# Absence of power-law behavior of the hypernetted chain equation

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The hypernetted chain equation is solved numerically near its critical point and the compressibility is found to deviate from power-law behavior. This failure can be traced to the asymptotic form of the bridge function, an analysis of which is given. A comparison is also made with the analytic behavior of the Percus-Yevick equation and suggestions for improved integral equations are discussed.

## I. INTRODUCTION

The thermodynamic functions of real fluids become singular at the liquid-gas critical point.[1] These divergences have been studied in the context of the integral-equation approach to the structure and thermodynamics of simple liquids. The hypernetted chain,[2-4] Percus-Yevick[2,5,6], and Yvon-Born-Green[7] equations all predict a liquid-gas instability. The Percus-Yevick (PY) equation leads to power-law behavior but with mean-field exponents. The Yvon-Born-Green equation (YBG) also leads to power-law behavior, but with non-classical exponents, indeed exponents close to those of real fluids.

Here we examine the isothermal compressibility of a simple fluid as determined from its description in terms of the hypernetted chain (HNC) equation. From the numerical solutions we find significant deviations from scaling behavior. As is well known, the HNC equation can be obtained from the diagrammatic resummation method by neglecting the contribution of the elementary diagrams, or the bridge function $E(r)$. We will present results below for the asymptotic critical behavior of $E(r)$, and from its role as an effective potential in a HNC-type of equation, we can account qualitatively for the failure of scaling. We are also able to show that the PY equation can also exactly describe a real system with an appropriately defined *effective* potential which differs, however, in a crucial way from the corresponding effective potential in the HNC equation. Finally, we shall use these insights to suggest possible modifications of the HNC equation.

## II. NUMERICAL SOLUTION OF HNC

Let $c(r)$ be the Ornstein-Zernike direct correlation function and $h(r)[=g(r)-1]$ the total correlation function. If $\phi(r)$ is the pair potential then the HNC equation is solved using a standard iterative procedure[4] on the equations

$$c(r) = \exp[-\beta\phi(r) + \theta(r)] - \theta(r) - 1,$$
$$[\theta(r) = h(r) - c(r)] \tag{1a}$$

and

$$\theta(k) = \rho c^2(k)/[1 - \rho c(k)]. \tag{1b}$$

The first equation is a statement of HNC, and the second is the Fourier transform of the Ornstein-Zernike equation for a homogeneous fluid with number density $\rho$. The system of equations (1a) and (1b) is particularly advantageous because the integrals for each transform are over the shortest ranged function in both real and reciprocal space. For the pair potential we choose

$$\phi(r) = (A\epsilon/r)(e^{-a(r-\sigma)} - e^{-b(r-\sigma)}) \tag{2}$$

whose range and strength can easily be varied. In particular the exponential damping leads to a distinct numerical advantage in that the correlation functions reach their asymptotic behavior relatively quickly in terms of the characteristic range of the potential. As a consequence the dependence on the range of the numerical integrations can be readily controlled and is much reduced, for example, compared with the Lennard-Jones potential. In what follows, temperatures are given in units of $\epsilon/k_B$ (we choose $A$ so that $\epsilon$ is the magnitude of the potential minimum) and lengths in units of $\sigma$, where $\phi(\sigma) = 0$. Computational and other details are given in the Appendix.

Given solutions for $c(r)$, we compute the isothermal compressibility at constant density and temperatures $T > T_c$ from the thermodynamic relation

$$\rho k_B T \kappa_T = [1 - \rho c(k=0)]^{-1}. \tag{3}$$

For a (reduced) temperature $T = 1.42$, a (reduced) density $\rho = 0.274$ maximizes $\kappa_T$. This density approximates the critical density. It is important to note, however, that the results we report are independent of the precise value of critical density assumed. The values of $\kappa_T$ as a function of $T$, as calculated from the iterative procedure, are summarized in Fig. 1. They diverge strongly
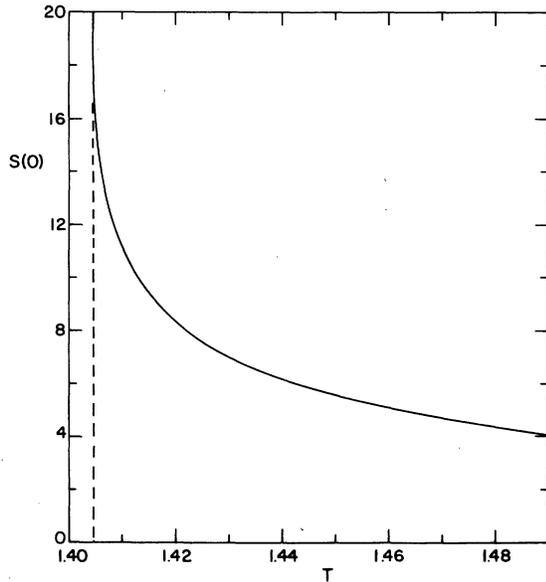
FIG. 1. $S(0)$ versus temperature in units of $\epsilon/k_B$ (see text). The dashed line indicates the position of the singularity.

