $\mathbf{r}$ be within the order of a correlation length from $\{\mathbf{r}_1,\mathbf{r}_2\}$. Since the coefficient of $\phi(\mathbf{q},\mathbf{r})$, averaged with its inversion, is

$$\tfrac{1}{2}[\tfrac{1}{2}\delta\beta(\mathbf{q})+\tfrac{1}{2}\delta\beta(\mathbf{r})-\delta\beta(\mathbf{R})]$$
$$+\tfrac{1}{2}[\tfrac{1}{2}\delta\beta(2\mathbf{R}-\mathbf{q})+\tfrac{1}{2}\delta\beta(2\mathbf{R}-\mathbf{r})-\beta(\mathbf{R})],$$

with leading term now going as $l^2\nabla\nabla\beta(\mathbf{R})$, the term T_1 may be dropped. The elimination of T_2 and T_3 proceeds in precisely the same fashion, while for T_4 an average over inversions is both impossible and unnecessary.

Thus only the asymptotic contributions to (4.20) remain, and the second of these vanishes for the same reason as that ascribed to T_3. Since the resulting relation is equally applicable to variations of $\bar{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ and $n_1(\mathbf{R})$, it follows that, as in (4.16),

$$\bar{n}_2[\mathbf{r}_1,\mathbf{r}_2; \beta(\mathbf{r})+\delta\beta(\mathbf{r})]-\bar{n}_2[\mathbf{r}_1,\mathbf{r}_2; \beta(\mathbf{r})+\delta\bar{\beta}]$$

$$=\left(\frac{\partial n_2(\mathbf{r}_1,\mathbf{r}_2)}{\partial n}\Big/\frac{\partial n_1(\mathbf{R})}{\partial n}\right)\{n_1[\mathbf{R}; \beta(\mathbf{r})+\delta\beta(\mathbf{r})]$$

$$-n_1[\mathbf{R}; \beta(\mathbf{r})+\delta\bar{\beta}]\}. \quad (4.21)$$

Combining with (4.16), we see that a uniform change of reciprocal temperature $\delta\bar{\beta}$ followed by an alteration of $\gamma(\mathbf{r})$ sufficient to bring $n_1(\mathbf{R}; \beta+\delta\bar{\beta})$ to its true value $n_1(\mathbf{R}; \beta+\delta\beta)$ results in a value of $\bar{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ identical with that produced by the nonuniform change $\delta\beta(\mathbf{r})$. This infinitesimal process can then be iterated to show that a slowly varying temperature, with no restriction on the magnitude of its change in the large, can be reduced insofar as $\bar{n}_2(\mathbf{r}_1,\mathbf{r}_2)$ is concerned to a uniform temperature $\beta(\mathbf{R})$ with modified $\gamma(\mathbf{r})$ and thus to the corresponding equilibrium distribution at $\beta(\mathbf{R})$, $n_1(\mathbf{R})$. As a consequence of the analyses of (4.16) and (4.21), the validity of (4.7) for $s=2$ has now been demonstrated.

In Appendix D, we show that the pattern of inference established above may be reversed, in that the asymptotic forms (2.22, 3.23) are themselves consequences of the local character of distribution functions together with the basic Ornstein-Zernike relation.

5. CONCLUSION

We have shown in this paper how the assumption of the existence of a finite correlation length in a fluid yields explicit expressions for the $(1/N)$ terms in the joint distribution of two sets of particles which are far apart compared to the correlation length. The form of these terms was then utilized to prove the local nature of the low order distributions in a system with spatially varying intensive parameters.

It appears to us that the central problem in the theory of equilibrium fluids is the proof of the existence of such a length. As mentioned in the introduction, this is related to the distinction between fluids and crystals and hence to phase transitions between these forms.

APPENDIX A

In this appendix we attempt to give a more rigorous mathematical formulation of the concepts of finite correlation length and asymptotic form of distribution functions. It is clear that these concepts can be made precise only when we have some procedure for letting the particle number N approach infinity. When the system is completely uniform, i.e., periodic boundary conditions, this passage to the limit is indeed straightforward: $N\to\infty$, $V\to\infty$, $N/V=n$ (although even here one may have to specify the ratios of the various sides).

For a nonuniform system, we may imagine the restriction to successively larger volumes V by imposition of an appropriate (short range and infinite) wall potential. All other conditions are to be held fixed at

predetermined values throughout space: internal and external (e.g., gravitational) potentials, as well as local (for a local-equilibrium ensemble) temperature and chemical potential. We assume then that these quantities are sufficiently bounded that if the particle number $N(V)$ for each volume is suitably chosen, the distributions $n_k(\mathbf{r}_1, \cdots, \mathbf{r}_k; N)$ of finite order k will possess limiting values $n_k(\mathbf{r}_1, \cdots, \mathbf{r}_k)$ as $N \to \infty$. The value of $n_k(\mathbf{r}_1, \cdots, \mathbf{r}_k)$ may of course depend on the way the volume becomes infinite. In the following we shall think particularly of two ways of passing to the limit: the first is such that the positions of all k particles become infinitely far from the walls, the second that some of the walls remain located at a finite distance from the k particles. As a prototype of the first situation we start with a cube defined by $-\frac{1}{2}L \leq x$, y, $z \leq \frac{1}{2}L$ and then let $L \to \infty$, while the second may be represented by starting instead with a cube $0 \leq x \leq L$, $-\frac{1}{2}L \leq y$, $z \leq \frac{1}{2}L$. The second situation is necessary for the examination of wall effects on the distributions in the limit of infinite L for an otherwise uniform system.

