

Asymptotic Behavior of the Radial Distribution Function*

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The pair distribution function in a uniform classical fluid is equivalent to the one-body density when one particle is fixed. An implicit relation for this nonuniform density is found by a functional expansion of the difference of chemical potential and external potential about its value for a system of uniform density. A linearization of this expansion, followed by retention of, at most, second derivatives of the inhomogeneity, reproduces the Ornstein-Zernicke relations for the asymptotic pair correlation. Linearization alone calls for the sum of internal potential and direct correlation function to vanish asymptotically. This relation is developed for the case of weak long-range forces, resulting in the Debye-Huckel expression for an electron gas, and reproducing the asymptotic correlations of the Kac-Uhlenbeck-Hemmer one-dimensional model. The relation is also shown to follow from the virial expansion for the direct correlation function.

1. INTRODUCTION

THE qualitative properties of the radial distribution function in a uniform classical fluid are still incompletely understood. Whereas the short-range character must depend explicitly upon the interaction potential, presumably in a quite complicated fashion, it has been suggested¹ on numerous occasions that the form of the radial distribution function well outside the range of the potential is essentially universal, with at most a few parameters determined by the potential. Indeed, as a critical point is approached, and random fluctuations predominate, the specific form of the potential might be completely masked in the asymptotic region. There are however only a few instances^{2,3} in which the asymptotic correlation function has been rigorously determined.

It is the aim of this paper to consider the problem of asymptotic correlations from the point of view of local characterizations of nonuniform systems, which we have previously presented.⁴ This enables us to discuss the assumptions of the basic Ornstein-Zernicke theory,⁵ and to weaken these assumptions, giving rise to a formulation of particular use in the case of weak long-range potentials. A comparison

with the rigorously derived correlations of the Kac-Uhlenbeck model³ provides support for the essential validity of the approach used.

2. REVIEW OF FORMALISM

A method previously developed⁴ for examination of distributions and thermodynamic parameters of nonuniform classical systems will be used here. In this study, it was shown that if

$$\begin{aligned} \gamma(\mathbf{r}) &= \lambda + \beta\mu - \beta U(\mathbf{r}), \\ \lambda &= \frac{3}{2} \ln(2\pi mkT/h^2), \\ \beta &= (kT)^{-1}, \end{aligned} \tag{2.1}$$

for a system with external potential U , chemical potential μ in a grand canonical ensemble, then the multiparticle distribution functions are obtainable by successive variational differentiation of the one-body density $n(\mathbf{r})$:

$$\hat{\mathcal{F}}_1(\mathbf{r}_1) = n(\mathbf{r}_1) \tag{2.2a}$$

$$\begin{aligned} \hat{\mathcal{F}}_2(\mathbf{r}_1, \mathbf{r}_2) &= n_2(\mathbf{r}_1, \mathbf{r}_2) - n(\mathbf{r}_1)n(\mathbf{r}_2) \\ &\quad + n(\mathbf{r}_1)\delta(\mathbf{r}_1 - \mathbf{r}_2) \\ &= \delta n(\mathbf{r}_1)/\delta\gamma(\mathbf{r}_2) \end{aligned} \tag{2.2b}$$

$$\hat{\mathcal{F}}_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \delta\hat{\mathcal{F}}_2(\mathbf{r}_1, \mathbf{r}_2)/\delta\gamma(\mathbf{r}_3), \dots \tag{2.2c}$$

Here $\hat{\mathcal{F}}_s$ is the s th Ursell function,⁴ in which however the component ordinary distributions are allowed to refer to identical particles:

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

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¹ F. H. Stillinger and H. L. Frisch, *Physica* **27**, 751 (1961); M. Fischer, *Physica* **28**, 172 (1962); M. S. Green, *J. Chem. Phys.* **33**, 1403 (1960).

² B. Kaufman and L. Onsager, *Phys. Rev.* **76**, 1244 (1949).

³ M. Kac, G. E. Uhlenbeck, and P. C. Hemmer, *J. Math. Phys.* **4**, 216 (1963).

⁴ J. L. Lebowitz and J. K. Percus, *J. Math. Phys.* **4**, 116 (1963), hereafter referred to as I.

⁵ L. S. Ornstein and F. Zernike, *Proc. Acad. Sci. Amsterdam* **17**, 793 (1914).