at a temperature $T = 1.4045$. Now, for real fluids this divergence can be summarized by the power law[1]

$$\kappa_T \sim \epsilon^{-\gamma}, \tag{4}$$

where $\epsilon = (T - T_c)/T_c$, and $\gamma = 1.2$–$1.24$.

In order to attempt to force our results to conform to such a law, we first adjust the choice of $T_c$ to produce linear behavior in a plot of $\log\kappa_T$ against $\log\epsilon$ over a significant range of $\log\epsilon$. We then examine $\log\kappa_T$ over the remainder of the range of $\log\epsilon$: in no case is linear behavior observed to continue to the lowest values of $\epsilon$ calculated. Typical results are presented in Fig. 2. They clearly show that $\kappa_T$ as obtained from the HNC equation via (3) deviates from a power law form, though the presence of a rapid divergence at $\epsilon \to 0$ clearly suggests the persistence of a singular point. The data is also plotted logarithmically in Fig. 3 and the fit to a power law is seen to be equally poor. Note that it is not feasible to compute $\kappa_T$ near $T_c$ from the virial equation for the pressure. Indeed Klein and Green[2] have shown that the virial singular point for HNC occurs well inside the spinodal curve computed from the compressibility equation: the algorithm used here fails in that region.

## III. FAILURE OF POWER LAWS: ANALYSIS

A deeper analysis of the HNC equation shows that the failure of power-law behavior is not unexpected. As noted above, HNC can be characterized by the approximation it makes for the
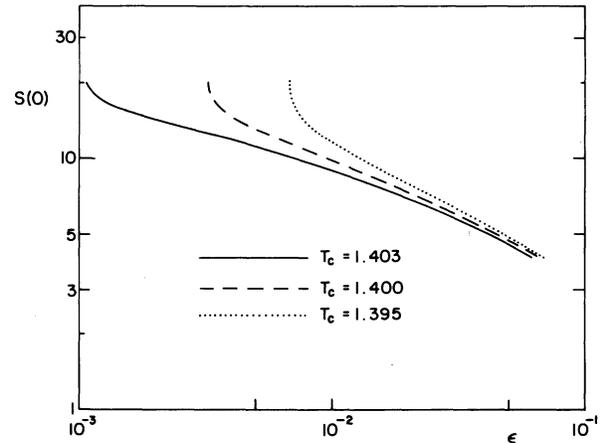


FIG. 2. Log-log plot of $S(0)$ versus reduced temperature, $\epsilon = (T - T_c)/T_c$, for three possible values of $T_c$. These curves demonstrate the deviations from power-law characteristic of HNC.

bridge function, $E(r) = 0$. It is well known that the bridge function can be defined within the framework of functional Taylor expansions for inhomogeneous fluids,[8] for which a hierarchy of direct correlation functions can also be defined,[9] namely,

$$c^{(1)}(1) = \delta \mathcal{F}_{\text{ex}}/\delta\rho(1),$$
$$c^{(2)}(1, 2) = \delta c^{(1)}(1)/\delta\rho(2), \tag{5}$$
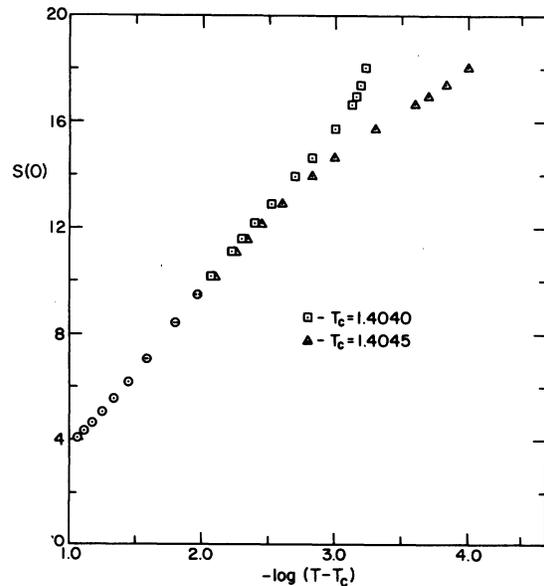$$c^{(3)}(1, 2, 3) = \delta c^{(2)}(1, 2)/\delta\rho(3), \text{ etc.},$$