We will now specialize our discussion to the one and two-particle distributions. The two-particle Ursell function for given N, V is

$$\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) \equiv n_2(\mathbf{r}_1, \mathbf{r}_2; N) - n(\mathbf{r}_1; N) n(\mathbf{r}_2; N). \quad \text{(A.1)}$$

$\mathfrak{F}$ vanishes when either of the particle coordinates is outside V and has the property that

$$\int_V \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) d\mathbf{r}_2 = -n(\mathbf{r}_1; N). \quad \text{(A.2)}$$

Our previous assumption assures the existence of

$$\lim_{N \to \infty} \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) = \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2) = n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1) n(\mathbf{r}_2). \quad \text{(A.3)}$$

The Ursell function $\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2)$ is defined in such a fashion that it vanishes for statistically independent particles. The correlation length of a fluid is therefore related to the scale on which $\mathfrak{F}_2$ vanishes as $|\mathbf{r}_{12}|$ increases. The possibility of correlation over large distances may be intrinsic, as in a crystal or at the critical point, or may be due simply to the constraint of a fixed number of particles in the system. It is clearly the second part of this long-range correlation with which we are concerned in this paper. The magnitude of this nonintrinsic correlation will vanish as the size of the system increases. Hence in the absence of intrinsic long-range correlation, which we here assume, we will in the limit have for some m

$$\int r_{12}{}^l |\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2)| d\mathbf{r}_2 = 0(1) \quad \text{for} \quad 0 < l < m. \quad \text{(A.4)}$$

The value of m determines the rate at which $\mathfrak{F}_2$ approaches zero as $r_{12} \to \infty$; if (A.4) holds for all l, the approach is exponentially fast.

In addition to vanishing rapidly at large separation, $\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2)$ will only have a small fractional deviation from $\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N)$ at small $\mathbf{r}_{12}$. Hence the difference

$$\phi_2(\mathbf{r}_1, \mathbf{r}_2; N) \equiv \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) - \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2) \quad \text{(A.5)}$$

(defined as vanishing outside of V) may be termed the asymptotic part of $\mathfrak{F}_2(N)$. In applications, use is made of the short-range character of $\mathfrak{F}_2$, coupled with properties of the integrals of $\phi_2(N)$ over the full volume, or more precisely of

$$\lim_{N \to \infty} \int_V \phi_2(\mathbf{r}_1, \mathbf{r}_2; N) \chi(\mathbf{r}_2) d\mathbf{r}_2, \quad \text{(A.6)}$$

where $\chi(\mathbf{r}_2)$ is a bounded function: $|\chi(\mathbf{r}_2)| < M$.

We shall first discuss the value of the integral (A.6) when $\chi(\mathbf{r}_2)$ is a constant. This will yield sufficient information about $\phi_2(N)$ that the properties of (A.6) will be obtained with few further assumptions. The advantage of the restriction to χ being a constant is that since

$$\int_V \phi_2(\mathbf{r}_1, \mathbf{r}_2; N) d\mathbf{r}_2 = -n(\mathbf{r}_1; N) - \int_V \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_2 \quad \text{(A.7)}$$

[employing (A.2) and (A.5)], then only the integral of $\mathfrak{F}_2$ is required, which being short-range can be found by integrating over a finite volume as $V \to \infty$.

Consider now the process discussed in Sec. 2 of dividing the volume V into V_A and $V_B = V - V_A$. Using the previous notation, we have

$$\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) = \langle n_2(\mathbf{r}_1, \mathbf{r}_2 | N_A, N - N_A) \rangle$$
$$- \langle n(\mathbf{r}_1) | N_A, N - N_A \rangle \langle n(\mathbf{r}_2) | N_A, N - N_A \rangle. \quad \text{(A.8)}$$

If $\mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N)$ is integrated over V_B with $\mathbf{r}_1$ in V_A, then from (A.8)

$$\int_{V_B} \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2; N) d\mathbf{r}_2 = \langle (N - N_A) n(\mathbf{r}_1 | N_A, N - N_A) \rangle$$
$$- \langle N - N_A \rangle \langle n(\mathbf{r}_1 | N_A, N - N_A) \rangle$$
$$= - \langle N_A n(\mathbf{r}_1 | N_A, N - N_A) \rangle$$
$$+ \langle N_A \rangle \langle n(\mathbf{r}_1 | N_A, N - N_A) \rangle$$
$$= - \sum_{k=2}^{\infty} \frac{\langle (\delta N_A)^k \rangle}{(\bar{N}_A)^{k-1}} \frac{\bar{n}_A{}^k}{k!} \left[\frac{\partial^k}{\partial \bar{n}_A{}^k} [\bar{n}_A n(\mathbf{r}_1 | \bar{N}_A, N - \bar{N}_A)] \right.$$
$$\left. - \bar{n}_A \frac{\partial^k n(\mathbf{r}_1 | \bar{N}_A, N - \bar{N}_A)}{\partial \bar{n}_A{}^k} \right] \quad \text{(A.9)}$$

