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Critical Point in the Percus-Yevick Theory[*]

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Some consequences of the Percus—Yevick theory are studies in the neighborhood of the critical point for adhesive hard spheres and for the 6 : 12 potential (truncated at 6σ). It is shown that the Percus—Yevick theory gives rise to classical behavior at the critical point. In particular, it is shown that for the compressibility equation of state the critical exponents γ and δ are 1 and 3, respectively, and for the energy equation of state the critical exponents α and β are 0 and $\frac{1}{2}$, respectively. In addition, the behavior of the Percus—Yevick distribution function in the neighborhood of the critical point is examined and it is shown that for the critical isochore the temperature derivative of the distribution function diverges with a critical exponent of $\frac{1}{2}$ which is independent of r and that for the critical isotherm the distribution function is a linear function of the density for all r.

I. INTRODUCTION

The theory of the behavior of a fluid near its critical point is one of the most intensively investigated areas of physics. In this paper we deal with the critical-point behavior of a fluid in the Percus—Yevick (PY) approximation.[1]

Let us consider a fluid of N molecules at a temperature T and occupying a volume V. Thus, the critical point is specified by T_c and ρ_c, where $\rho = N/V$. Experimentally it is found that a number of quantities vanish or diverge at the critical point. Critical exponents can be used to characterize the behavior of these quantities near the critical point. For example, the heat capacity at constant density C is given by

$$C \simeq \text{const} \times |T - T_c|^{-\alpha} \tag{1}$$

TABLE I. Values of critical indices.

	Expt.	Classical	Lattice gas
α	0.04—0.06	0	$\sim \frac{1}{8}$
β	0.35—0.36	$\frac{1}{2}$	$\sim \frac{5}{16}$
γ	1.2—1.3	1	$\sim \frac{5}{4}$
δ	4.4—4.6	3	~ 5

along the critical isochore $\rho = \rho_c$. Similarly,

$$\rho - \rho_c \simeq \text{const} \times |T - T_c|^{\beta} \tag{2}$$

along the liquid-vapor coexistence curve. Also, the isothermal bulk modulus B is given by

$$B = \frac{1}{k_B T} \left(\frac{\partial p}{\partial \rho} \right)_T \simeq \text{const} \times |T - T_c|^{\gamma}, \tag{3}$$

where k_B is Boltzmann's constant along the critical isochore. In addition, the pressure p has the form

$$p - p_c \simeq \text{const} \times |\rho - \rho_c|^{\delta} \tag{4}$$

along the critical isotherm $T = T_c$.

Inasmuch as T_c may be approached along a critical isochore from above and below it is necessary to allow for different critical exponents. Thus, α and α' and γ and γ' should be distinguished. The primed exponent indicates that it is one appropriate for $T < T_c$. Experimental values[2] of the critical exponents are listed in Table I. Experimentally $\alpha \simeq \alpha'$ and $\gamma \simeq \gamma'$.

Clearly it is desirable to obtain the critical exponents theoretically. The van der Waals theory gives the results

$$\alpha = \alpha' = 0, \quad \beta = \frac{1}{2},$$
$$\gamma = \gamma' = 1, \quad \delta = 3. \tag{5}$$

The result $\alpha = 0$ for the van der Waals theory is not a complete statement and can lead to misleading conclusions. The value $\alpha = 0$ can mean either a logarithmic divergence of C or a finite value for C at the critical point. In the case of the van der Waals theory, $\alpha = 0$ has the latter meaning. Thus, even though $\alpha = 0$ is numerically close to the experimental value $\alpha \simeq 0.05$, the van der Waals C is nondivergent and qualitatively different from the experimental C.

A rather large number of approximate theories give the above values, Eq. (5), of the critical exponents. The common feature of most of these theories is that they assume that the thermodynamic properties are analytic at the critical point and that the critical point is a point of inflection. As a result, the thermodynamic properties can be expanded in a Taylor series in $T - T_c$ and

$\rho - \rho_c$. If such an expansion is valid one can show quite generally that the critical exponents given in (5) follow regardless of the precise form of the equation of state.[3] Such theories are called *classical theories*.

To obtain nonclassical behavior it is necessary to obtain the thermodynamic properties of some model system exactly or with high accuracy. The lattice gas is a model system which is simple enough so that thus it is possible, but which is still realistic enough to give good values for the critical exponents. The lattice gas values of the critical exponents[4] are compared with the experimental and classical values in Table I. They are among the best theoretical estimates of the critical exponents presently available. Although it is only conjecture that the critical exponents of the three-dimensional lattice gas are rational numbers, we follow the conventional practice and display them as rational numbers. The lattice-gas exponents also appear to satisfy $\alpha = \alpha'$ and $\gamma = \gamma'$ although the question is still open.