FIG. 3. $S(0)$ versus $-\log_{10}(T - T_c)$ for two possible values of $T_c$ demonstrating the deviation from logarithmic behavior. For $-\log_{10}(T - T_c) < 2.0$ the points for the two different $T_c$'s are not distinguishable on this scale, and are combined as shown (circles).

where $\mathcal{F}_{ex}$ is the excess Helmholtz free energy. It follows that

$$c^{(2)}(1,2) = \delta[\beta V(1) + \ln\rho(1)]/\delta\rho(2), \qquad (6)$$

where $V$ is an external one-body potential. The definition of $h(1,2)$ and the Ornstein-Zernike equation give, respectively,

$$\rho(1)\rho(2)h(1,2) = \rho^{(2)}(1,2) - \rho(1)\rho(2) \qquad (7)$$

and

$$h(1,2) - c(1,2) = \int d3\,\rho(3)h(1,3)c(3,2). \qquad (8)$$

To obtain the familiar result for a homogeneous fluid

$$g(r) = \exp[-\beta\phi(r) + h(r) - c(r) + E(r)], \qquad (9)$$

we first expand $\ln[\rho(1)e^{\beta V(1)}]$ in terms of the density variation induced by an external potential that arises from the addition of an extra particle placed at 2 [i.e., $V \equiv \phi(1.2)$]. Applying (8) and exponentiating the expansion gives the inhomogeneous generalization of (9) with

$$E(1,2) = \tfrac{1}{2} \iint d3\,d4\, c^{(3)}(1,3,4)\rho(3)h(2,3)\rho(4)h(2,4)$$

$$+ \tfrac{1}{6} \iiint d3\,d4\,d5\, c^{(4)}(1,3,4,5)\rho(3)h(2,3)$$

$$\times \rho(4)h(2,4)\rho(5)h(2,5) + \cdots . \qquad (10)$$

This series expansion for $E$ can be rewritten in a more useful form as follows: Recall that the density-density correlation function is defined by

$$g(1,2) = \beta^{-1}\delta\rho(1)/\delta u(2), \qquad (11)$$

where $u(2) = \mu - \beta V(2)$, $\mu$ being the chemical potential. It is related to the other correlation functions by

$$g(1,2) = \rho(1)\rho(2)h(1,2) + \rho(1)\delta(1,2) \qquad (12)$$

and

$$g^{-1}(1,2) = \delta(1,2)\rho^{-1}(1) - c^{(2)}(1,2). \qquad (13)$$

A further functional differentiation of (13) now gives

$$\frac{\delta g^{-1}(1,2)}{\delta\rho(3)} = \frac{-\delta(1,2)\delta(1,3)}{\rho^2(1)} - c^{(3)}(1,2,3) \qquad (14)$$

which involves the third-order direct correlation function. Some elementary manipulations now lead to the following:

$$\int d3\, g(1,3)\frac{\delta g^{-1}(3,2)}{\delta\rho(4)} = \int d3\, \frac{\delta\rho(3)}{\delta u(1)}\frac{\delta^2 u(2)}{\delta\rho(3)\delta\rho(4)}$$

$$= \frac{\delta^2 u(2)}{\delta\rho(4)\delta u(1)} = 0 \qquad (15)$$

and

$$\iint d3\,d4\, g(1,3)g(1,4)\frac{\delta g^{-1}(3,2)}{\delta\rho(4)}$$

$$= \beta^{-1} \iint d3\,d4\, \frac{\delta\rho(3)}{\delta u(1)}\frac{\delta\rho(4)}{\delta\mu(1)}\frac{\delta^2 u(2)}{\delta\rho(3)\delta\rho(4)}$$