The principal technique for examining nonuniform systems consisted of transforming from an initial (uniform) $n_0(\mathbf{r})$ to the final desired $n(\mathbf{r})$ by a functional Taylor expansion

$$f[n] = f[n_0] + \int \frac{\delta f[n]}{\delta n(\mathbf{r}_1)} \Big|_0 \Delta n(\mathbf{r}_1) d\mathbf{r}_1 + \frac{1}{2} \iint \frac{\delta^2 f[n]}{\delta n(\mathbf{r}_1) \delta n(\mathbf{r}_2)} \Big|_0 \Delta n(\mathbf{r}_1) \Delta n(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 + \dots, \tag{2.3}$$

where

$$\Delta n(\mathbf{r}) = n(\mathbf{r}) - n_0(\mathbf{r}).$$

The required density derivatives were obtained in terms of known γ derivatives by the chain rule

$$\frac{\delta}{\delta n(\mathbf{r}_1)} = \int \frac{\delta \gamma(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)} \frac{\delta}{\delta \gamma(\mathbf{r}_2)} d\mathbf{r}_2. \tag{2.4}$$

The quantity $\delta \gamma(\mathbf{r}_2) / \delta n(\mathbf{r}_1)$ was written as

$$\frac{\delta \gamma(\mathbf{r}_2)}{\delta n(\mathbf{r}_1)} \equiv \frac{\delta(\mathbf{r}_1 - \mathbf{r}_2)}{n(\mathbf{r}_1)} - X(\mathbf{r}_1, \mathbf{r}_2), \tag{2.5}$$

and, as the matrix inverse to (2.26), thereby satisfied⁶

$$\frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} - 1 = X(\mathbf{r}_1, \mathbf{r}_2) + \int \left[\frac{n_2(\mathbf{r}_1, \mathbf{r}_2)}{n(\mathbf{r}_1)n(\mathbf{r}_2)} - 1 \right] n(\mathbf{r}_3) X(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3, \tag{2.6}$$

so that X is to be identified with the generalization to nonuniform systems of the direct correlation function of Ornstein and Zernicke.⁵

3. ASYMPTOTIC FORM OF RADIAL DISTRIBUTIONS

We now make use of our general formalism to investigate some properties of uniform fluids. This will be done by considering the response of the fluid to an external potential $U(\mathbf{r})$ induced by keeping a fluid particle fixed at $\mathbf{r} = 0$,⁷ i.e. $U(\mathbf{r}) = \varphi(\mathbf{r})$, the intermolecular potential. Then $n(\mathbf{r})$ becomes the density of particles at \mathbf{r} when it is known that there is a particle at the origin:

$$n(\mathbf{r}) = \rho_2(\mathbf{r}) / \rho = \rho + G(\mathbf{r}), \tag{3.1}$$

where ρ and $\rho_2(\mathbf{r})$ are the singlet and pair densities, and $G(\mathbf{r})$ the normalized radial correlation function in the uniform fluid.

An implicit equation for the density $G(\mathbf{r})$ can now be obtained by applying (2.3) to $\gamma(\mathbf{r})$ of (2.1),

⁶ Equations (2.5) and (2.6) are identical to Eqs. (2.10) and (2.12) of I with the relation between X and C (used in I) given in Eq. (4.1) of I.

⁷ See, e.g., J. K. Percus, Phys. Rev. Letters 8, 462 (1962).

which is known to within the constant chemical potential μ . If the uniform comparison system is that at density ρ , then μ is unaltered by the potential, and we have, from (2.2)-(2.5), with $\Delta n(\mathbf{r}) = G(\mathbf{r})$,

$$\begin{aligned} \gamma(\mathbf{r}) - \beta\mu - \lambda &= -\beta\varphi(\mathbf{r}) \\ &= \int [\rho^{-1} \delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})] G(\mathbf{x}) d\mathbf{x} \\ &\quad - \frac{1}{2} \int \dots \int \mathfrak{F}_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) \\ &\quad \times [\rho^{-1} \delta(\mathbf{r}_1 - \mathbf{x}_1) - X(\mathbf{r}_1 - \mathbf{x}_1)] \\ &\quad \times [\rho^{-1} \delta(\mathbf{r}_2 - \mathbf{x}_2) - X(\mathbf{r}_2 - \mathbf{x}_2)] \\ &\quad \times [\rho^{-1} \delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})] \\ &\quad \times G(\mathbf{r}_1) G(\mathbf{r}_2) d\mathbf{r}_1 \dots d\mathbf{x}_2 + \dots. \end{aligned} \tag{3.2}$$

A superior expansion for many purposes, using a generally smaller expansion parameter, is obtained by taking the uniform comparison system for evaluation of $\gamma(\mathbf{r})$ as that at the local density $n(\mathbf{r})$. Then

$$\Delta n(\mathbf{x}) = n(\mathbf{x}) - n(\mathbf{r}) = G(\mathbf{x}) - G(\mathbf{r}), \tag{3.3}$$

