Structure of the Triplet Distribution Function near the Critical Point

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Asymptotic long-range properties of the triplet distribution function of a fluid near its critical point are inferred from known properties of the pair distribution function and the second equation in the Bogoliubov-Born-Green-Kirkwood-Yvon hierarchy. The inverse correlation range κ and the critical exponent η are related to coefficients in this asymptotic form. This structural information can be used, in some cases, to test whether a proposed functional relationship between the distribution functions is consistent with realistic critical behavior.

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The idea that the equilibrium correlations of pairs of local variables are related has appeared in a number[1-8] of places in the literature and takes several forms, of which I mention three. General plausibility arguments have been given,[1] supported and extended by specific calculations,[1-3] that all pair correlations of local variables should have a universal Ornstein-Zernike form at large distances except on "special" lines in the thermodynamic state space. A rather stronger relationship[4,5] is assumed in the "algebra of fluctuating variables" approach where, at the critical point of a system, it is supposed that the pair correlations of any two local variables can be written as linear combinations of some fundamental set of correlations and that the coefficients in these linear combinations form a certain algebra. Finally, a bewildering variety of relations between various correlations have been assumed by many authors in order to decouple infinite hierarchies of equations, involving infinitely many different correlations, such as arise in the Green's-function[6] theories of many-body systems or the Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY) hierarchy[7] for the equilibrium state reduced distribution functions. Perhaps the oldest relation of this type is the Kirkwood superposition[8] assumption relating the triplet and the pair distribution functions. This assumption, with the second equation of the BBGKY hierarchy, gives rise to a well-known equation in the theory of fluids, whose behavior near its critical point has recently received considerable study.[9] These studies show that the superposition approximation fails to give the correct asymptotic relation between the pair and the triplet distribution functions near the critical point, at least for spatial dimension $d < 4$, but they do not make clear the reasons for this failure or what the correct asymptotic relation might be.

In this paper, I give arguments for a certain asymptotic relationship between the pair and triplet distribution functions in the critical region and show that the inverse correlation length κ and the critical exponent η are related to the coefficients appearing in this relationship. This asymptotic form makes clear in what respect the superposition assumption fails in the critical region and provides a norm against which other decoupling assumptions can be tested.

This argument combines the second equation in the BBGKY hierarchy with known properties of the pair distribution function to infer properties of the triplet distribution function in the critical region. I will first show that a simple asymptotic relation between the pair and triplet correlations will yield a pair distribution function with the correct critical behavior. Then I will invert the argument to show in what sense this assumed relationship might be unique.

The second member of the BBGKY hierarchy is[7]

$$\nabla_1 f_2(\vec{r}_1, \vec{r}_2) = -f_2(\vec{r}_1, \vec{r}_2)\nabla_1 u(\vec{r}_1, \vec{r}_2) - \int f_3(\vec{r}_1, \vec{r}_2, \vec{r}_3)\nabla_1 u(\vec{r}_1, \vec{r}_3) d^3 r_3, \tag{1}$$

where f_2 and f_3 are the usual pair and triplet reduced distribution functions and $u = \varphi/k_B T$ is the reduced intermolecular potential. u is assumed to be translationally and rotationally invariant, $u(\vec{r}_1, \vec{r}_2) = u(|\vec{r}_1 - \vec{r}_2|)$, and of finite range, $u(r) = 0$ if $r > r_0$. For $\vec{r}_2$ far from $\vec{r}_1$ (and $\vec{r}_3$) the distribution functions satisfy, for one-phase states,

$$f_2(\vec{r}_1, \vec{r}_2) \to \rho^2, \quad f_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) \to \rho f_2(\vec{r}_1, \vec{r}_3),$$

where ρ is the number density. It is convenient to use two dimensionless correlation functions which vanish as $\vec{r}_2 \to \infty$,

$$h_2(\vec{r}_1, \vec{r}_2) = [f_2(\vec{r}_1, \vec{r}_2) - \rho^2]/\rho^2, \quad (2)$$

$$h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2) = [f_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) - \rho f_2(\vec{r}_1, \vec{r}_3)]/\rho^3. \quad (3)$$

In terms of these correlations, (1) can be written, for $|\vec{r}_2 - \vec{r}_1| > r_0$, as

$$\nabla_1 h_2(\vec{r}_1, \vec{r}_2) = -\rho \int h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2) \nabla_1 u(\vec{r}_1, \vec{r}_3) d^3 r_3, \quad (4)$$

where the rotational invariance of u and of f_2 have been used.

