Critical Point Correlations of the Yvon-Born-Green Equation

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The critical behavior of the Yvon-Born-Green integral equation for fluids is analyzed by a moment expansion which yields a nonlinear differential equation accurately describing the long-range correlations. Phase plane analyses show that for dimensions $d \leq 4$ a critical point is characterized by $\eta = 4 - d$ with $g(\tau) - 1$ negative for large distances, $\tau$, in contrast to normal expectations. For $d > 4$ the differential equation allows $\{g(\tau) - 1\}$ $> 0$ and $\eta = 0$ or $4 - d$. The compressibility never diverges if $d = 1$.

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Recently, Green, Luks, Lee, and Kozak have reported theoretical values for the critical exponents $\beta$, $\gamma$, and $\delta$ for a fluid derived from numerical solutions of the Yvon-Born-Green (YBG) equation, which utilizes the Kirkwood superposition approximation. The values reported, e.g., $\gamma = 1.24 \pm 0.04$, are surprisingly close to those believed to be correct for three-dimensional systems with a scalar order parameter. This naturally leads to the speculation that the YBG equation might yield an essentially correct description of the critical region of a fluid which would directly utilize the intermolecular interaction potential, $\varphi(\vec{r})$, and be free of the approximations, on the one hand, of a discrete lattice structure as in Ising models or, on the other hand, of a field-theoretic momentum cutoff and an unbounded continuously varying local order parameter as in the Landau-Ginsburg-Wilson models. It is to be noted, however, that the value of the critical-point decay exponent $\eta$ was not determined numerically in the studies reported in Ref. 1, primarily because convergence problems in the calculations made it difficult to obtain reliable numerical solutions with correlation lengths, $\xi$, exceeding about $6R_o$, where $R_o$ denotes the finite range of the hard-core plus square-well potential considered.

This situation makes it particularly desirable to investigate by analytic means the nature of those solutions of the YBG equation which have the smooth, slowly decaying behavior believed characteristic of the true correlation functions in the critical region. To this end we introduce here a systematic expansion procedure which leads to the approximation of the YBG equation for distances $r \approx 2R_o$ by a nonlinear differential equation whose solutions are much easier to study than those of the full integral equation. We thereby demonstrate that the critical-point pair correlation functions given by the YBG equation are, for three-dimensional systems, neither classical (with $\eta = 0$) nor in agreement with accepted critical-point phenomenology. It is interesting, nevertheless, to discover that the YBG equation displays an upper borderline dimension $d_a = 4$ in agreement with current renormalization-group theory. Our method is independent of the details of the intermolecular potential $\varphi(\vec{r})$, can be applied in general dimension $d$, and becomes more accurate as the instability limit (of infinite compressibility) is approached.

The YBG equation may be written as

$$\frac{d}{dr} \ln g(\tau) = \frac{du(\tau)}{dr} + \rho \int \frac{g(s) - 1}{s} ds,$$

where $g(\tau)$ is the pair correlation function which in a one-phase region approaches unity as $r \to \infty$, $u(\tau) = \varphi(\vec{r})/k_B T$ is the reduced intermolecular potential, and $\rho$ is the molecular number density.

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the inhomogeneous term in (1) vanishes for \( r > R_0 \); likewise, the range of integration is just \( \frac{4}{3} \ll R_0 \).

In the critical region, say for \( \xi \approx 4R_0 \), one would expect \( g(r) \) (a) to be long-range and (b), for \( r \approx 2R_0 \), to vary slowly on the scale set by \( R_0 \).

These surmises are well confirmed by the numerical solutions for \( d = 3 \). They serve to justify a moment expansion of the integral transform in (1). This is generated by first expanding \( \tilde{T} = \mathbb{E} \) about \( \frac{4}{3} = 0 \) in powers of \( s/r \) (which is small for \( r \approx 2R_0 \)) and then expanding the net correlation function \( h([\tilde{T} - \mathbb{E}]) = g([\tilde{T} - \mathbb{E}]) - 1 \) in a Taylor series expansion, i.e., in powers of \( sd/\rho \) [which is small by assumption (b)]. For the leading approximation all terms of order \( (s/r)^m \) \( \text{dr} / \rho \text{d}r \) with \( m + n < 3 \) must be retained. No assumption need be made concerning the relative size of the two parameters, i.e., the size of \( r \text{d}r \). The angular integrations on \( \mathbb{E} \) may be performed explicitly and the resulting equation can be integrated once with respect to \( r/\rho \) by use of the boundary condition, \( h(r) \to 0 \) as \( r \to \infty \), appropriate to the one-phase region. The result is