One of the most widely used theories of fluids is that of PY.[1] For a time the PY theory was thought to be useful only at high temperatures. However, recent work[5-7] has shown the PY theory to be reasonably satisfactory even at liquid temperatures. Thus, it is of interest to investigate the behavior of the PY thermodynamic properties and distribution function at the critical point.

In this paper we examine the critical point in the PY theory. Before doing so we emphasize that the PY theory gives unambiguous results only for the radial distribution function (RDF). There are several equations relating the RDF to the thermodynamic functions. These equations would yield the same results if exact RDF were used. However, if the PY RDF is used, these equations yield different results. Thus, the PY theory will give different thermodynamic functions and may give differing critical exponents when differing routes to thermodynamics are used. In this paper we calculate the pressure and compressibility only from the compressibility equation and the energy and heat capacity only from the energy equation. These are the most direct and numerically accurate routes to these particular thermodynamic properties.

Other methods are possible. For example, the energy and heat capacity may be calculated from the compressibility equation and the pressure and compressibility may be calculated from the energy equation. However, each of these methods requires numerical integration followed by double numerical differentiation. This can be done. For example, the latter procedure was followed by Henderson et al.[7] However, it is doubtful whether such calculations could be made

numerically with sufficient accuracy to determine values for critical exponents.

We find that, when the compressibility equation is used, $\gamma = 1$ and $\delta = 3$ and, when the energy equation is used, $\alpha = 0$ and $\beta = \frac{1}{2}$. These values are identical with the classical values. The PY values of the critical exponents of the RDF are more fundamental. We find that the RDF is a linear function of ρ for $T = T_c$ and that its temperature derivative varies inversely as $|T - T_c|^{1/2}$ for $\rho = \rho_c$.

II. PERCUS-YEVICK THEORY

If the total potential energy Φ results solely from the additive contributions of a pair potential $u(r)$, i.e.,

$$\Phi(\vec{r}_1, \cdots, \vec{r}_N) = \sum_{i<j} u(r_{ij}) , \tag{6}$$

where the $\vec{r}_\lambda$ are the positions of the molecules and $\vec{r}_{ij} = |\vec{r}_i - \vec{r}_j|$, then the thermodynamic properties can be calculated from either the *pressure equation*

$$\frac{pV}{Nk_BT} = 1 - \frac{2\pi\rho}{3k_BT} \int_0^\infty \frac{du}{dr} g(r) r^3 \, dr , \tag{7}$$

the *compressibility equation*

$$k_BT \left(\frac{\partial \rho}{\partial p}\right)_T = 1 + 4\pi\rho \int_0^\infty [g(r) - 1] r^2 \, dr , \tag{8}$$

or the *energy equation*

$$U = \tfrac{3}{2} Nk_BT + 2\pi N\rho \int_0^\infty u(r) g(r) r^2 \, dr . \tag{9}$$

In Eqs. (7)–(9), p and U are the pressure and energy of the fluid, respectively. The function $g(r)$ is the RDF which is proportional to the probability of finding two molecules a distance r apart. The proportionality constant is chosen so that $g(r) \to 1$ as $r \to \infty$.

It is convenient to introduce two additional functions related to $g(r)$. We define the *total correlation function* $h(r)$ by

$$h(r) = g(r) - 1 \tag{10}$$

and the *direct correlation function* $c(r)$ by

$$h(12) = c(12) + \rho \int h(13) c(23) \, d\vec{r}_3 , \tag{11}$$

where $h(12) = h(r_{12})$, etc.

If we define the Fourier transform $\tilde{f}(k)$ of a function $f(r)$ by

$$\tilde{f}(k) = \int e^{i\vec{k}\cdot\vec{r}} f(r) \, d\vec{r}$$

$$= (4\pi/k) \int_0^\infty \sin kr f(r) r \, dr , \tag{12}$$

then (11) becomes

$$\tilde{h}(k) = \tilde{c}(k) + \rho\tilde{h}(k)\tilde{c}(k) . \tag{13}$$

In particular, for $k = 0$,

$$1 + \rho\tilde{h}(0) = [1 - \rho\tilde{c}(0)]^{-1} \tag{14}$$

and thus an alternative form of (8) is

$$\frac{1}{k_BT} \left(\frac{\partial p}{\partial \rho}\right)_T = 1 - 4\pi\rho \int_0^\infty c(r) r^2 \, dr . \tag{15}$$