where $\bar{n}_A = \bar{N}_A / V_A$, $\delta N_A = N_A - \bar{N}_A$. By taking the limit of N, $V \to \infty$, with V_A remaining fixed, it follows

that

$$\int_{V_A} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = \int_{V_A} \lim_{N\to\infty} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2$$

$$= \lim_{N\to\infty} \int_{V_A} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2$$

$$= -n(\mathbf{r}_1) - \lim_{N\to\infty} \int_{V_B} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2$$

$$= -n(\mathbf{r}_1) + \sum_{k=2}^{\infty} \frac{\langle(\delta N_A)^k\rangle}{(\bar{N}_A)^{k-1}} \frac{\bar{n}_A^k}{k!}$$

$$\times \left[\frac{\partial^k}{\partial \bar{n}_A^k}[\bar{n}_A n(\mathbf{r}_1|\bar{N}_A, N-\bar{N}_A)] \right.$$

$$\left. -\bar{n}_A \frac{\partial^k n(\mathbf{r}_1|\bar{N}_A, N-\bar{N}_A)}{\partial \bar{n}_A^k} \right], \quad (A.10)$$

where all quantities on the right-hand side are to be taken in the limit of V becoming infinite.

Next let $\bar{N}_A$ increase to infinity. The quantities inside the square brackets in (A.10) are of at most $O(1)$, and this remains true if for the purposes of rigor the series is truncated, the final term being evaluated at other than $\bar{N}_A$. We now assume that the fluctuations in N_A are bounded in order of magnitude by the fluctuations in a grand canonical ensemble, where it can be shown that

$$\langle(\delta N_A)^k\rangle \leq O(\bar{N}_A^{k/2}). \quad (A.11)$$

This yields, for V_A approaching infinity in such a way that $\mathbf{r}_1$ becomes infinitely far from the interface S_A (although not necessarily far from the container walls),

$$\int_{V_A} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2$$
$$= -n(\mathbf{r}_1) + n^2 kT\bar{\chi}\partial n(\mathbf{r}_1)/\partial n + o(1), \quad (A.12)$$

where we have defined

$$\lim_{\bar{N}_A\to\infty} \frac{\langle(\delta N_A)^2\rangle}{\bar{N}_A} = nkT\bar{\chi}, \quad (A.13)$$

with the understanding that to order $o(1)$ in N_A, $nkT\bar{\chi}(\bar{N}_A)$ and $n(\mathbf{r}_1,\bar{N}_A)$ coincide with their limiting values. But according to (A.4),

$$\int \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 = \int_{V_A} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2 + o(1). \quad (A.14)$$

It follows from (A.7) and (A.12) that

$$\lim_{N\to\infty} \int \phi_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2 = -n^2 kT\bar{\chi}\frac{\partial n(\mathbf{r}_1)}{\partial n}, \quad (A.15)$$

which is the result desired.

At fixed $\mathbf{r}_1$, characterization of $\phi_2(\mathbf{r}_1,\mathbf{r}_2; N)$ will entail two regions of interest. For $\mathbf{r}_2$ separated microscopically from $\mathbf{r}_1$, the general argument following (2.10) suggests that the effect of the boundary may cause $\mathfrak{F}_2(N)$ to deviate from $\mathfrak{F}_2$ by the order of $(1/N)O(N^{\frac{2}{3}}) = O(N^{-\frac{1}{3}})$. For $\mathbf{r}_2$ outside an intrinsic correlation length from $\mathbf{r}_1$, the effect of the constraint (of precisely N particles in V) could still introduce terms of order $O(N^{-\frac{1}{3}})$. However, this could certainly not be true in a uniform sense, due to the existence of the integral (A.15). We would like to argue that in this region, the dominant term in $\phi_2(N)$ is given by the second term on the right-hand side of (2.19), which is of order $O(1/N)$. This is certainly compatible with Eq. (A.15) and as we shall see is almost implied by it.

A very strong argument for this behavior of $\phi_2(N)$ can be made by considering rather than $\phi_2(\mathbf{r}_1,\mathbf{r}_2; N)$ a very similar quantity

$$\phi_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) \equiv \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) - \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2) \quad (A.16)$$

where

$$\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) = \lim_{N\to\infty} \mathfrak{F}_2(\mathbf{r}_1, \mathbf{r}_2|\bar{N}_A, N-\bar{N}_A).$$

$\phi_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A)$ is the deviation of the Ursell function for an infinite system without any constraints from the one for the same system when a given volume V_A is constrained to contain $\bar{N}_A$ particles. As far as the constraint of a fixed number of particles is concerned, the subsystem inside V_A may be regarded as a closed system with a special type of boundary. The function $\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A)$ should therefore mimic for $\mathbf{r}_1$, $\mathbf{r}_2$ inside V_A the behavior of the function $\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2; \bar{N}_A)$ for a closed system of $\bar{N}_A$ particles inside the container V_A. Indeed, as far as the integral over V_A is concerned, the two functions have the same behavior:

$$\int_{V_A} \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A)d\mathbf{r}_2 = -n(\mathbf{r}_1|\bar{N}_A). \quad (A.17)$$