Because of the short range of the potential, only configurations for which $|\vec{r}_1 - \vec{r}_3| < r_0$ appear in (4). Hence $h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2)$ can be regarded as the correlation of two local variables, the local particle density $\rho(\vec{r}_2)$ and a product density $\rho(\vec{r}_1)\rho(\vec{r}_3)$ localized in the vicinity of $\vec{r}_1$ and $\vec{r}_3$. Now the arguments given in Refs. 1–5 suggest, for $\vec{r}_2$ well separated from $\vec{r}_1$ and $\vec{r}_3$, that h_3 should be proportional to $h_2(R)$, where $\vec{R}$ is a vector from $\vec{r}_2$ to some point near $\vec{r}_1$ and $\vec{r}_3$. It is necessary to write this asymptotic proportionality in a way that explicitly reflects the symmetry of f_3 and h_3 under interchange of the positions of particles 1 and 3. There are several natural ways of doing this, all of which lead to equivalent results. To simplify the notation we set $\vec{r} = \vec{r}_1 - \vec{r}_2$, $\vec{t} = \vec{r}_3 - \vec{r}_2$, and $\vec{s} = \vec{r}_1 - \vec{r}_3$. The assumed asymptotic relation between h_3 and h_2, for $s < r_0$ and r and t large compared to r_0, can be written

$$h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2) \simeq \tfrac{1}{2} a(s)[1 + (s/r)^2 b + O(s^4/r^4) + \cdots] h_2(r) + \tfrac{1}{2} a(s)[1 + (t/r)^2 b + O(t^4/r^4) + \cdots] h_2(t), \quad (5)$$

where $a(s)$ is an undetermined function of s and b is a constant. This has the required symmetry since interchange of $\vec{r}_1$ and $\vec{r}_3$ interchanges $\vec{r}$ with $\vec{t}$ and replaces $\vec{s}$ with $-\vec{s}$. I will come back to the questions of the uniqueness of this expression and the nature of possible higher-order terms. Equation (5) in (4) gives a linear integro-differential equation for h_2 which should be valid for r large compared to the range r_0 of the potential $u(r)$. The slowly varying solutions of this equation can be investigated by a gradient expansion technique.[9] That is, since $\vec{t} = \vec{r} - \vec{s}$ and $s \ll r$, Eq. (5) can be well approximated by its Taylor expansion about $\vec{t} = \vec{r}$, for slowly varying h_2. There are two small parameters, s/r and $s\,d/dr$, in this expansion and their relative size need not be specified. The leading approximation to the integral equation is given by expanding (5) to terms of order $(s/r)^m \times (s\,d/dr)^n$ with $m + n \leqslant 3$. The expansion has the general form

$$h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2) = \sum_{m,n} a_m{}^n (s, \hat{r} \cdot \hat{s}) \left(\frac{s}{r}\right)^m s^n \frac{d^n h_2(r)}{dr^n}. \quad (6)$$

The particular form (5) gives, upon expansion, the following values for the coefficients in (6):

$$a_0{}^0 = a(s), \quad a_1{}^0 = 0, \quad a_2{}^0 = b a(s), \quad a_3{}^0 = (\hat{r} \cdot \hat{s}) b a(s),$$
$$a_0{}^1 = -(\hat{r} \cdot \hat{s}) a(s)/2, \quad a_1{}^1 = [1 - (\hat{r} \cdot \hat{s})^2] a(s)/4,$$
$$a_2{}^1 = -a_1{}^2 - a_3{}^0/2, \quad a_0{}^2 = (\hat{r} \cdot \hat{s})^2 a(s)/4, \quad (7)$$
$$a_1{}^2 = -(\hat{r} \cdot \hat{s})[1 - (\hat{r} \cdot \hat{s})^2] a(s)/4,$$
$$a_0{}^3 = -(\hat{r} \cdot \hat{s})^3 a(s)/12.$$

The general form (6) substituted into the radial component of (4) gives

$$-\frac{dh_2(r)}{dr} = \sum_{m,n} A_m{}^n \frac{1}{r^m} \frac{d^n h_2(r)}{dr^n}, \quad (8)$$

where

$$A_m{}^n = \rho \int (\hat{r} \cdot \hat{s}) \frac{du(s)}{ds} a_m{}^n (s, \hat{r} \cdot \hat{s}) s^{m+n} d^3 s. \quad (9)$$

If the integral in (9) is done in polar coordinates with the z axis along $\hat{r}$ so that $\cos\theta = \hat{r} \cdot \hat{s}$, then only the part of $a_m{}^n(s, \hat{r} \cdot \hat{s})$ odd in $\hat{r} \cdot \hat{s}$ contributes to the coefficient $A_m{}^n$.