so that

$$\gamma(\mathbf{r}) - \lambda = \tag{3.4}$$

$$\begin{aligned} \beta\mu - \beta\varphi(\mathbf{r}) &= \beta\mu_0(\rho + G(\mathbf{r})) + \int [n^{-1}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{x}) \\ &\quad - X_0(\mathbf{r} - \mathbf{x})] [G(\mathbf{x}) - G(\mathbf{r})] d\mathbf{x} \\ &\quad - \frac{1}{2} \int \dots \int \mathfrak{F}_{30}(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) [n^{-1}(\mathbf{r}) \delta(\mathbf{r} - \mathbf{x}) \\ &\quad - X_0(\mathbf{r} - \mathbf{x})] [n^{-1}(\mathbf{r}) \delta(\mathbf{r}_1 - \mathbf{x}_1) - X_0(\mathbf{r}_1 - \mathbf{x}_1)] \\ &\quad \times [n^{-1}(\mathbf{r}) \delta(\mathbf{r}_2 - \mathbf{x}_2) - X_0(\mathbf{r}_2 - \mathbf{x}_2)] [G(\mathbf{r}_1) - G(\mathbf{r})] \\ &\quad \times [G(\mathbf{r}_2) - G(\mathbf{r})] d\mathbf{r}_1 \dots d\mathbf{x}_2 + \dots, \end{aligned}$$

where subscript zero indicates that the quantity is to be taken in a uniform system of density $n(\mathbf{r}) = \rho + G(\mathbf{r})$.

To the extent that X_0 and \mathfrak{F}_{30} of (3.4) are short range, $G(\mathbf{x}) - G(\mathbf{r})$ may be expanded in a Taylor series about \mathbf{r} within the integrals, and we find

$$\begin{aligned} \beta\mu &= \beta\varphi(\mathbf{r}) + \beta\mu_0(\rho + G) - \frac{1}{6} \frac{\Lambda_0^2 \beta}{(\rho + G)^2 \chi_0} \nabla^2 G \\ &\quad - \frac{1}{6} \frac{l_0^2}{(\rho + G)^4} \left(\frac{\beta}{\chi_0} \right)^2 (\nabla G)^2 + \dots, \end{aligned} \tag{3.5a}$$

where

$$\Lambda_0^2 = \int x^2 X_0(\mathbf{x}) d\mathbf{x} / \int [n^{-1}(\mathbf{r}) \delta(\mathbf{x}) - X_0(\mathbf{x})] d\mathbf{x}$$

$$\begin{aligned}
 &= (n^2 \chi_0 / \beta) \int x^2 X_0(\mathbf{x}) d\mathbf{x} \\
 &= \int x^2 G_0(\mathbf{x}) d\mathbf{x} / \int [\delta(\mathbf{x}) + G_0(\mathbf{x})] d\mathbf{x}, \quad (3.5b)
 \end{aligned}$$

$$\begin{aligned}
 l_0^2 &= \int \hat{\mathfrak{F}}_{30}(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) [n^{-1}(\mathbf{r}) \delta(\mathbf{x}) \\
 &\quad - X_0(\mathbf{x})] \mathbf{x}_1 \cdot \mathbf{x}_2 d\mathbf{x} d\mathbf{x}_1 d\mathbf{x}_2. \quad (3.5c)
 \end{aligned}$$

Here $\chi_0 = n^{-1} (\partial p / \partial n)^{-1} |_0$ is the isothermal compressibility, entering through the relation

$$\int [n^{-1}(\mathbf{r}) \delta(\mathbf{x}) - X_0(\mathbf{x})] d\mathbf{x} = \beta / (n^2 \chi_0). \quad (3.6)$$

The earliest work on the asymptotic behavior of $G(\mathbf{r})$, where $G(\mathbf{r})$ is small compared to ρ , was done by Ornstein and Zernike⁵ (O.Z.), and is essentially equivalent to (a) keeping only terms linear in G , and (b) cutting off the series in (3.5) after the ∇^2 term. This yields

$$\frac{\partial \mu_0(\rho)}{\partial \rho} G_a(\mathbf{r}) - \frac{1}{6} \frac{\Lambda^2}{\rho^2 \chi} \nabla^2 G_a(\mathbf{r}) = -\varphi(\mathbf{r}), \quad (3.7)$$

where G_a is the asymptotic value of G . Since $\varphi(\mathbf{r})$ is the intermolecular potential, it will generally have a short range, i.e., it will vanish in the region in which G assumes its asymptotic form, and the right-hand side of (3.7) can be set equal to zero. This leads at once to the usual O-Z equation (noting $\rho \partial \mu / \partial \rho = \partial p / \partial \rho$)

$$\nabla^2 G_a = (6/\Lambda^2) G_a. \quad (3.8)$$

The "advantage" of our analysis over a purely macroscopic derivation of Eq. (3.8) is that we have here an explicit expression for the coefficient of $\nabla^2 G_a$, in terms of G (but not necessarily of G_a), an advantage shared by other treatments as well.⁸

The solution of (3.8) in three dimensions is

$$G_a = A r^{-1} \exp[-(6^{1/2}/\Lambda)r], \quad (3.9)$$

and in one dimension, where the factor 6 in (3.5), (3.8) should be replaced by two,

$$G_a = A \exp[-(2^{1/2}/\Lambda)r]. \quad (3.10)$$

It is easily verified that the use of G_a itself for computing Λ in (3.5b) leads to a contradiction which becomes less severe when the integral of G_a , which in this approximation would be proportional to the compressibility, is very large. This is consistent

with the O-Z theory which was developed for the vicinity of the critical point, where the compressibility is indeed very large, (see also Sec. 6 and reference 11).