The properties of $\phi_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A)$ can be found from an expansion similar to that leading to (A.9), which yields, as a development in $(1/\bar{N}_A)$,

$$\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) = \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2) - \langle(\delta N_A)^2\rangle \left[\frac{\partial^2}{\partial \bar{N}_A^2}\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) \right.$$

$$\left. + \frac{\partial}{\partial \bar{N}_A}n(\mathbf{r}_1|\bar{N}_A)\frac{\partial}{\partial \bar{N}_A}n(\mathbf{r}_2|\bar{N}_A) \right] + \cdots. \quad (A.18)$$

For $\mathbf{r}_1$ and $\mathbf{r}_2$ far from each other, this expression reduces to

$$\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2|\bar{N}_A) - \mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)$$

$$= \frac{1}{\bar{N}_A}nkT\bar{\chi}\frac{\partial n(\mathbf{r}_1)}{\partial \bar{n}_A}\frac{\partial n(\mathbf{r}_2)}{\partial \bar{n}_A} + \cdots, \quad (A.19)$$

if $\mathbf{r}_1$ and $\mathbf{r}_2$ are both interior to V_A (the correction term vanishes otherwise). The right-hand side of the expression is indeed of the same form as that found in (2.19) for the function $\phi_2(\mathbf{r}_1,\mathbf{r}_2; \bar{N}_A)$.

Let us now return to the discussion of $\phi_2(\mathbf{r}_1,\mathbf{r}_2; N)$. On the basis of (A.15), we divide $\phi_2(N)$ into two parts:

$$\phi_2(\mathbf{r}_1,\mathbf{r}_2; N)=N^{-1}\phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2; N)+\phi_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2; N). \quad (A.20)$$

Here $\phi_2^{(0)}(N)$ is to remain bounded as $N \to \infty$, i.e., $\phi_2^{(0)}(N)=O(1)$, and satisfies

$$\lim_{N\to\infty} \frac{1}{N} \int \phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2= -n^2kT\bar{\chi}\frac{\partial n(r_1)}{\partial n}; \quad (A.21)$$

the remainder $\phi_2^{(1)}(N)$ may be of order greater than $O(1/N)$ but by virtue of (A.15) must satisfy

$$\lim_{N\to\infty} \int \phi_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2=0. \quad (A.22)$$

The decomposition (A.20) is of course not unique, since one can for example add and subtract any term of order $o(1/N)$.

The vanishing in the limit of the integral (A.22) can occur in two basic ways. First, the part of $\phi_2^{(1)}(N)$ which is of order greater than $O(1/N)$ may be effectively restricted to a finite region. Second, $\phi_2^{(1)}(N)$ may be of order greater than $O(1/N)$ over the full volume, but have an oscillatory character leading to a vanishing integral. We assume now that in a fluid the latter situation does not arise and express this formally by the condition that a decomposition (A.20) exists for which

$$\lim_{N\to\infty} \int |\phi_2^{(1)}(\mathbf{r}_1,\mathbf{r}_2; N)| d\mathbf{r}_2=0. \quad (A.23)$$

This assumption implies that

$$\lim_{N\to\infty} \int \chi(\mathbf{r}_1,\mathbf{r}_2)\phi_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2$$

$$= \lim_{N\to\infty} \frac{1}{N} \int \chi(\mathbf{r}_1,\mathbf{r}_2)\phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2, \quad (A.24)$$

where χ is an arbitrary bounded function of $\mathbf{r}_1$ and $\mathbf{r}_2$. Hence in all applications in this paper we need only be concerned with the value of $\phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2; N)$.

Consider now a homogeneous system. Let us denote the limiting value of $\phi_2^{(0)}(N)$ by $\phi_2^{(0)}$,

$$\lim_{N\to\infty} \phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2; N)=\phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2), \quad (A.25)$$

and its asymptotic part by ψ,

$$\lim_{|\mathbf{r}_2|\to\infty} \phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\psi(\mathbf{r}_1), \quad (A.26)$$

both of which limits we assume to exist. The existence

of these limits means that we discard the possibility of $\phi_2^{(0)}(N)$ having an oscillatory behavior extending the length of the container. The limit $|\mathbf{r}_2| \to \infty$ is here to be taken in such a way that $\mathbf{r}_2$ moves infinitely far from the walls. Combining Eqs. (A.21) and (A.26) yields

$$\psi(\mathbf{r}_1)= -n^3kT\bar{\chi}\partial n(r_1)/\partial n, \quad (A.27)$$

so that finally, using (A.24),

$$\int \chi(\mathbf{r}_1,\mathbf{r}_2)\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2; N)d\mathbf{r}_2= \int \chi(\mathbf{r}_1,\mathbf{r}_2)\mathfrak{F}_2(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2$$

$$-n^3kT\bar{\chi}\frac{\partial n(r_1)}{\partial n}\left[N^{-1}\int \chi(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_2\right]+o(1). \quad (A.28)$$