The PY approximation is

$$c(r) = [e(r) - 1] y(r) , \tag{16}$$

where

$$e(r) = e^{-u(r)/k_BT} \tag{17}$$

and

$$y(r) = g(r)/e(r) . \tag{18}$$

Substitution of (16) into (11) gives the PY equation

$$y(12) = 1 + \rho \int [e(13) y(13) - 1][e(23) - 1] y(23) \, d\vec{r}_3. \tag{19}$$

III. ADHESIVE HARD SPHERES

Baxter[8] has recently solved the PY equation for adhesive hard spheres, where

$$u/k_BT = \psi(r) = \infty \qquad , \quad r < R'$$
$$= \ln\left(12\tau \frac{R - R'}{R}\right), \quad R' < r < R \tag{20}$$
$$= 0 \qquad , \quad r < R$$

and where $R - R'$ is allowed to become infinitesimally small. The parameter τ is a dimensionless measure of the temperature. The relation between τ and T is *arbitrary*. For simplicity, we assume $\tau \propto T$.

Baxter has obtained an analytic solution of the PY equation for (20). In particular, for $r < R$,

$$g(r) = 0 \qquad , \qquad r < R'$$
$$= \frac{\lambda}{12} \frac{R}{R - R'} + 0(1) , \quad R' < r < R . \tag{21}$$

The parameter λ depends on T and ρ and is given by

$$\lambda = (6/\eta) [\mu - (\mu^2 - \nu)^{1/2}] , \tag{22}$$

where

$$\mu = \tau + \eta/(1 - \eta) , \tag{23}$$

$$\nu = \eta(2 + \eta)/6(1 - \eta)^2 , \tag{24}$$

and $\eta = \frac{1}{6}\pi\rho R^3$. Baxter's original calculation of the heat capacity involved a slight problem in taking a limit. To avoid the question as to whether the assumptions involved in taking this limit lead to errors in the form of the heat capacity near the critical point, we use an alternative method, based on the work of Watts *et al.*,[9] which avoids this limit entirely.

Neglecting the ideal-gas terms which do not lead to singular terms, the Helmholtz free energy A

is given by

$$\frac{A}{Nk_B T} = -\ln \int \prod_{i<j} e^{-\psi(r_{ij})} \, d\vec{r}_1 \cdots d\vec{r}_N . \quad (25)$$

Thus,

$$\left(\frac{\partial A/Nk_B T}{\partial \tau}\right)_V = -\tfrac{1}{2}\rho \int \frac{d\psi}{d\tau} \, g(r) \, d\vec{r} . \quad (26)$$

Now

$$\frac{d\psi}{d\tau} = \frac{1}{\tau} \quad (27)$$

for $R' < r < R$ and is zero elsewhere. Thus

$$\left(\frac{\partial A/Nk_B T}{\partial \tau}\right)_V = \frac{\eta\lambda}{\tau} . \quad (28)$$

Equation (28) is the energy equation of state for adhesive hard spheres.

The compressibility equation critical point is given by

$$\tau_c = \tfrac{1}{6}(2 - \sqrt{2}) , \quad (29)$$

$$\eta_c = \tfrac{1}{2}(3\sqrt{2} - 4) , \quad (30)$$

and

$$\mu_c^2 = \nu_c = \tfrac{1}{18} . \quad (31)$$

Expanding the energy equation about τ_c at $\eta = \eta_c$ gives

$$\left(\frac{\partial A/Nk_B T}{\partial \tau}\right)_V = \frac{6}{\tau_c} \left[\mu_c - (2\mu_c)^{1/2} (\tau - \tau_c)^{1/2}\right] . \quad (32)$$

Thus

$$C \propto -\left(\frac{\partial^2 A/Nk_B T}{\partial \tau^2}\right)_V = \frac{3(2\mu_c)^{1/2}}{\tau_c} (\tau - \tau_c)^{1/2} . \quad (33)$$

Thus it appears that for $\eta = \eta_c$, C diverges at τ_c.

Despite Eq. (33), one cannot assign the value $\tfrac{1}{2}$ to α. To determine the critical point in the energy equation of state we must integrate Eq. (28) to obtain the free energy. If this is done a constant of integration, which is of course only a function of density, arises. This constant of integration must be determined by fitting the free energy at some temperature. If infinite tempera ture is used, the energy equation critical temperature lies above τ_c,[9] the compressibility critical point. With this choice of the constant of integration, $\alpha = 0$ since the heat capacity will be finite at the energy equation-of-state critical point.