4. LONG-RANGE POTENTIALS

We may attempt to minimize the assumptions leading to (3.7) by avoiding assumption (b) and supposing only that (3.4) can be linearized in G . This leads directly to the result

$$\begin{aligned}
 -\beta \varphi(\mathbf{r}) &= \beta (\partial \mu_0(\rho) / \partial \rho) G + \int [\rho^{-1} \delta(\mathbf{r} - \mathbf{x}) \\
 &\quad - X(\mathbf{r} - \mathbf{x})] [G(\mathbf{x}) - G(\mathbf{r})] d\mathbf{x} \\
 &= X_1(\mathbf{r}), \quad (4.1)
 \end{aligned}$$

where the subscript one indicates the result of linearization in G . If one again restricts attention to the asymptotic region, in order to justify retaining only linear terms in G , then, for a short range $\varphi(\mathbf{r})$, (4.1) implies that $X(\mathbf{r})$ also vanishes asymptotically. This arises from the fact that in (3.4), it is not sufficient to know $G_a(\mathbf{r})$ alone even where r is large, since G appears in integrals over the whole domain of r . Indeed there may be no general way of separating the asymptotic part of G . However, when the intermolecular forces are weak everywhere, i.e., when φ is always small, then (4.1) does become correct, representing the lowest order in φ in an expansion of X . In fact, a virial expansion of X starts with the term $X = e^{-\beta \varphi} - 1$, which is precisely what one obtains by expanding $\exp[\gamma(\mathbf{r})]$ rather than γ in Eq. (3.2) or (3.4) [see Appendix].

When φ is not only small but also has a finite range, the corresponding G must also assume the form $G = -\rho \beta \varphi \sim \rho (e^{-\beta \varphi} - 1)$. It is only when φ has a very large range, i.e. the moments of φ are not small even though φ is, that we get an interesting situation. This can be seen most easily by going over to the Fourier transform of X and G . We have then from (4.1)

$$X_1(\mathbf{k}) = -\beta \varphi(\mathbf{k}), \quad (4.2)$$

but since from (2.6)

$$G(\mathbf{k}) = \rho X(\mathbf{k}) / [1 - \rho X(\mathbf{k})], \quad (4.3)$$

then correspondingly

$$G_1(\mathbf{k}) = -\beta \rho \varphi(\mathbf{k}) / [1 + \beta \rho \varphi(\mathbf{k})]. \quad (4.4)$$

If $\varphi(\mathbf{r})$ has a finite range, then $\varphi(\mathbf{k})$ will be small everywhere and (4.4) can again be expanded to give $G_1(\mathbf{k}) = -\beta \rho \varphi(\mathbf{k})$. However where $\varphi(\mathbf{r})$ has

⁸ See, e.g., L. J. Goldstein in *Symposium on the Many-Body Problem*, edited by J. K. Percus, (Interscience Publishers, Inc., New York, 1963), Chap. XIX.

a long range, $\varphi(\mathbf{k})$ will be large near $\mathbf{k} = 0$, and such an expansion cannot be made.

The Electron Gas

An example of the foregoing is the case of an electron gas embedded in a uniform positive background. Here

$$\varphi(\mathbf{r}) = (4\pi\epsilon_0)^{-1}e^2/r, \quad (4.5)$$

$$\varphi(\mathbf{k}) = \begin{cases} (e^2/\epsilon_0) 1/k^2 & \mathbf{k} \neq 0 \\ 0 & \mathbf{k} = 0. \end{cases} \quad (4.6)$$

Thus

$$G_1(\mathbf{k}) = -[1 + (\epsilon_0/\beta\rho e^2)k^2]^{-1}, \quad (4.7)$$

and

$$G_1(\mathbf{r}) = -\rho(\beta e^2/4\pi\epsilon_0)r^{-1}e^{-r/D} = \rho(g - 1),$$

where

$$D = (\epsilon_0/\beta\rho e^2)^{\frac{1}{2}}, \quad (4.8)$$

and g is the radial distribution function. Equation (4.8) is the well-known Debye-Hückel⁹ form of G to lowest order in e^2 . As is also well-known, (4.8) does not give a sensible result near $r = 0$, i.e., for $r < (4\pi\epsilon_0/\beta e^2) = r_0$. This is not surprising since $\varphi(\mathbf{r})$ near the origin is not only not small but is in fact infinite.

The difficulty of infinite $\varphi(\mathbf{r})$ and correspondingly infinite $-\gamma(\mathbf{r})$ can be overcome as previously mentioned if the expansion (3.4) of $\gamma(\mathbf{r})$ is replaced by an expansion of $e^{\gamma(\mathbf{r})}$. Doing so, (4.4) is replaced by

$$G_1(\mathbf{k}) = \rho f(\mathbf{k})/[1 - \rho f(\mathbf{k})],$$

where

$$f(\mathbf{r}) = e^{-\beta\varphi(\mathbf{r})} - 1, \quad (4.9)$$

but the anomaly of a negative g is still not eliminated, for the "effective" $\beta\varphi$, while not infinite, does reach unity at the origin. Indeed, (4.8) is expected to be correct at most asymptotically, i.e., for $r \geq D \gg r_0$. Furthermore, in a real system, φ is strongly modified near the origin. It is thus more reasonable to consider the case of an intermolecular potential made up of two parts: a strong short-range part and a weak long-range part.