For a system which is not completely uniform, the limit (A.26) may still exist if the system is asymptotically uniform, in which case (A.28) clearly remains valid. However, if the region $|\mathbf{r}_2| \to \infty$ is not uniform, (A.26) will not hold and must be replaced by the strong assumption of statistical independence of distant parts, i.e.,

$$\lim_{|\mathbf{r}_{12}|\to\infty} \phi_2^{(0)}(\mathbf{r}_1,\mathbf{r}_2)=\psi(\mathbf{r}_1)\psi(\mathbf{r}_2). \quad (A.26')$$

This is perhaps the strongest assumption we have made and it may possibly be violated at low temperatures. If we do make this assumption, then (A.28) again holds, and we further have on combining with previous equations

$$\phi_2(N)=\frac{1}{N}n^3kT\bar{\chi}\frac{\partial n_1(\mathbf{r}_1)}{\partial n}\frac{\partial n_1(\mathbf{r}_2)}{\partial n}$$

$$+\phi_2'(N)+o(1/N), \quad (A.29)$$

where

$$\int |\phi_2'(N)| d\mathbf{r}_2=o(1).$$

The generalization of the above discussion to higher Ursell functions is quite direct and will not be carried out, but the final expression will be written down in Appendix C.

APPENDIX B

In this Appendix, we extend Eq. (2.22) for the asymptotic value of a distribution function to fluid mixtures. This result is then applied along the lines of Ornstein and Zernike to the scattering of visible light from mixtures. For simplicity, we shall consider explicitly only the case of a two-component fluid consisting of N_a atoms of one kind and N_b of another kind.

The joint distribution of m_1 particles of species a and m_2 of species b will be written as $n_{m_1 m_2}$. The asymptotic values of $n_{q_1+p_1 q_2+p_2}$ when the subset consisting of q_1 particles of a and q_2 particles of b is very far from the other particles can be found by an

investigation similar to that used for the one-component fluid. It yields

$$n_{q_1+p_1\ q_2+p_2} \rightarrow n_{q_1q_2}n_{p_1p_2}$$

$$-\sum_{\alpha\beta}\left(kT\frac{\partial N_\alpha}{\partial\mu_\beta}\right)\frac{\partial n_{q_1q_2}}{\partial N_\alpha}\frac{\partial n_{p_1p_2}}{\partial N_\beta}, \quad (B.1)$$

where α and β can assume the values a and b, and

$$\partial N_\alpha/\partial\mu_\beta = \partial N_\beta/\partial\mu_\alpha. \quad (B.2)$$

When a parallel incident beam of radiation of intensity I_0 and frequency ν falls upon this fluid, the intensity of the radiation at distance r which has been scattered at angle θ may be computed in a way entirely analogous to that used for a single component fluid.[16] It is given by

$$I(\theta)=\tfrac{1}{2}(1+\cos^2\theta)I_0(r_0/r)^2\left\{N_af_a^2+N_bf_b^2+\int\int\left[f_a^2n_{aa}\right.\right.$$

$$\left.\left.+2f_af_bn_{ab}+f_b^2n_{bb}\right]e^{i\mathbf{K}\cdot\mathbf{r}_{12}}d\mathbf{r}_1d\mathbf{r}_2.\right\} \quad (B.3)$$

Here f_a and f_b are the atomic scattering factors for single atoms of type a and b, respectively, $r_0=e^2/m_ec^2$ is the classical radius of the electron, the $n_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)$ denote the two self- and one mutual- two-body distributions, and $\mathbf{K}$ is the change in wave vector on scattering [$K=(4\pi\nu/c)\sin\tfrac{1}{2}\theta$].

In the above, we can subtract a constant term from any $n_{\alpha\beta}$ since for a system of volume V this will contribute only when $K\sim V^{-\frac{1}{3}}$ and is thus indistinguishable from the transmitted beam as $V\rightarrow\infty$. We shall therefore subtract the corresponding asymptotic value. The integrand in (A.3) then exists only for small values of r_{12}, of the order of the correlation length. Further, if the system is uniform, then

$$n_{\alpha\beta}(\mathbf{r}_1,\mathbf{r}_2)=n_\alpha n_\beta g_{\alpha\beta}(r_{12}), \quad (B.4)$$

and Eq. (B.3) can be rewritten as

$$I(s)=\tfrac{1}{2}(1+\cos^2\theta)I_0(r_0/r)^2Vj(s), \quad (B.5)$$

where

$$j(s)=n_af_a^2+n_bf_b^2+\int_0^\infty\{f_a^2n_a^2[g_{aa}(r)-g_{aa}(\infty)]$$

$$+2f_af_bn_an_b[g_{ab}(r)-g_{ab}(\infty)]$$

$$+f_b^2n_b^2[g_{bb}(r)-g_{bb}(\infty)]\}4\pi r^2\left(\frac{\sin rs}{rs}\right)dr, \quad (B.6)$$