At first sight, one might think that the constant of integration could be chosen so as to make the energy and compressibility critical isotherms coincide and thus be lead to a divergent heat capacity. However, the portion of B which arises from Eq. (28) in the absence of the contribution of the constant of integration diverges to minus infinity at

τ_c. Thus, the second derivative of such a constant of integration would diverge at $\eta = \eta_c$ with the result that B would diverge along the critical isochore. Such behavior is unphysical and we conclude that $\alpha = 0$.

Wheeler and Chandler[10] have previously pointed out the error of using the compressibility equation critical point when examining the energy equation heat capacity.

Earlier we have shown[9] that, in the energy equation of state, the coexistence curve may be constructed by means of the Maxwell construction. Thus $\beta = \tfrac{1}{2}$ when determined from the energy equation of state. Expansion of the compressibility equation of state shows that $\gamma = 1$ and $\delta = 3$, respectively.[8]

IV. 6 :12 FLUID

The adhesive-hard-sphere system is somewhat unphysical. For this reason we also consider the 6 : 12 fluid, where

$$u(r) = 4\epsilon \left[(\sigma/r)^{12} - (\sigma/r)^6\right] . \quad (34)$$

In solving the PY equation numerically, it is necessary to perform integrations over some finite region. In calculating the thermodynamic properties one must make some assumptions about the form of $g(r)$ for large r. For most applications these corrections are small and so no appreciable error is introduced. However, in our case, because we are working near the critical point where $h(r)$ becomes of infinite range, these corrections become important. For example, the energy and compressibilities are affected slightly differently
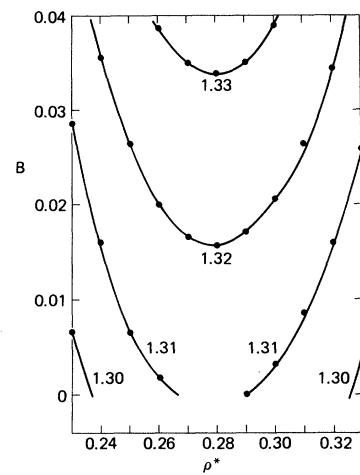

FIG. 1. Isothermal bulk modulus of 6:12 fluid. The points are the results of our numerical calculations. The curves are isotherms drawn between the points and are labeled with the appropriate reduced temperature.

so that C and B^{-1} *appear* to diverge at slightly different temperatures. Hence, to avoid the necessity of making any assumptions with their resulting possible errors, we truncate (34) at 6σ. All our results are for this truncated 6 : 12 potential.

We have solved the PY equation in the neighborhood of the 6 : 12 critical point both by an iterative method equivalent to that of Mandel *et al.*[5] which is based on the original form of the PY equation and by Watts's method[6,7] which is based on Baxter's alternative form[11] of the PY equation.

Away from the critical point, these methods are equivalent. However, near the critical point we found appreciable differences between the results of the two methods. This was particularly true for the heat capacity. Baxter's form of the PY equation, and thus Watts's method, gives $g(r)$ correctly for $r < 6\sigma$ whereas the iterative method introduces errors in the region $3\sigma < r < 6\sigma$. Normally the effect of these latter errors is small. However, in the neighborhood of the critical point the long-range behavior of $g(r)$ is important. Thus, Watts's method is more suitable for our calculations. The results we report here are based on this method. We have verified that as the range of the integrations in the iterative method is increased, the results obtained by that method approach those obtained from Watts's method.

In displaying results for the 6 : 12 fluid we define the reduced temperature, pressure, and density by $T^* = k_B T/\epsilon$, $p^* = p\sigma^3/\epsilon$, and $\rho^* = \rho\sigma^3$, respectively. In Fig. 1, we have plotted values of B in the neighborhood of the critical point and in Fig. 2 we have plotted the locus of points for which $B = 0$. From these figures we have obtained the critical constants $T_c^* = 1.311$ and $\rho_c^* = 0.278$. These values are slightly different from usual PY critical constants for the 6 : 12 potential[7] because our potential is truncated at 6σ.