⁹ P. Debye and E. Hückel, Z. Physik 24, 185 (1923).

5. THE KAC MODEL

An example of a potential with strong short-range and weak long-range parts has recently been studied in detail by Kac, Uhlenbeck, and Hemmer (K-U-H).³ This one-dimensional model is of great interest because it can be solved rigorously (with great skill and great labor), and it leads to a first-order phase transition, something never before found rigorously. The potential has the form

$$\begin{aligned} \varphi(x) &= \varphi_h(x) + \varphi_l(x), \\ \varphi_h(x) &= \begin{cases} \infty & |x| < \delta \\ 0 & |x| > \delta \end{cases}, \\ \varphi_l(x) &= -\alpha_0\gamma e^{-\gamma x}, \end{aligned} \quad (5.1)$$

where x is now a one-dimensional variable and $\gamma\delta \ll 1$. The asymptotic region is defined by $x \geq \gamma^{-1}$ and there is a parameter of smallness $\gamma\delta$. In the limit $\gamma \rightarrow 0$, this model exhibits a phase change described by the van der Waals equation:

$$\begin{aligned} p &= \beta^{-1}\rho/(1 - \rho\delta) - \alpha_0\rho^2 \\ &= \beta^{-1}/(l - \delta) - \alpha_0/l^2. \end{aligned} \quad (5.2)$$

If (4.1) is now considered in the asymptotic region, where G and X are small, then $X_1(r)$, which we shall now call $X_a(r)$, has the form

$$X_a(r) = -\beta\varphi_l = \alpha_0\beta\gamma e^{-\gamma r} \quad (5.3)$$

and

$$X_a(k) = 2\beta\alpha_0/(1 + \gamma^{-2}k^2). \quad (5.4)$$

It is seen from (5.3) and (5.4) that the even moments of $X_a(r)$ will be of order $(1/\gamma^2)^m$. Stated differently, if we expand $X_a(k)$ in a power series in k , we find

$$X_a(k) = 2\beta\alpha_0[1 - (k^2/\gamma^2) + (k^2/\gamma^2)^2 + \dots]. \quad (5.5)$$

Hence all coefficients in the series (5.5), except for the zeroth, will be very large. The correct $X(k)$ would presumably have a power series expansion whose coefficients, except for the zeroth-order term, are essentially the same as those given in (5.5). This would, for example, be the result of a virial expansion of X (or G). (It is a peculiarity of this type of potential that the moments of G or X , other than zero, diverge for all densities in the limit $\gamma \rightarrow 0$, which may limit the inferences that can be drawn from it.)

For the purpose of finding the asymptotic form of G , for $x \geq \gamma^{-1}$, it is thus sufficient to modify

$X_s(k)$ at $k = 0$ to have its correct value there¹⁰:

$$X(k) = X_s(k) + [X(0) - X_s(0)]$$

$$= 2\beta\alpha_0/(1 + \gamma^{-2}k^2) + \rho^{-1}s. \quad (5.6)$$

Using (5.6) to find $G(k)$, in order to obtain the asymptotic form of G , yields

$$G(k) = \rho X(k)/(1 - \rho X(k))$$

$$= \frac{s}{1-s} + \frac{2\beta\rho\alpha_0}{(1-s)^2} \left[\frac{k^2}{\gamma^2} + \frac{1-s-2\beta\rho\alpha_0}{1-s} \right]^{-1} \quad (5.7)$$

and this in turn leads to

$$G_s(r) = \frac{\beta\rho\alpha_0\gamma}{(1-s)^2} \left(\frac{1-s-2\beta\rho\alpha_0}{1-s} \right)^{\frac{1}{2}}$$

$$\times \exp \left[-\gamma r \left(\frac{1-s-2\beta\rho\alpha_0}{1-s} \right)^{\frac{1}{2}} \right]. \quad (5.8)$$

We now employ Eqs. (3.6) and (5.2) for $X(0)$ and p to find s :

$$s = (X(0) - X_s(0))\rho = (1 - \beta dp/d\rho) - 2\beta\rho\alpha_0$$

$$= 1 - (1 - \rho\delta)^{-2} = 1 - \beta\delta p_h/\delta\rho, \quad (5.9)$$

where p_h is the part of the pressure which comes from the hard core alone. There finally results

$$G_s(r) = \gamma \frac{(l - \delta)^4}{l^4} \beta\alpha_0 \left[\frac{dp_h}{dl} / \frac{d\rho}{dl} \right]^{\frac{1}{2}}$$

$$\times \exp \left[-\gamma r \left[\frac{dp}{dl} / \frac{d\rho}{dl} \right]^{\frac{1}{2}} \right], \quad (5.10)$$

which is precisely the expression obtained by K-U-H. when the system is not too close to the critical point, at which dp/dl vanishes. Had we taken s to be a function of k , independent or weakly dependent on γ , with the correct value for $k = 0$, the exponent and coefficient in (5.10) would have been modified by terms which vanish when $\gamma \rightarrow 0$.¹¹