and

$$s=(4\pi\nu/c)\sin\tfrac{1}{2}\theta$$

(reducing correctly to the one-component case when $f_a=f$, $g_{\alpha\beta}=g$, $n_a+n_b=n$). Equations (B.5) and (B.6) are appropriate for determining the long-wavelength

limit. If ν is sufficiently low that

$$c/\nu\gg l, \quad (B.7)$$

where l is the correlation length—beyond which the integrand in (B.6) must vanish—then $s\ll 1/l$, and we may replace $\sin rs/rs$ by 1. Writing

$$n_{\alpha\beta}(\infty)=n_\alpha n_\beta-(1/V)\gamma_{\alpha\beta}, \quad (B.8)$$

it readily follows that

$$j(s)\rightarrow j(0)=\gamma_{aa}f_a^2+\gamma_{bb}f_b^2+2\gamma_{ab}f_af_b. \quad (B.9)$$

But according to (B.1), we can write

$$\gamma_{\alpha\beta}=kT\left(\frac{\partial n_\alpha}{\partial\mu_\beta}\right)\Bigg|_{T,V,\mu_\alpha}. \quad (B.10)$$

Equations (B.9) and (B.10) constitute the result desired.

APPENDIX C

We now extend Eq. (2.22) to the asymptotic value of the intrinsic correlation functions. These may be defined by the sequence of relations

$$\mathcal{F}_1(\mathbf{r})=n_1(\mathbf{r}),$$

$$\mathcal{F}_2(\mathbf{r},\mathbf{r}')=n_2(\mathbf{r},\mathbf{r}')-n_1(\mathbf{r})n_1(\mathbf{r}'),$$

$$\mathcal{F}_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')=n_3(\mathbf{r},\mathbf{r}',\mathbf{r}'')-n_2(\mathbf{r},\mathbf{r}')n_1(\mathbf{r}'') \quad (C.1)$$

$$-n_2(\mathbf{r},\mathbf{r}'')n_1(\mathbf{r}')-n_2(\mathbf{r}',\mathbf{r}'')n_1(\mathbf{r})$$

$$+2n_1(\mathbf{r})n_1(\mathbf{r}')n_1(\mathbf{r}'')\cdots.$$

The fundamental property possessed by $\mathcal{F}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)$ is that of vanishing in any region in which the set $\mathbf{r}_1,\ \cdots,\ \mathbf{r}_s$ decomposes into two or more independent subsets, i.e., such that the distribution functions n_t correspondingly decompose into products. This is because all correlations due to subsets have been subtracted in forming $\mathcal{F}_s$ from n_s, leaving only the "intrinsic" s-body correlation.

The connection between the n_s and the $\mathcal{F}_s$ may be defined more concisely. For this purpose, introduce a "test function" $f(\mathbf{r})$, and integrate to form the constants (functionals of f)

$$n_s[f]=\int\cdots\int n_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)f(\mathbf{r}_1)\cdots f(\mathbf{r}_s)d\mathbf{r}_1\cdots d\mathbf{r}_s,$$
$$\quad (C.2)$$

$$\mathcal{F}_s[f]=\int\cdots\int \mathcal{F}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s)f(\mathbf{r}_1)\cdots f(\mathbf{r}_s)d\mathbf{r}_1\cdots d\mathbf{r}_s,$$

and the combinations

$$n[f]=\sum_0^\infty n_s[f]/s!,\quad n_0\equiv 1 \quad (C.3)$$

$$\mathcal{F}[f]=\sum_1^\infty \mathcal{F}_s[f]/s!.$$

[16] Reference 13, Chap. 3, Sec. 1.

The distribution functions may be recovered by variational differentiation:

$$n_s(\mathbf{r}_1,\cdots,\mathbf{r}_s) = \frac{\delta^s n[f]}{\delta f(\mathbf{r}_1)\cdots\delta f(\mathbf{r}_s)}\bigg|_{f=0},$$

$$\mathfrak{F}_s(\mathbf{r}_1,\cdots,\mathbf{r}_s) = \frac{\delta^s \mathfrak{F}[f]}{\delta f(\mathbf{r}_1)\cdots\delta f(\mathbf{r}_s)}\bigg|_{f=0}. \quad (\text{C.4})$$

It is then found that the sequence (C.1) achieves the very concise form

$$\mathfrak{F}[f] = \ln n[f]. \quad (\text{C.5})$$

The required extension of (2.22, 3.23) is now readily accomplished. From (3.17), we have

$$n[f] = n^{(0)}[f] - \frac{1}{N}\frac{n\bar\chi}{2\beta}n^2\frac{\partial^2}{\partial n^2}n^{(0)}[f]\cdots, \quad (\text{C.6})$$

and (C.5) becomes

$$\mathfrak{F}[f] = \ln n^{(0)}[f] - \frac{1}{n^{(0)}[f]}\frac{1}{N}\frac{n\chi}{2\beta}n^2\frac{\partial^2 n^{(0)}[f]}{\partial n^2}\cdots$$

$$= \left(1 - \frac{1}{N}\frac{n\bar\chi}{2\beta}n^2\frac{\partial^2}{\partial n^2}\right)\ln n^{(0)}[f]$$

$$- \frac{1}{N}\frac{n\bar\chi}{2\beta}\left(n\frac{\partial\ln n^{(0)}[f]}{\partial n}\right)^2\cdots. \quad (\text{C.7})$$