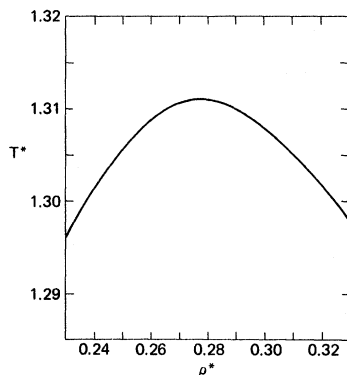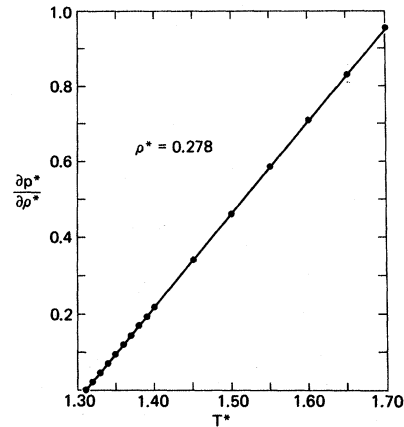In Fig. 3, we have plotted $\partial p^*/\partial \rho^*$ as a function

FIG. 3. $\partial p^*/\partial \rho^*$ of a 6:12 fluid for $\rho = \rho_c$. The points are the results of our calculations and the curve is a linear fit of these results.

of T for $\rho = \rho_c$ and have found a linear dependence consistent with $\gamma = 1$. In Fig. 4, we have plotted $B^{1/2}$ as a function of ρ for $T = T_c$ and have found a linear dependence consistent with $\delta = 3$.

We have also calculated C by numerically differentiating U, given by (9). In Fig. 5, we have plotted C in the neighborhood of the compressibility critical temperature T_c, and in Fig. 6 we have plotted C^{-2} as a function of T for $\rho = \rho_c$. For T near T_c, C^{-2} varies linearly with T.

The Helmholtz free energy A and pressure may be calculated[6,7] from the energy

$$(A - A_0)/Nk_B T = -\tfrac{1}{2}\rho \int_{\beta_0\epsilon}^{\beta\epsilon} G \, d(\beta\epsilon) , \tag{35}$$

where

$$\epsilon G(T,\rho) = 4\pi \int_0^\infty g(R) u(R) R^2 \, dR \tag{36}$$

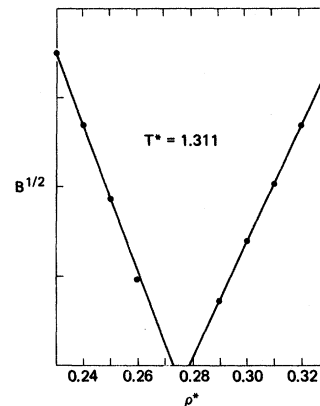FIG. 2. Locus of points for which the isothermal bulk modulus is zero.

FIG. 4. Isothermal bulk modulus of a 6:12 fluid for $T = T_c$. The points give the results of our calculations and the curve is a linear fit of these results.
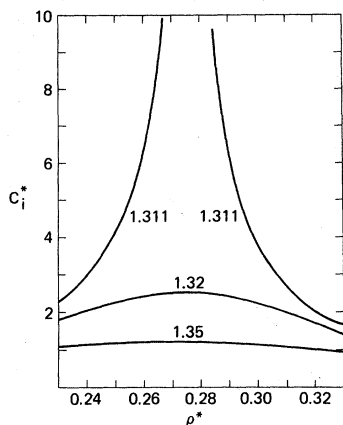
FIG. 5. Heat capacity at constant density of a 6:12 fluid near the critical point. The curves are labeled with the appropriate reduced temperature.

FIG. 7. Radial distribution functions of a 6:12 fluid for $\rho = \rho_c$.

and A_0 is the Helmholtz free energy at the inverse temperature $\beta_0 \epsilon$. Again, if we choose A_0 and $\beta_0 \epsilon$ so that the energy equation of state is correct at some high temperature, we find that the energy critical temperature is greater than the compressibility critical point.[7] Hence, C is finite at the energy critical point and we have $\alpha = 0$ and $\beta = \frac{1}{2}$.

Other critical exponents which might be sought are the values of α and β in the compressibility equation of state and the values of γ and δ in the energy equation of state. Each of these calculations involves both numerical integration and dif-

ferentiation. It is doubtful that sufficient accuracy could be maintained so that meaningful values of these exponents could be obtained. However, this might be an interesting problem. The calculation of β in the compressibility equation of state is made difficult because for subcritical temperatures there is a range of values of ρ for which the PY equation has no solution.

