Critical Scattering and Integral Equations for Fluids

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Critical scattering predictions of the Percus-Yevick, hypernetted-chain, and Yvon-Born-Green integral equations for fluids are described for general dimensions d. The first two equations are unsatisfactory. The Yvon-Born-Green equation predicts critical scattering of Ornstein-Zernike form for $d>4$, but for $d \leqslant 4$ the compressibility, K_T, remains bounded unless the net correlation function, $g(r)-1$, becomes negative near criticality for intermediate and large r: In that case scaling behavior occurs with $\eta=4-d$ and $K_T \rightarrow +\infty$ for $d>d_0 \simeq 2.2$.

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Approximate integral equations for classical fluids have long been a cornerstone of modern theories of fluids.[1] The study of such equations is also instructive because they are prototypes of more complex equations for many-body quantal systems. At low densities the usual equations, in particular the Percus-Yevick (PY), hypernetted-chain (HNC), and Yvon-Born-Green (YBG) equations, are satisfactory since, for a given pair potential, $\varphi(r)$, they reproduce correctly the leading virial coefficients. The predictions of these equations for the *critical region* of a fluid, however, have remained obscure and unrelated to modern theories of critical behavior where the spatial dimensionality, d, play a central role.[2] This has impeded the construction of unified theories for fluids that would encompass, in a reasonably quantitative way, both proper critical behavior and the effects of realistic, continuum potentials.

Here we report analytical work which bears on the nature of the critical scattering predicted by the PY, HNC, and YBG equations for general d. Ideally, one would like, for $d=2$ and 3, to obtain reasonably, nonclassical values of the critical exponents,[2] particularly γ, which specifies the divergence of the compressibility, K_T, on the critical isochore (i.e., at density $\rho=\rho_c$), and η, which describes the critical point decay of the net pair-correlation function, $h(r;\rho,T)=g(r)-1$, as $1/r^{d-2+\eta}$. For $d \geqslant 4$ the classical values $\gamma=1$ and $\eta=0$ should appear.[2] One might also hope to find scaling behavior[2] in terms of the correlation length, ξ, and the density deviation, $(\rho-\rho_c)$, as observed experimentally. In this light we conclude that both the PY and HNC equations are quite unsatisfactory.

The YBG equation, however, has excited interest recently because numerical studies[3] for $d=3$ have suggested exponents agreeing well with experiment, e.g., $\gamma \simeq 1.24$. To examine this we have extended a new analytical approach[4] [for finite-range potentials, i.e., $\varphi(r)=0$ for $r>R_0$][5] which had revealed apparently anomalous behavior precisely *at* criticality. We find, first, (A) that for $d>4$ the YBG scattering function in the critical region is, indeed, asymptotically of classical or Ornstein-Zernike (OZ) form[6] just as renormalization-group ideas imply.[2] In addition, for all $d \leqslant 4$ we show there are only two possibilities: Either (B) as $\xi \equiv 1/\kappa(T,\rho)$ diverges on approach to criticality, the correlations obey the asymptotic scaling relation

$$h(T,\rho;r) \approx r^{-(d-2+\eta)} D(\kappa r), \tag{1}$$

with $\eta=4-d$, while $h(r)$ becomes *negative* for intermediate and large r in the critical region (see below); or (C) the YBG equation exhibits *no criticality,* in the sense that K_T remains uniformly bounded. In fact, only (C) applies for $d<2$ (as has been shown separately[4] for $d=1$). Despite the unexpected and, perhaps, unphysical negativity of $h(r)$ under (B) the compressibility [as computed from $K_T \sim \chi = 1+\rho\int h(r)\, d^d r$] diverges to $+\infty$ provided $d>d_0 \simeq 2.2$; however, for $2 \leqslant d < d_0$ a divergence to $-\infty$ is implied! But if the YBG (p,ρ) isotherms vary smoothly, as essential physically, this latter behavior is self-contradictory, leaving only the possibility (C). For $d=3$ the best current numerical solutions[3,7] still suggest that $h(r)$ stays positive (for $r>2R_0$), so that the YBG equation for ordinary space may well exhibit no true criticality at all!

To explain the arguments underlying our conclusions consider first the PY equation. For short-range potentials[5] it insists that the direct correlation function[1] is *always* of finite range. It follows directly that the critical scattering is of OZ form for *all d*; specifically Eq. (1) holds with $\eta=0$ while $D(x) \equiv D_{OZ}(x)$ is x^{d-2} times the Fourier transform of $1/(1+q^2)$. However, even though the PY equation fails to exhibit the anticipated nonclassical scattering behavior[2] for $d<4$, the OZ form is a fairly good approximation for real fluids and $\eta(d=3)\simeq 0.03$ is rather small. Nevertheless, although one can also show,[8] on the basis of Baxter's exact solution for sticky hard spheres,[1] that the PY equation of state *scales* with classical exponents (including $\gamma=1$), the scaling function displays a *nonclassical singularity:* In particular, the usual asymptotic gas-liquid symmetry, which is well confirmed by experiment, is strongly violated, with K_T diverging more strongly for $\rho>\rho_c$. Furthermore, the specific heat, $C_V(T)$, diverges logarithmically ($\alpha=0$) not only *on* the critical isochore $\rho=\rho_c$, which is a plausible approximation to reality ($\alpha \simeq 0.12$), but *also*[8] at $T=T_c$ for *all* $\rho>\rho_c$: This, of course, is completely unphysical. Comparison with the numerical solutions of Henderson and Murphy (see Ref. 1) for a Lennard-Jones potential indicates that the unphysical behavior of the PY equation for $d=3$ is not just an artifact of the sticky-hard-sphere model. For $d=2$ the unphysical PY-OZ prediction $h_c(r)\sim -\ln r \to -\infty$ should also be recalled.