We may perhaps understand the region of breakdown near the critical point by considering that in the derivation of (4.1) from (3.4) we have neglected terms of order G^2 compared to $(\partial\mu_0(\rho)/\partial\rho)G$. Near the critical point, dp/dl and, hence, $d\mu/d\rho$, of course vary as $(l - l_c)^2$, and as $T - T_c$, where l_c and T_c are critical volume and temperature. Since $G \sim$

$\gamma(dp/dl)^{-\frac{1}{2}}$, we are assuming (in suitable units) that $\gamma^2(dp/dl)^{-1} \ll \gamma(dp/dl)^{\frac{1}{2}}$, or $\gamma \ll (dp/dl)^{\frac{1}{2}}$. We are thus limited to the region $\gamma \ll (l - l_c)^3$, $\gamma \ll (T - T_c)^{\frac{1}{2}}$, which are the same as the limits found by K-U-H.

6. DISCUSSION

G_s as given in (5.10) is of the same form, exponential, as that given by the O-Z theory for a short-range potential, Eq. (3.10). It is clear, however, that (1) when the O-Z theory, Eq. (3.7), is applied to this potential, it will yield a G_s which is the sum of two exponentials with the wrong exponents and coefficients, and (2) the simple exponential form of (5.10) is here due entirely to the precise form of the assumed long-range part of φ . This is certainly so if our method of arriving at (5.10) is essentially valid and can be used as well for other forms of φ_l . It is easy to construct φ_l 's—shallow square-well sum of exponentials—for which G_s would be a sum of exponentials, or decaying oscillatory exponentials, or change from one to the other as a function of density. We may also surmise that the single exponential form is not universal from the fact that (5.10) may be expanded in a virial series the lowest-order term of which $-\rho\beta\varphi_l$ is given correctly by the usual expansion; presumably the higher-order terms also follow correctly. This would not be true if G_s were a single exponential, but φ_l were not.¹²

There remains the question of the validity of the linearization of (3.4). If we are interested in the asymptotic region from the outset, we may equally well use (3.2) as our starting point. Combining terms as before, this reduces to

$$-\beta\varphi(\mathbf{r}) = X(\mathbf{r}) - \frac{1}{2} \iiint \mathfrak{F}_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2) X(\mathbf{x}_1) X(\mathbf{x}_2)$$

$$\times [\rho^{-1} \delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})] d\mathbf{x} d\mathbf{x}_1 d\mathbf{x}_2 + \dots, \quad (6.1)$$

and this may profitably be rewritten as

$$-\beta\varphi(\mathbf{r}) = X(\mathbf{r}) - \frac{1}{2} \iint [\delta\mathfrak{F}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r})]$$

$$\times X(\mathbf{x}_1) X(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \dots \quad (6.2)$$

Keeping the Kac-Uhlenbeck model in mind as prototype, it is clear that for large r , the regions $x_1 \sim x_2 \sim r$; $x_1 \sim r$, x_2 far from r ; and $x_2 \sim r$, x_1 far from r in the second term of (6.2) all con-

¹⁰ The corresponding modification in the case of the electron gas would yield corrections to G_s of higher order in e^2 .

¹¹ Note added in proof: The *ad hoc* prescription given here for obtaining G_s from X_s , to lowest order in γ , can be made rigorous and generalized to obtain also higher-order terms in G_s from a limited knowledge of X . It is interesting to note from Eq. (5.10) that when α_0 is negative, i.e., we have a weak long-range repulsive potential, then, the range of the radial distribution function is smaller than that of the direct correlation function.

¹² P. C. Hemmer has shown: (1) that our analysis yields the correct result for G_s when φ_l consists of a sum of exponentials and (2) that near the critical point (but still $(l - l_c)^3 \gg \gamma$, $(T - T_c)^{\frac{1}{2}} \gg \gamma$) one exponential will dominate the long-range part of G . There is thus approximate agreement with the O-Z theory in this range, though there is no way of determining both A & Λ appearing in (3.10) from the O-Z theory alone, c.f. discussion at the end of Sec. 3.