When the specific values (7) of the $a_m{}^n$ are used in (9), two types of angular integrals appear, corresponding to factors $(\hat{r} \cdot \hat{s})^2$ and $(\hat{r} \cdot \hat{s})^4$ in the integrands. These angular integrals have the values

$$C_2 = \frac{\pi^{d/2}}{d\,\Gamma(d/2)}, \quad C_4 = \frac{3\pi^{d/2}}{d(d+2)\Gamma(d/2)}, \quad (10)$$

where d is the spatial dimensionality of the fluid. In addition, two radial integrals, R_2 and R_4, appear, where

$$R_n = \rho \int_0^\infty \frac{du(s)}{ds} a(s) s^{d+n} ds. \quad (11)$$

The nonzero $A_m{}^n$ computed from (7) are

$$A_3{}^0 = b C_2 R_2, \quad A_0{}^1 = -C_2 R_0/2,$$
$$A_2{}^1 = -A_1{}^2 - A_3{}^0/2, \quad (12)$$
$$A_1{}^2 = -(C_2 - C_4) R_2/4, \quad A_0{}^3 = -C_4 R_2/12.$$

These values, placed in (8), yield

$$\frac{d^3h_2}{dr^3}+\frac{(d-1)}{r}\frac{d^2h_2}{dr^2}-\frac{(d-1)}{r^2}\frac{dh_2}{dr}+\frac{2(d+2)b}{r^2}\frac{dh_2}{dr}-\frac{4(d+2)b}{r^3}h_2-\kappa^2\frac{dh_2}{dr}=0, \tag{13}$$

where a factor of $A_0{}^3$ has been divided out, (11) and (10) have been used, and

$$\kappa^2=12(1-C_2R_0/2)/C_4R_2. \tag{14}$$

Equation (13) can be integrated once, with the boundary condition $h(r)\to 0$ as $r\to\infty$, to give

$$\frac{d^2h_2(r)}{dr^2}+\frac{(d-1)}{r}\frac{dh_2(r)}{dr}+\frac{2(d+2)b}{r^2}h_2(r)-\kappa^2h_2(r)=0. \tag{15}$$

Equation (15) is a generalization of the classical Ornstein-Zernike ($b=0$) equation. The solution of (15) which vanishes at large r has the properties

(i) $h_2(r)\propto e^{-\kappa r}/r^{(d-1)/2}$, for $\kappa r\gg 1$,

(ii) $h_2(r)\propto 1/r^{d-2+\eta}$, for $\kappa r\ll 1$,

where η is the positive root of

$$\eta(d-2+\eta)+2(d+2)b=0. \tag{16}$$

This gives the critical index η in terms of the parameter b in the asymptotic relation (5). The expected dependence of η on d requires that $b=0$ for $d\geqslant 4$ and $b<0$ for $d<4$. Note that if $h(r)$ satisfies (15) then $j(r)=r^{-\eta}h(r)$ satisfies the Ornstein-Zernike ($b=0$) equation for a shifted dimensionality $d'=d+2\eta$.

Thus, the specific asymptotic relation (5) implies an Eq. (15) capable of describing realistic pair correlations in the critical region. I will now try to make it plausible that (5) is unique up to terms $m+n\leqslant 3$ in the expansion (6). First it is plausible to assume that a general relationship of the form (6) holds between h_3 and h_2 for $r\gg r_0$. The arguments of Refs. 1–3 imply a relationship between h_3 and h_2 for $\kappa r\gg 1$ and (6) is a natural attempt to generalize that relationship to the region $\kappa r<1$ by including higher-order terms in the small parameters s/r and $s\,d/dr$. There may be other types of terms in (6). The algebra of fluctuating variables approach of Refs. 4 and 5 suggests that (6) might contain terms involving energy density fluctuations. I will assume that, if such terms are present, they do not contribute in low enough order to affect the subsequent argument. Second, it is reasonable to require the pair distribution function in the critical region, and for $r\gg r_0$, to satisfy an equation of the form (15) simply as a correct phenomenological description of the expected properties of $h_2(r)$. So I will assume the general form (6), that $h_2(r)$ satisfies (15), and that (6) is invariant under the interchange of $\vec{r}_1$ and $\vec{r}_3$.