Less can be said analytically at present about the HNC equation; however, careful extension of an argument due to Green[9] shows that the critical point decay exponent must be $\eta=\frac{1}{3}(6-d)$ for $d\leqslant 6$ but sticks at $\eta=0$ for $d\geqslant 6$. Thus the HNC equation does exhibit a borderline dimensionality, but at $d_>=6$ rather than 4.[2] Although positive η is predicted for $d=2$ (as needed physically) the numerical values for $d=2$, 3, and 4 are *all* poor. Furthermore, numerical solutions for $d=3$ demonstrate that K_T diverges at most very weakly,[10] say[11] $\gamma \lesssim 0.04$, which is completely unrealistic!

Our analysis of the YBG equation[12] rests on a reduction[4] of the full integral equation[1] to a second-order nonlinear differential equation for $h(r)$, valid for small κR_0 and $r\gtrsim 2R_0$, and subject to the boundary condition $h(\infty)=0$. The original discussion[4] focused mainly on $\kappa=0$, the critical point itself, and revealed changes in behavior at $d=4$ suggestive of the correct borderline dimensionality[2]; it was noted, however, that, physically, the limit $\kappa\to 0+$ represents the crucial issue. To elucidate this we take two further steps. First, we impose a second, "short-distance" boundary condition, $h(a)=h_a(T,\rho)$, where $a\gtrsim 2R_0$ is fixed: The precise value of h_a entails solution of the YBG equation at short distances ($\lesssim 2R_0$) but only its boundedness is needed here. Second, by putting

$$h(r)\equiv(c/r)^2 Z(x;\kappa), \quad \text{with} \quad x\equiv e^w=\kappa r, \tag{2}$$

where $c(T,\rho)$ varies slowly, the nonlinear equation[4] can be cast in the scaled form

$$\frac{d^2Z}{dw^2}+(d-6)\frac{dZ}{dw}+\tfrac{1}{2}(4\epsilon+Z)Z=x^2Z, \quad \epsilon=4-d. \tag{3}$$

The boundary conditions become (a) $Z/x^2\to 0$ as $x\to\infty$; (b) $Z(\kappa a;\kappa)\to z_a\equiv h_a a^2/c^2$ as $\kappa\to 0$. Note that the explicit dependence on κ in (2) enters through the new condition (b).

Now when (3) is linearized the solutions satisfying (a) yield $h(r)$ in precisely OZ form[4]; furthermore $Z(x)$ then varies as x^{4-d} for $x\lesssim 1$. Conversely, to satisfy (b) requires $x\to 0$ and allowance for the nonlinear term; but (3) then becomes autonomous and analysis in the phase plane, $(Y=dZ/dw, Z)$, where there are just two fixed points, $O_1=(0,0)$ and $O_2=(0,-4\epsilon)$, is revealing.[4] For $d>4$ one readily discovers a unique class of solutions, $Z_0(kx)$, which flow into O_1 and are parametrized only by $k>0$. By choosing k, the condition (b) can be satisfied [provided only $z_a\leqslant Z_0^{\max}\simeq d(d-4)$ and, for $d<6$, $z_a>0$]. One also finds that $Z_0(x)$ varies as $Z^\infty x^{4-d}$ for $x\gtrsim x_0(\kappa)\ll 1$ with $Z^\infty>0$. This crucial fact enables the autonomous solution to be matched smoothly onto a linearized, OZ-type solution with errors of relative order $\kappa^{|\epsilon|}\to 0$.[12] The scaled matching point, $x_0\equiv\kappa r_0$, is found to *vanish* like $(\kappa a)^{|\epsilon|/(d-2)}$, so that (1) holds asymptotically with $\eta=0$ and $D(x)=D_{OZ}(x)$, as stated. Note, however, that the function $Z_0(x)$ determines the behavior of $h(r)$ for r up to r_0, which actually diverges to ∞ as $\kappa\to 0$! In summary, the YBG equation exhibits correct OZ scattering behavior above the correct borderline, $d_>=4$.[2] This implies $\chi\sim\kappa^{-2}$ and scaling relations such as $\gamma=2\nu$, but we have not been able to show convincingly that, e.g., γ takes its classical value.