\[
\ln[1 + h(r)] = u_{1} h(r) + u_{2} \left( \frac{\partial \rho^2}{\partial r^2} + \frac{d - 1}{r} \frac{\partial h}{\partial r} \right),
\]

which should be valid for \( r \approx 2R_0 \). The coefficients are defined by

\[
u_{d}(r, T) = \frac{\partial A_{d, T}}{\partial \rho \text{d}r} \int_{0}^{\rho_{c}} \frac{\partial g(r)}{\partial r} g(r)^{d+4} \text{d}r,
\]

where \( A_{d, T} = \frac{\pi^{d+2}}{2 \rho^{d+1}} \Gamma(\frac{d+3}{2}) \). It is evident from (3) and (1) that \( u_{1} \) and \( u_{2} \) depend only on the values of \( g(r) \) for \( r \approx 2R_0 \), but they must be found by solving the full YBG equation (1).

For large \( r \) the condition \( h(\infty) = 0 \) justifies an expansion of \( \ln(1 + h) \) in powers of \( h \). In fact, the numerical solutions of (1) for \( d = 3 \) demonstrate that \( |h(r)| \) is small (\( \approx 0.05 \)) in the critical region even for \( r \approx 2R_0 \). The quadratic term in the expansion must be kept because, on the stability locus, defined by \( u_{d}(r, T) = 1 \), terms linear in \( h \) cancel from (2). Finally the long-distance form of the YBG equation becomes

\[
\frac{d^{2}h}{dr^{2}} + \frac{d - 1}{r} \frac{dh}{dr} = \kappa^{2} h - \lambda h^{2},
\]

where \( \kappa^{2}(r, T) = (1 - u_{d})/u_{d} \) and \( \lambda(r, T) = 1/2u_{2} \).

Equation (4) is subject to the boundary condition \( h(\infty) = 0 \).

The accuracy of this representation of the YBG equation has been tested numerically in the vicinity of the stability locus, defined now by \( \kappa(r, T) \) = 0, against the solutions of the full equation. For \( \kappa \) small but nonzero and \( r \) sufficiently large that \( |\kappa h| \ll |\lambda h|^{2} \), the differential equation (4) becomes linear and has solutions of Ornstein-Zernike form with

\[
h(r) \approx D_{o} e^{-\sigma} / \rho^{(d-1)/2} \text{ for } \kappa r \gg 1,
\]

the standard result of linear theory. The correlation length should evidently be identified with \( \xi = 1/\kappa \); therefore \( \kappa^{2}(r, T) \) should be positive for high enough temperatures or for low and high densities. This is borne out numerically. The \( \kappa^{2} \) becomes small in the critical region: \( \theta = \varepsilon/k_{B}T \approx 0.37 \) (where \( \varepsilon \) is the square-well depth) and \( 4R_{0} \approx 2.3 \) (the relevant density being determined by the locus of maximum compressibility at fixed \( T \)).

Likewise the parameter \( \lambda(r, T) \) in (4) should be slowly varying and positive in the critical region; the calculations confirm this, yielding \( u_{2} = \lambda_{2} \approx 0.76R_{0}^{2} \) and \( \lambda_{1}/u_{2} = 1.8 \). We have reliable numerical solutions of (1) corresponding to \( \xi \) in the range 3.5\( R_0 \) to 5.5\( R_0 \). These solutions can be matched, to their known accuracy, by numerical solutions of (4) over the range \( 4R_{0} < r < 90R_{0} \) at \( r \approx 4R_{0} \), \( h(r) \approx 10^{-2} \) and the solutions agree to 0.05%. At \( r \approx 30R_{0} \), \( h(r) \approx 10^{-6} \) and the solutions agree to 3%. The quadratic term in (4) plays an essential role in the fit, particularly for the smaller values of \( r \). Thus (3) and (4) do indeed provide an accurate description of the long-range behavior of the full YBG solutions and the general variation of \( \kappa \) and \( \lambda \) is as expected.