Equation (8) follows from assuming (6). In order that (15) follow from (8), restrictions have to be put on the coefficients $A_m{}^n$. For example, a second-order approximation of (8) yields (15) only if $A_0{}^0$, $A_2{}^0$, $A_0{}^2$ are not zero and if $A_1{}^0=0$, $A_0{}^1=-1$, $A_1{}^1/A_0{}^2=d-1$, and terms for which $m+n>2$ are neglected. I will show shortly that $A_0{}^0=0$, so that the second-order approximation does not give (15). The other possibility is that a third-order approximation of (8) will give the derivative of (15), i.e., an equation of the form of (13), and (15) then follows by one integration and with the boundary condition $h_2(r)\to 0$ at $r\to\infty$, as was the case for the particular form (5). In order for this to happen, the ten coefficients $A_m{}^n$, $m+n\leqslant 3$, must satisfy the six relations

$$\begin{gathered}A_0{}^0=A_1{}^0=A_1{}^1=A_0{}^2=0,\quad A_1{}^2/A_0{}^3=d-1,\\ A_1{}^2+A_2{}^1+A_3{}^0/2=0.\end{gathered} \tag{17}$$

Now separate the $a_m{}^n$ into parts odd and even in the variable $\hat{r}\cdot\hat{s}$, $a_m{}^n=o_m{}^n+e_m{}^n$. From (9) the $A_m{}^n$ depend only on the $o_m{}^n$, so it would appear that (17) puts only six restrictions on the ten $o_m{}^n$ and none on the ten $e_m{}^n$. However, requiring the form (6) to be invariant under the interchange of $\vec{r}_1$ and $\vec{r}_3$ leads to expressions for each of the ten $o_m{}^n$ in terms of just six of the $e_m{}^n$ and their derivatives. The complete calculation of these symmetry relations is straightforward but tedious and some of the resulting expressions are long and so the details will be published elsewhere. These symmetry relations show that $A_0{}^0=0$ so that (15) does not arise from a second-order approximation of (8). The ten symmetry relations combined with the conditions (17) are sufficient to provide a strong argument that the coefficients $a_m{}^n$ must have the form given in (7), that is, that (5) is unique up to order $m+n\leqslant 3$ in the expansion (6).

Finally I have a few comments concerning the failure of the superposition assumption in the critical region. The superposition assumption

$$f_3(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \rho^{-3} f_2(\vec{r}_1, \vec{r}_2) f_2(\vec{r}_1, \vec{r}_3) f_2(\vec{r}_2, \vec{r}_3),$$

implies that

$$h_3(\vec{r}_1, \vec{r}_3 | \vec{r}_2) = \frac{f_2(s)}{\rho^2} \left[h_2(r) + h_2(t) + h_2(r) h_2(t)\right].$$

Comparing this to (5) gives $a(s) = f_2(s)/\rho^2$ and $b = 0$. Since $b = 0$, the exponent $\eta = 0$. Note, however, that decoupling assumptions of this kind may also imply nonlinear terms [here $h_2(r)h_2(t)$] in the expansion (6). Whether or not these terms have to be kept in the subsequent analysis depends on their size relative to the nonzero linear terms in Eqs. (8) and (15). It is known[9] in the case of the superposition approximation that the linear theory (15) is not stable against the addition of quadratic terms in $h_2(r)$ for $d < 4$. This apparently has the effect of preventing the equation from having a true critical point for $d < 4$. So even if one were to find a decoupling assumption for which $b \neq 0$ and which in the linear theory gave realistic results, the presence of nonlinear terms might change the nature of the correlations. The stability of the critical solutions of the linear equation (15) against the addition of a nonlinear term $h^p(r)$ depends on the power p, the dimension d, and the coefficient b. A simple comparison of the linear and nonlinear terms suggests that the linear theory is stable if $d > 2 - \eta + 2/(p-1)$; however, a complete analysis similar to Ref. 9 is not yet available. This relation implies, for example, that a functional relation between f_3 and f_2, for which $b \neq 0$, and containing only cubic or higher ($p \geq 3$) nonlinearities, would give rise to an integro-differential equation which would allow realistic critical behavior for $d = 3$.

I have had the benefit of several discussions on this general topic with Professor J. J. Kozak and Dr. E. K. Lee.

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