$$= \frac{\delta^2\mu(2)}{\delta u(1)\delta u(1)} = 0. \qquad (16)$$

If we now substitute (12) and (14) into (15) and (16) we obtain

$$\iint d3\,d4\,\rho(3)h(1,3)\rho(4)h(1,4)c^{(3)}(2,3,4)$$

$$= c^{(3)}(1,1,2) - h^2(1,2). \qquad (17)$$

Note that in arriving at these results some care has to be exercised to avoid spurious delta functions that can arise from two-site coincidences. It is important to work directly with the averages of the density operators. Applying similar arguments to the higher order terms in the series for $E(1,2)$ and then taking the homogeneous limit [where $c^{(2)}(1,2) = c(r)$] we find

$$E(r) = -\tfrac{1}{2}h^2(r) + \tfrac{1}{3}h^3(r) - \cdots + \mathcal{C}(r)$$

$$= \ln(1+h) - h + \mathcal{C}(r), \qquad (18)$$

where

$$\mathcal{C}(r) = \mathcal{C}(1,2) = \tfrac{1}{2}c^{(3)}(1,1,2)$$

$$- \tfrac{1}{6}c^{(4)}(1,1,1,2) + \cdots . \qquad (19)$$

Finally, substituting (18) into (9) gives

$$c(r) = -\beta\phi(r) + \mathcal{C}(r) \qquad (20)$$

which shows that $\mathcal{C}(r)$, as defined by (19), is the correction to the familiar long-range approximation for $c(r)$.

The definition of $\mathcal{C}(r)$ in terms of third- and higher-order functional derivatives suggests that it should be small and short ranged. [Observe that the PY and HNC equations can be obtained by ignoring terms of the same order as $\mathcal{C}(r)$.] Now, near the critical point $c(r)$ becomes long ranged. Since $\phi(r)$ is short ranged, we conclude that near the critical point $\mathcal{C}(r) \approx c(r)$ for large $r$. But at the critical point[1] for $d > 2$ (and $\eta < 2$) we have

$$h(r) \sim r^{-(d-2+\eta)}$$

and an argument due to Green[10] shows that

$$c(r) \sim r^{-(d+2-\eta)}$$

where $d$ is the dimensionality. From this behavior we note that for $d < 6$ the dominant term in the asymptotic expansion for $E(r)$ [see (18)] must be $-\tfrac{1}{2}h^2(r)$. From this we can conclude that $E(r)$

is negative and both its *magnitude* and its *range* increase as $h^2(r)$ as the critical point is approached.

The next step in the argument is to return to the exact statement (9) and observe that the correlation functions for potential $\phi$ can be obtained, in principle without approximation, by solving a HNC equation for a potential $\beta\bar{\phi} = \beta\phi - E$. If we invert this line of reasoning, the solution of the HNC equation appropriate to potential $\bar{\phi}$ gives the exact correlation functions for the system with potential $\beta\phi = \beta\bar{\phi} + E$. It then follows that the HNC result for potential $\bar{\phi}$ at each temperature $T$ corresponds to a system with potential $\phi$ and its associated critical temperature $T_c^{\text{eff}}(T)$. Near this point the potential $\phi$ has the asymptotic form

$$\beta\phi \simeq \beta\bar{\phi} - \tfrac{1}{2}h^2 + \cdots , \qquad (21)$$

and as it is approached $\phi$ acquires an increasingly stronger and increasingly long-ranged attractive tail by virtue of the fact that $h(r)$ itself has this behavior. Because of the overall increasing strength of $\phi$, $T_c^{\text{eff}}(T)$ *increases* as $T$ *decreases* toward the true critical point. It is this unavoidable variation of the effective critical temperature which leads to the absence of the usual power-law behavior. Furthermore, the sense of the variation of $T_c^{\text{eff}}$ implies the existence of a temperature $\bar{T}$, being simply the solution to $T = T_c^{\text{eff}}(T)$. Thus the HNC equation should indeed lead to a spinodal line. Note, however, that for any given $\bar{\phi}(r)$ the existence of a corresponding $\phi(r)$ is not rigorously guaranteed. The qualitative conclusions should still hold, however, even if the correspondence is not exact.