At the critical point the isothermal compressibility \( K \) should diverge which, if \( K \) is computed in the standard way by integrating \( g(r) \), can occur only as \( \kappa \) vanishes. We thus assume that the critical-point correlations may be described by (4) with \( \kappa = 0 \). Since the equation is of second order and we impose only the single boundary condition \( h(\infty) = 0 \), there will be a family of solutions among which the (presumably) unique critical-point solution of the YBG equation must be found. The problem then is to characterize the large-\( r \) behavior of all solutions of Eq. (4) with \( \kappa = 0 \) which vanish as \( r \to \infty \). General solutions in analytic form are not available for arbitrary \( d \); nevertheless, a fairly complete account of the behavior for large \( r \) can be given for all solutions for any (including noninteger) \( d \geq 1 \).

Before presenting this, it is instructive to try the simple power-law form \( h(r) = D_{o} / r^{\xi} \). This is a solution if and only if \( \xi = 2 \) and

\[
D_{o} = 2(d-4)/\lambda = 4(4 - d)u_{2}.
\]
For \( d > 4 \) the amplitude is positive, as expected physically, but the decay exponent corresponds to \( \eta = 4 - d \) rather than to 0 as believed correct\(^6\). Conversely, for \( d < 4 \) the amplitude of this solution is negative, which appears to be quite unphysical! Thus a correct upper borderline dimensionality \( d_c = 4 \) emerges from the equation but the behavior for \( d \) on either side of the border is not as expected. The negative amplitude will be seen in the following to be a property of all \( d < 4 \) solutions.

To proceed more systematically, note that if \( \kappa = 0 \), Eq. (5) admits a homology transformation\(^6\): specifically, if \( h(\gamma) \) is a solution then so is \( \tilde{h}(\gamma) = l^2 h(l\gamma) \) for any \( l \neq 0 \). This represents an equivalence relation which partitions all solutions into disjoint homology classes. The equivalence property is exploited by the change of variables \( w = \ln r, z(w) = wr^2 h(\gamma), \) and \( y(w) = dz/dw = z'(w) \), yielding the equivalent set of coupled first-order equations

\[
y'(w) = (6 - d)y + 2(d - 4)x - x^2, \quad z'(w) = y(w),
\]

with boundary condition \( e^{2w} h(w) = 0 \) as \( w \to \infty \).

Since these equations are autonomous (no explicit \( w \) dependence) their solutions define fixed trajectories in the phase plane \((y,z)\). If \( [y(w),z(w)]\) is a solution then so is \( [y(w+w_0),z(w+w_0)]\) and each trajectory corresponds to a single homology class of solutions.

The large-\( \gamma \) behavior of \( h(\gamma) \) is determined by the variation of \( z(w) \) as \( w \to \infty \). The theory of two-variable autonomous equations\(^6\) allows just three possibilities as \( w \to \infty \); the phase point \((y,z)\) may move on a trajectory which (a) recedes to \( \infty \), (b) is a closed (periodic) trajectory or approaches a closed trajectory (limit cycle behavior), or (c) which terminates in the phase plane at a fixed point (defined by \( y' = z' = 0 \)). Solutions of (7) of type (a) can readily be shown to reach infinity at finite \( w \) (or \( \gamma \)) and hence are physically unacceptable. As regards (b), Bendixon's criterion (essentially Green's lemma) applied to (7) shows that there can be no closed trajectories unless \( d = 6 \). When \( d = 6 \) the equations can be integrated analytically and there are periodic solutions. Thus, except for the case of \( d = 6 \), the large-\( w \) behavior is determined entirely by the phase portrait of the trajectories near the two fixed points \( O_1 = (0,0) \) and \( O_2 = (0,D_0) \) [see (6)]. Each trajectory leading into one of the fixed points describes a one-parameter family (homology class) of solutions of (7). The local phase portraits can be found in the standard way by linearizing about \( O_1 \) and about \( O_2 \) except for \( d = 4 \), when the two fixed points coincide and the linearized equations have a zero eigenvalue. Relevant results of this analysis are as follows. First, for \( d = 4 \), (i) no trajectories terminate at \( O_1 \) and so there are no corresponding solutions; and (ii) precisely two trajectories terminate at \( O_2 \), and so there are two families of solutions, all of which approach \( z = D_0 \) as \( w \to \infty \), corresponding to the asymptotic behavior \( h(\gamma) \approx D_0/\gamma^2 \). This implies a critical exponent \( \eta = 4 - d \) but, as before, it follows from (6) that \( h(\gamma) \) is negative, contrary to physical expectations. Second, for \( d > 4 \), (iii) two trajectories terminate at \( O_1 \), yielding two families of solutions. For large \( w \) these all have the form \( \zeta \approx De^{(w-\epsilon)/D_0} \) where \( D \) parametrizes the solutions. For these solutions \( h(\gamma) \approx D/\gamma^{d-2} \) at large \( \gamma \) and thus they have the classical Ornstein-Zernike critical form with \( \eta = 0 \). (iv) If \( 4 < d < 6 \) no trajectories terminate at \( O_2 \) and there is only the isolated solution corresponding to \( h(\gamma) = D_0/\gamma^2 \) as found before. However, \( D_0 \) is now positive so the solution is not unreasonable physically. (v) When \( d = 6 \) the trajectories near \( O_2 \) are all closed orbits and there is a two-parameter family of solutions with asymptotic behavior like \( [D_0 + D_1 \cos \ln(r/r_0)]/\gamma^2 \) with \( |D_1| < D_0 \), the envelope corresponding again to \( \eta = 4 - d \). (vi) For \( d > 6 \) all trajectories near \( O_2 \) spiral in towards \( O_2 \) and terminate there. This yields a two-parameter family of solutions all asymptotic to the previous special solution \( h(\gamma) \approx D_0/\gamma^2 \). Thus for all \( d > 4 \) two possibilities emerge: (a) \( \eta = 0 \) or (b) \( \eta = 4 - d \), with both cases allowing a positive \( h(\gamma) \). Further analysis is needed to decide which of these cases, if either, describes the actual solutions of the YBG equation.\(^6\)