tribute $0(\gamma^2)$. In the first case both $X(x_1)$ and $X(x_2)$ would be of order γ while in the second case $\hat{\mathfrak{F}}_2$ and one of the X 's would be of order γ . We still have to show that when x_1 and x_2 are both far from r then $\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r})$ is of order γ^2 . To do this we consider an expansion of $\gamma(\mathbf{r})$, similar to (3.2), with the nonuniform density $n(\mathbf{r})$ caused by keeping two fluid particles fixed at \mathbf{x}_1 and \mathbf{x}_2 . In this case,

$$n(\mathbf{r}) = \rho_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)/\rho_2(\mathbf{x}_1, \mathbf{x}_2), \tag{6.3}$$

where, as in section three, ρ_l refers to the l -particle distribution in a uniform system of density ρ . Thus, to lowest order,

$$\begin{aligned} & -\beta[\varphi(\mathbf{r} - \mathbf{x}_1) + \varphi(\mathbf{r} - \mathbf{x}_2)] \\ &= \int [\rho^{-1}\delta(\mathbf{r} - \mathbf{x}) - X(\mathbf{r} - \mathbf{x})] \\ & \times \left[\frac{\rho_3(\mathbf{x}, \mathbf{x}_1, \mathbf{x}_2)}{\rho_2(\mathbf{x}_1, \mathbf{x}_2)} - \rho \right] d\mathbf{x} + \dots \tag{6.4} \end{aligned}$$

After some manipulation, started by expressing ρ_3 in terms of $\hat{\mathfrak{F}}_3$, Eq. (6.4) may be put in the form

$$\begin{aligned} \frac{\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)}{\delta n(\mathbf{r})} &= -\hat{\mathfrak{F}}_2(\mathbf{x}_1 - \mathbf{x}_2)\{X(\mathbf{r} - \mathbf{x}_1) + \beta\varphi(\mathbf{r} - \mathbf{x}_1) \\ & + X(\mathbf{r} - \mathbf{x}_2) + \beta\varphi(\mathbf{r} - \mathbf{x}_2) + \rho^{-1}[\delta(\mathbf{r} - \mathbf{x}_1) \\ & + \delta(\mathbf{r} - \mathbf{x}_2)]\} + \delta(\mathbf{r} - \mathbf{x}_1)\delta(\mathbf{r} - \mathbf{x}_2). \tag{6.5} \end{aligned}$$

We see that taking $X(\mathbf{y}) = -\beta\varphi(\mathbf{y}) + 0(\gamma^2)$ for $y \gg \delta$ leads to $\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)/\delta n(\mathbf{r}) \sim 0(\gamma^2)$ for \mathbf{r} far from \mathbf{x}_1 and \mathbf{x}_2 which in turn makes the second term in (6.2) of $0(\gamma^2)$. We have also verified this explicitly for the lowest order in the density.

The virial expansion of $X(\mathbf{r})$ may actually be used to verify (4.1) directly to lowest order in γ . As is well-known, all the clusters appearing in the virial series for X must be at least doubly connected. In fact,¹³

$$\begin{aligned} X(\mathbf{r}_{12}) &= f(\mathbf{r}_{12}) + \sum_{k=2}^{\infty} \frac{\rho^{k-1}}{(k-1)!} \\ & \times \int S_k(1, 2, \dots, k+1) d\mathbf{r}_3 \dots d\mathbf{r}_{k+1}, \end{aligned}$$

where S_k is the irreducible cluster sum of the f 's connecting (at least doubly) $k+1$ particles. It is easy to convince oneself that for r_{12} large, i.e. of order γ^{-1} , all the terms in the sum will be of order γ^2 at least. Thus the term proportional to ρ is

$$f(\mathbf{r}_{12}) \int f(\mathbf{r}_{13})f(\mathbf{r}_{23}) d\mathbf{r}_3.$$

For large \mathbf{r}_{12} , $f(\mathbf{r}_{12})$ will be of order ν and so will the integral. In general it is sufficient to look at the ring diagrams for clearly none of the other clusters will give (lower)-order γ contributions. In the term proportional to ρ^3 there will be a ring diagram which contains $f(\mathbf{r}_{12})$ and this will behave essentially like the three-particle ring. Similar considerations show that the term

$$\int f(\mathbf{r}_{13})f(\mathbf{r}_{14})f(\mathbf{r}_{23})f(\mathbf{r}_{24}) d\mathbf{r}_3 d\mathbf{r}_4$$

is again of order γ^2 , for r_{12} large (we simply have to enumerate all the possibilities: $\mathbf{r}_3, \mathbf{r}_4$ close to \mathbf{r}_1 or \mathbf{r}_2 ; \mathbf{r}_3 close \mathbf{r}_4 far, etc.) and the same holds for all other ring clusters.¹⁴ The same analysis will also apply to the case where φ_l is the sum of exponentials.¹²

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APPENDIX. ALTERNATE EXPANSIONS