To find $\mathfrak{F}_{q+l}$, we must apply $\delta^{q+l}/\delta f(\mathbf{r}_1)\cdots\delta f(\mathbf{r}_{q+l})|_{f=0}$. But suppose that the sets q, l are asymptotically separated. Then according to (3.22), the $n_s^{(0)}$ decompose accordingly, so that $\mathfrak{F}_{q+l}^{(0)}$ obtained from $\ln n^{(0)}[f]$ must vanish. In the same fashion, there can be no contribution from the $[n\partial\ln n^{(0)}[f]/\partial n]^2$ term unless the complete set of derivatives corresponding to the set q operates on one factor, those for set l on the other. We conclude at once that

$$\mathfrak{F}_{q+l} \to -\frac{1}{N}\frac{n\bar\chi}{\beta}n\frac{\partial\mathfrak{F}_q}{\partial n}n\frac{\partial\mathfrak{F}_l}{\partial n}, \quad (\text{C.8})$$

the desired result. It should be pointed out that our final expression (C.8) depends only upon the asymptotic form of the distribution functions, and its validity is therefore not restricted to the gas region for which the separation into $n^{(0)}$ and a remainder [necessary for (C.6)] is possible.

We may note that $\mathfrak{F}_s$ becomes a higher order infinitesimal than $1/N$ if its particles divide into three or more groups. Another consequence of the asymptotic form (C.8), which was previously discussed (see Appendix A) for the case of $\mathfrak{F}_2$, is an expression for the integrals of $\mathfrak{F}_{q+l}$ in an infinite system. Indicating the explicit dependence of Ursell functions on particle

number N, we have generally (where $q>0$)

$$\int \mathfrak{F}_{q+l}(\mathbf{r}_1\cdots\mathbf{r}_{q+l}; N)d\mathbf{r}_{q+1}\cdots d\mathbf{r}_{q+l}$$

$$= (-1)^l\frac{(q+l-1)!}{(q-1)!}\mathfrak{F}_q(\mathbf{r}_1\cdots\mathbf{r}_q; N). \quad (\text{C.9})$$

Consider now the corresponding integral for the difference of $\mathfrak{F}_{q+l}$ and its asymptotic value $\mathfrak{F}_{q+l}^{(\text{as.})}$ given by (C.8),

$$\int [\mathfrak{F}_{q+l}(\mathbf{r}_1\cdots\mathbf{r}_{q+l}; N)$$

$$- \mathfrak{F}_{q+l}^{(\text{as.})}(\mathbf{r}_1\cdots\mathbf{r}_{q+l}; N)]d\mathbf{r}_{q+1}\cdots d\mathbf{r}_{q+l}$$

$$= (-1)^l\left[\frac{(q+l-1)!}{(q-1)!}\mathfrak{F}_q(N)\right.$$

$$\left.- (l-1)!nkT\bar\chi n\frac{\partial\mathfrak{F}_q(N)}{\partial n}\right]. \quad (\text{C.10})$$

The integrand of (C.10) is of a local nature. We can therefore pass to the limit of $N\to\infty$ inside the integral sign, yielding finally

$$\int \mathfrak{F}_{q+l}(\mathbf{r}_1,\cdots,\mathbf{r}_{q+l}; \infty)d\mathbf{r}_{q+1}\cdots d\mathbf{r}_{q+l}$$

$$= (-1)^l\left[\frac{(q+l-1)!}{(q-1)!}\mathfrak{F}_q(\infty)\right.$$

$$\left.- (l-1)!nkT\bar\chi n\frac{\partial\mathfrak{F}_q(\infty)}{\partial n}\right], \quad q\geq 1 \quad (\text{C.11})$$

of which the Ornstein-Zernike relation is a special case.

APPENDIX D

Here, we "close the circle" and show, using the well-known special case $q=l=1$, that the asymptotic formula (2.22, 3.23) is implied by the local character of distribution functions. This may be done in two stages.

First consider the conditional distribution $n_q(\mathbf{r}_1,\cdots, \mathbf{r}_q|\mathbf{r}_{q+1})$ when $\mathbf{r}_{q+1}$ is far from the set $\mathbf{r}_1, \cdots, \mathbf{r}_q$ of center of mass $\mathbf{R}$. Now the effect of fixing $\mathbf{r}_{q+1}$ is to change the local density at $\mathbf{R}$ from $n(\mathbf{R})$ to

$$n'(\mathbf{R}) = n(\mathbf{R}|\mathbf{r}_{q+1})$$

$$= n(\mathbf{R}) - \frac{1}{N}\frac{n\bar\chi}{\beta n(\mathbf{r}_{q+1})}\frac{n\partial n(\mathbf{R})}{\partial n}\frac{n\partial n(\mathbf{r}_{q+1})}{\partial n}. \quad (\text{D.1})$$