### IV. EFFECTIVE POTENTIALS IN THE PERCUS-YEVICK APPROXIMATION

We next remark that the solution of the PY equation for a potential $\bar{\phi}(r)$ can also be regarded as an exact solution for a system described by a certain potential $\phi(r)$. Let $F(r)$ be defined by

$$F(r) = E(r) - 1 - \ln\bar{y}(r) + \bar{y}(r) , \qquad (22)$$

where

$$\bar{y}(r) = g(r)e^{\beta\phi(r) - F(r)} \equiv g(r)e^{\beta\bar{\phi}(r)} .$$

In (22), $E(r)$ is the bridge function *for the potential* $\phi(r)$. We now substitute this in the exact relation (7) and obtain

$$c(r) = g(r)(1 - e^{\beta\bar{\phi}(r)}) . \qquad (23)$$

We note that (23) is the standard PY approximation for a system with pair potential $\bar{\phi}$. If $\bar{\phi}(r)$ is *short ranged,* then for large $r$, $\bar{y}(r) \simeq g(r)$.

From this it follows that $F(r) \simeq \mathfrak{c}(r)$. The potential $\phi$ will therefore have a smaller shorter-ranged state-dependent contribution than the $h^2(r)$ term in the corresponding HNC case. Consequently the PY equation should lead to critical behavior that is somewhat closer to that found in real fluids since its *effective* critical temperature will vary less. This is verified by the work of Henderson and Murphy[6] who showed that the Percus-Yevick equation *does* lead to power-law behavior, though with mean-field exponents. The lack of an additional long-ranged attractive tail in the PY effective potential also implies lower effective critical temperatures than in the corresponding HNC case. This was shown to be so by Watts.[3]

### V. POSSIBLE IMPROVED INTEGRAL EQUATIONS

As shown by Rosenfeld and Ashcroft,[11] provided thermodynamic conditions remote from the critical point are chosen, the HNC equation can be substantially improved by including an approximation for $E(r)$ in the choice of effective potential. Near the critical point we have seen that $E \sim -\tfrac{1}{2}h^2(r)$ at large $r$. If this is taken as the approximation to $E$, then an argument similar to that given by Green[10] shows that the resulting integral equation leads to a critical exponent $\eta = \tfrac{1}{2}$. This is an improvement over the simple HNC ($\eta = 1$) but still far from the expected $\eta \simeq 0.04$. The equation leads to a critical dimensionality of 4, in agreement with behavior expected of real fluids (note that HNC has a critical dimensionality[12] of 6). The approximation

$$E(r) = \ln(1 + h) - h$$

for large $r$ should lead to Ornstein-Zernike behavior since at large $r$ we then have

$$c(r) = -\beta\bar{\phi}(r) .$$

Evidently the development of an integral equation leading to correct critical behavior will require an independent determination of the function $\mathfrak{c}(r)$. The statement embodied in (19) above may be useful in this respect.

### APPENDIX: COMPUTATIONAL DETAILS

The parameters chosen for $\phi$ were $A = 2.03\sigma$, $a = 14.7\sigma^{-1}$, and $b = 2.69\sigma^{-1}$. These lead to a poten-

tial which very well approximates the Lennard-Jones 6–12 form. The calculations were carried out on grids in real and reciprocal space with $\Delta r = 0.02\sigma$ and $\Delta \kappa = 0.05\sigma^{-1}$. The use of smaller steps was found to make no significant difference in the results. Real and reciprocal-space integrations were normally terminated at $20\sigma$ and $50\sigma^{-1}$, respectively; for the most singular points, the calculations were repeated with real-space termination at $30\sigma$ and $40\sigma$. Again, there were no significant changes in the results.

In all of the calculations carried out the corre-

lation length remained relatively small ($\approx 5\sigma$). Because of this it was not possible to make a meaningful determination of $\eta$ directly from the behavior of $h(r)$. In Ornstein-Zernike theory ($\eta = 0$), $S(0)$ is proportional to $\xi^2$. Our results for $S(0)$ show, however, that the variation with $\xi$ is somewhat weaker than this, indicating that $\eta$ is large. This is expected for HNC. To obtain a rough idea of the shape of the spinodal curve, we note $S(0)$ diverges for densities of $\frac{2}{3}\rho_c = 0.183$ and $\frac{4}{3}\rho_c = 0.366$ at temperatures of 1.360 and 1.349, respectively.

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