We describe here several alternate expansions to the one developed in Sec. 3 for obtaining the properties of a uniform system in terms of a non-uniform system with an external potential induced by keeping one of the particles fixed at the origin. We have already referred to the expansion of $e^{\gamma(\mathbf{r})}$. This yields according to (2.2)-(2.5) with

$$\Delta n(\mathbf{r}) = G(\mathbf{r}), \tag{A1}$$

$$\frac{\delta e^{\gamma(\mathbf{r})}}{\delta n(\mathbf{x})} = e^{\gamma(\mathbf{r})} \frac{\delta \gamma(\mathbf{r})}{\delta n(\mathbf{x})}, \tag{A2}$$

$$\begin{aligned} (e^{-\beta\varphi(\mathbf{r})} - 1) &\equiv f(\mathbf{r}) = X(\mathbf{r}) + \frac{1}{2!} X^2(\mathbf{r}) \\ &- \frac{1}{2!} \int \frac{\delta\hat{\mathfrak{F}}_2(\mathbf{x}_1, \mathbf{x}_2)}{\delta n(\mathbf{r})} X(\mathbf{x}_1)X(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \dots \tag{A3} \end{aligned}$$

It is interesting to note that the series in (A3) can be partially summed to start with $(e^{X(\mathbf{r})} - 1)$.

We consider next the inverse process of Eqs. (3.2) and (A3), i.e., instead of expanding $\gamma(\mathbf{r})$ or $e^{\gamma(\mathbf{r})}$ in a Taylor series in $\Delta n(\mathbf{r}')$ we expand $n(\mathbf{r})$ in a series in $\Delta\gamma(\mathbf{r}')$ or $\Delta e^{\gamma(\mathbf{r}'')}$ (cf. Sec. 3 in I). In

¹⁴ Note added in proof: Similar results for the lowest γ order in X_a were also obtained by E. Helfand and M. Fischer. We have also obtained a very simple expression for the γ^2 term in X_a from graphical consideration. This agrees with the second-order term in G_a obtained by Uhlenbeck, Kac and Hemmer, first from their integral equation, and later from direct graphical analysis of G_a .

¹³ M. J. von Leeuwen, J. Groenewald, and J. de Boer, *Physica* 25, 792 (1959); F. H. Stillinger and F. P. Buff, *J. Chem. Phys.* 37, 1 (1962).

the first case we find for

$$\begin{aligned} n(\mathbf{r}) &= G(\mathbf{r}) + \rho, \\ \Delta\gamma(\mathbf{r}) &= -\beta\varphi(\mathbf{r}), \end{aligned} \tag{A4}$$

$$\begin{aligned} G(\mathbf{r}) &= -\beta \int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})\varphi(\mathbf{x}) d\mathbf{x} \\ &+ \frac{\beta^2}{2!} \int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)\varphi(\mathbf{x}_1)\varphi(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \dots \\ &= -\beta\rho\varphi(\mathbf{r}) - \beta\rho \int G(\mathbf{r} - \mathbf{x})\varphi(\mathbf{x}) d\mathbf{x} \\ &+ \frac{\beta^2}{2} \int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)\varphi(\mathbf{x}_1)\varphi(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \dots \end{aligned} \tag{A5}$$

When φ is both weak and short range then, to lowest-order $G = \beta\rho\varphi$, as discussed in Sec. 4, which results from the first term in (A5). For the electron gas where φ is assumed weak everywhere but is long range, the first two terms in (A5) would again yield the Debye-Huckel result. For the Kac potential, however, where $\varphi(x)$ is long range and in addition is infinite for $|x| < \delta$, (A5) cannot be used at all even for r large. This indicates that we try

expanding $n(\mathbf{r})$ in $\Delta e^{\gamma(\mathbf{r})} = e^{\lambda + \beta\mu f(\mathbf{r})}$. Writing thus

$$\frac{\delta n(\mathbf{r})}{\delta e^{\gamma(\mathbf{x})}} = e^{-\gamma(\mathbf{x})} \frac{\delta n(\mathbf{r})}{\delta \gamma(\mathbf{x})}, \tag{A6}$$

we find

$$\begin{aligned} G(\mathbf{r}) &= \int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})f(\mathbf{x}) d\mathbf{x} + \frac{1}{2!} \left\{ - \int \hat{\mathfrak{F}}_2(\mathbf{r}, \mathbf{x})f^2(\mathbf{x}) d\mathbf{x} \right. \\ &\quad \left. + \int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)f(\mathbf{x}_1)f(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 \right\} + \dots \\ &= \rho f(\mathbf{r}) + \rho \int G(\mathbf{r} - \mathbf{x})f(\mathbf{x}) d\mathbf{x} \\ &\quad - \frac{1}{2}\rho f^2(\mathbf{r}) - \frac{1}{2}\rho \int G(\mathbf{r} - \mathbf{x})f^2(\mathbf{x}) d\mathbf{x} \\ &\quad + \frac{1}{2!} \int \hat{\mathfrak{F}}_3(\mathbf{r}, \mathbf{x}_1, \mathbf{x}_2)f(\mathbf{x}_1)f(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2 + \dots \end{aligned} \tag{A7}$$

It is seen from (A7) that, unlike (4.1), the higher terms in the Taylor expansion will contain terms of order γ , so that terminating the expansion after one or two terms will not yield G_s correctly even to the lowest order in γ . This agrees with our analysis of Secs. 5 and 6.