Finally, when \( d = 4 \) the phase portrait around the coincident fixed points \( O_1 = O_2 = (0,0) \) cannot be obtained by linearization. However, one can show that there is a unique trajectory terminating at \( O_1 \), which corresponds to solutions with asymptotic behavior \( h(\gamma) \approx -2/\gamma r_0^2 [\ln(r/r_0) - \ln(r/r_0)] \), where \( r_0 \) is a constant. This corresponds to \( \eta = 0 \) even though it is not purely algebraic; however, \( h(\gamma) \) is always negative for these solutions just as it is for \( d < 4 \).

These results make it clear that any solutions of the YBG equation on the stability locus and at the critical point are, for \( d < 4 \), in serious disagreement with the accepted critical behavior for real systems; the value of \( \eta \) is unrealistically large for \( d < 4 \) and the predicted critical point correlations are negative.
The question of the behavior of solutions of (4) for $\kappa > 0$ and their relation to the solution of the full YBG equation is harder. In fact, it is more reasonable to identify the critical-point behavior with the limit $\kappa \to 0$ rather than with $\kappa = 0$. In principle the limiting behavior could be different (although for $d < 4$ numerical studies demonstrate that this is not the case; but see also Ref. 8). The issue can, however, be approached easily for $d = 1$ since (4) [as also (2)] is then integrable in closed form for all $\kappa$. It is found that any positive solutions which satisfy $h(\infty) = 0$ are bounded above by $3\kappa^2/2\lambda$ and hence vanish when $\kappa \to 0$. Conversely, any solutions not vanishing when $\kappa \to 0$ approach the form $D_0/\nu_0^2$ and are always negative. In all cases, however, the total compressibility remains bounded (assuming $g(\nu)$ is bounded for small $\nu$] and no true critical behavior of the usual type can occur. Insofar as one-dimensional fluids with short-range forces cannot exhibit phase transitions this is a positive feature of the YBG equation. One would, however, like to show that the stability locus $\kappa^2 = 0$ cannot be reached at all for $d \neq 1$. That, however, requires a detailed analytic understanding of the short-range behavior of the YBG equation which is beyond the scope of our present approach.

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4The hard core diameter is taken as $\sigma = R_0/1.85$ in order to simulate argon (see Ref. 1).
5The approach was developed independently by the first three authors, who announced their preliminary results in a talk contributed to the Fourteenth International Conference on Thermodynamics and Statistical Mechanics, University of Alberta, Edmonton, 17–22 August 1980, and by the last two authors, who reported the dimensionality dependence in the ensuing discussion at that conference.
7In the latest improved numerical calculations a cutoff distance of $5\sigma R_0$ or greater is used.
8The imposition of a second boundary condition at short distances has been investigated by M. E. Fisher and S. Fishman (to be published) and yields a description of the critical behavior of the correlations for small nonzero $\kappa$.