Further, if $\bar n_q(\cdots; n)$ denotes the joint distribution function for a uniform density n, the local dependence of n_q on $\mathbf{R}$ tells us [see (4.13, 4.17)] that

$$n_q(\mathbf{r}_1,\cdots,\mathbf{r}_q) = \bar n_q[\mathbf{r}_1,\cdots,\mathbf{r}_q; n(\mathbf{R})]$$

$$+ \nabla n(\mathbf{R})\cdot\mathbf{A}_q(\mathbf{r}_1,\cdots,\mathbf{r}_q; n(\mathbf{R})) + \cdots \quad (\text{D.2})$$

for some appropriate vector function A_q. Also, $n_q(\mathbf{r}_1,\cdots,\mathbf{r}_q|\mathbf{r}_{q+1})$ is similarly expressed, with $n'(\mathbf{R})$ replacing $n(\mathbf{R})$. Hence

$$n_q(\mathbf{r}_1\cdots\mathbf{r}_q|\mathbf{r}_{q+1})-n_q(\mathbf{r}_1\cdots\mathbf{r}_q)$$

$$=\bar{n}_q(\mathbf{r}_1\cdots\mathbf{r}_q;n'(\mathbf{R}))-\bar{n}_q[\mathbf{r}_1\cdots\mathbf{r}_q;n(\mathbf{R})]$$

$$+\nabla n'(\mathbf{R})\cdot A_q[\mathbf{r}_1\cdots\mathbf{r}_q;n'(\mathbf{R})]$$

$$-\nabla n(\mathbf{R})\cdot A_q[\mathbf{r}_1\cdots\mathbf{r}_q;n(\mathbf{R})]+\cdots$$

$$=[n'(\mathbf{R})-n(\mathbf{R})]\frac{\partial\bar{n}_q[\mathbf{r}_1\cdots\mathbf{r}_q;n(\mathbf{R})]}{\partial n}\Big/\frac{\partial n(\mathbf{R})}{\partial n}$$

$$+[\nabla n'(\mathbf{R})-\nabla n(\mathbf{R})]\cdot A_q[\mathbf{r}_1\cdots\mathbf{r}_q;n(\mathbf{R})]$$

$$+[n'(\mathbf{R})-n(\mathbf{R})]\nabla n(\mathbf{R})$$

$$\cdot\frac{\partial A_q[\mathbf{r}_1\cdots\mathbf{r}_q;n(\mathbf{R})]}{\partial n}\Big/\frac{\partial n(\mathbf{R})}{\partial n}+\cdots. \quad (D.3)$$

Since the only $\mathbf{R}$ dependence of $n'(\mathbf{R})-n(\mathbf{R})$ is through the factor $\partial n(\mathbf{R})/\partial n$, it follows that

$$\nabla[n'(\mathbf{R})-n(\mathbf{R})]$$

$$=[n'(\mathbf{R})-n(\mathbf{R})]\nabla\Big(\frac{\partial n(\mathbf{R})}{\partial n}\Big/\frac{\partial n(\mathbf{R})}{\partial n}\Big)+\cdots. \quad (D.4)$$

Inserting in (D.3) and comparing with $\partial n_q(\mathbf{r}_1\cdots\mathbf{r}_q)/\partial n$ from (D.2), we obtain

$$n_q(\mathbf{r}_1\cdots\mathbf{r}_q|\mathbf{r}_{q+1})-n_q(\mathbf{r}_1\cdots\mathbf{r}_q)$$

$$=[n'(\mathbf{R})-n(\mathbf{R})]\frac{\partial n_q(\mathbf{r}_1\cdots\mathbf{r}_q|\mathbf{r}_{q+1})}{\partial n}\Big/\frac{\partial n(\mathbf{R})}{\partial n}$$

$$+\cdots. \quad (D.5)$$

Substituting from $n'(\mathbf{R})-n(\mathbf{R})$ of (D.1) and multiplying by $n(\mathbf{r}_{q+1})$ now results in the q, 1 case for asymptotic separation:

$$n_{q+1}(\mathbf{r}_1\cdots\mathbf{r}_q\mathbf{r}_{q+1})\to n_q(\mathbf{r}_1\cdots\mathbf{r}_q)n(\mathbf{r}_{q+1})$$

$$-\frac{1}{N}\frac{n\bar{\chi}}{\beta}\frac{n\partial n_q(\mathbf{r}_1\cdots\mathbf{r}_q)}{\partial n}\frac{n\partial n(\mathbf{r}_{q+1})}{\partial n}. \quad (D.6)$$

Next consider $n_l(\mathbf{r}_{q+1}\cdots\mathbf{r}_{q+l}|\mathbf{r}_1\cdots\mathbf{r}_q)$. The effect of fixing $\mathbf{r}_1$, $\cdots$, $\mathbf{r}_q$ is to change the local density at $\mathbf{R}'$ (center of mass of the set of l particles) from $n(\mathbf{R}')$ to $n_q(\mathbf{R}'|\mathbf{r}_1\cdots\mathbf{r}_q)$, which we have just obtained. Applying the above argument to the set of l particles then recovers the full relation (2.22, 3.23).