For $d\leqslant 4$ the situation is more complicated. First, the autonomous equation for $d<4$ has no solutions which approach O_1 as $x\to\infty$ (that might be matched to OZ, linearized solutions). (For $d=4$ there are such solutions for $Z\leqslant 0$ but they play only a subsidiary role.)[12,13] Rather, any positive solution of the autonomous equation flows to a point where $Z=0$ and $dZ/dw<0$: One can prove that such solutions of the full Eq. (3) can never satisfy (a) as $x\to\infty$.[12] Next one shows that for small x, needed for (b), the only positive solutions of (3) satisfy[12,13] $Z(x)=A_+x^\epsilon(1+\cdots)+A_-x^2+\cdots$, but that if (a) is satisfied the amplitudes A_+ and A_- are bounded above: Of course, this is not hard to check by numerical integration. It then follows that, as $\kappa \to 0$ with $h_a, z_a > 0$, it will eventually become *impossible* to satisfy *both* conditions (b) and (a). Current numerical studies of the full $d=3$ YBG equation check the accuracy[3] of (3) for small κR_0, but as yet reveal no unequivocal signs that κ becomes small enough to encounter this conflict.[3,7] Nonetheless, if $h(r)$ remains positive for fixed $r > 2R_0$, it follows that κ cannot become too small: Thus the compressibility integral, χ, can at most yield a large but finite K_T, in accord with alternative (C) stated above.

If h_a (and so z_a) becomes negative in the critical region the relevant solutions for small x are determined by the fixed point O_2 as $Z(x) = -4\epsilon + x^2 + Bx^{-\zeta} + \cdots$ with $\zeta(4) = 0 < \zeta(d) < \zeta(1) = 1$ for $1 < d < 4$.[12,13] The phase plane trajectories reveal that any value of z_a (<0) yields a solution which, as $\kappa \to 0$, approaches the *principal solution,* $Z^\dagger(x)$, of (3) which satisfies (a) *and the modified condition* (b′) $Z(x) \to -4\epsilon$ as $x \to 0$ (corresponding to the coefficient B, of the term $x^{-\zeta}$ above, vanishing). Since (3) is of second order, (a) and (b′) should, and indeed do, suffice to determine a unique solution which, however, must be computed numerically. Via (3) we have thus established that (1) holds with $D(x) = c^2 Z^\dagger(x)$ and $\eta = 4-d$, as stated. The negativity of $h(r)$ for intermediate and larger r follows[13] because (b′) implies $Z^\dagger(x) < 0$ for small x. The scaling implies $K_T \sim \kappa^{2-d}$ for $d > 2$, and $\sim \ln\kappa$ for $d=2$; but the sign of divergence is fixed by the integral $I^\dagger = \int_0^\infty Z^\dagger(x) x^{d-3} dx$: For $d > d_0 \simeq 2.2$ this is positive since $Z^\dagger(x)$ becomes positive for large x.[12] However $I^\dagger$ is negative for $d < d_0$ and diverges as $-8/(d-2)$ when $d \to 2+$. Finally, K_T cannot diverge for $d < 2$ even if $\kappa \to 0$.

In overall summary, while the YBG equation is the only one of the standard integral equations for fluids to exhibit the desired transition to classical critical behavior at the correct borderline dimensionality, $d_> = 4$, its analytic character for $d \leqslant 4$ leaves much to be desired: As explained in the opening paragraphs, it is quite possible that, even though K_T becomes comparatively large, no true critical point arises; if there is one, the pair correlations must become negative in a peculiar and, thus far, unobserved manner.

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[1] See J. A. Barker and D. Henderson, Rev. Mod. Phys. 48, 587 (1976), and references therein.

[2] See, e.g., M. E. Fisher, Rev. Mod. Phys. 46, 597 (1974), and references therein.

[3] K. A. Green *et al.*, Phys. Rev. Lett. 42, 985 (1979), and Phys. Rev. A 21, 356 (1980).

[4] G. L. Jones, J. J. Kozak, E. Lee, S. Fishman, and M. E. Fisher, Phys. Rev. Lett. 46, 795, 1350(E) (1981).

[5] Although, important aspects of our analysis can be extended to potentials with power law decay: e.g., S. Fishman, to be published.

[6] Note that this explicitly rules out the possibility $\eta = 4-d$, left open for $d > 4$ in Ref. 3.

[7] G. L. Jones and K. A. Green-Luks, private communication.

[8] S. Fishman and M. E. Fisher, to be published.

[9] M. S. Green, J. Chem. Phys. 33, 1403 (1960).

[10] M. I. Guerrero, G. Saville, and J. S. Rowlinson, Mol. Phys. 29, 1941 (1975).

[11] S. M. Foiles and N. W. Ashcroft, Cornell University Materials Science Center Report No. 4378 (unpublished).

[12] M. E. Fisher and S. Fishman, to be published.

[13] For simplicity we omit the various special considerations, factors of $1/|\ln x|$, etc., needed at $d=4$.