We now turn our attention to the behavior of the RDF in the neighborhood of the critical point. The critical exponents of the RDF are more fundamental in the sense that they determine the critical exponents of the thermodynamic properties and provide more detailed information.
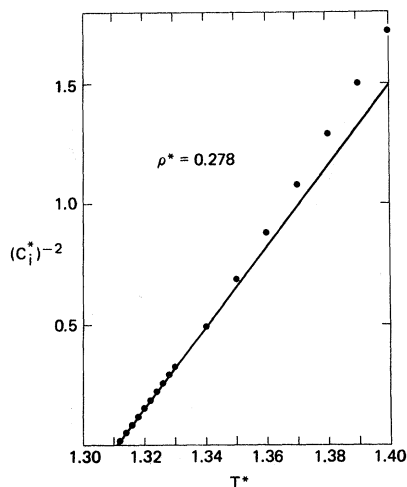

FIG. 6. Internal heat capacity at constant density of a 6:12 fluid for $\rho = \rho_c$. The points give the results of our calculations and the curve is a linear fit of the results for $T \sim T_c$.
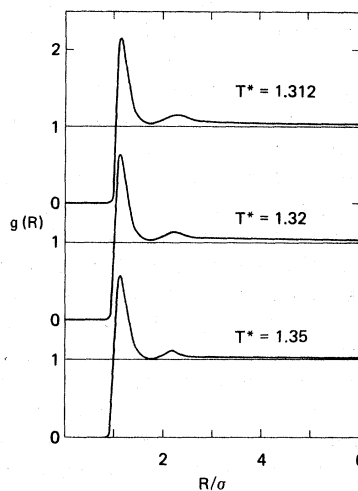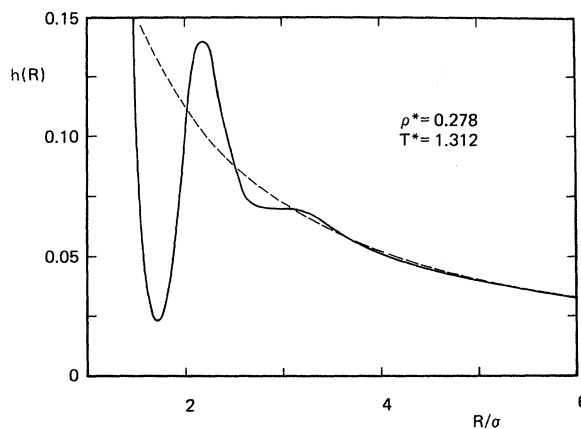

FIG. 8. $h(R)$ of 6:12 fluid near the critical point. The solid curve gives the PY results and the broken curve gives the results of Eq. (37).
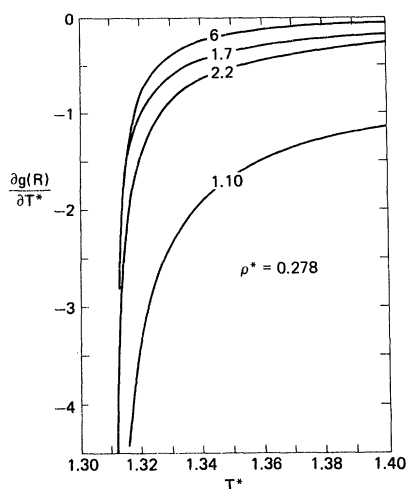
FIG. 9. $\partial g/\partial T$ at constant density of a 6:12 fluid for $\rho = \rho_c$. The curves are labeled with the appropriate values of R/σ.

FIG. 11. $y(R)$ of a 6:12 fluid for $T = T_c$. The curves are labeled with the appropriate values of R/σ.

V. DISTRIBUTION FUNCTIONS

In Fig. 7, we have plotted $g(r)$ as a function of T for $\rho = \rho_c$. The RDF changes rapidly as $T \to T_c$. Also it is to be noted that the RDF decays monotonically to unity for large r. Fisher and Widom[12] have suggested that the critical point is well inside the region of monotonic decay. We have examined $g(r)$ for a fairly wide range of temperatures and densities. Our results *appear* to be consistent with the conjectures of Fisher and Widom. For temperatures of the order of T_c, the PY $g(r)$ of the 6:12 fluid appears to decay monotonically for den-

sities at least 30% greater than ρ_c. We cannot be more definite because it is impossible to make any firm statements concerning whether $g(r)$ has a finite or an infinite number of oscillations at higher densities when we know $g(r)$ only for $r < 6\sigma$.

For an Ornstein-Zernike[13] system

$$h(r) = (1/4\pi\rho\lambda)\ (e^{-\kappa r}/r) \tag{37}$$

for r large. In (37) the parameter

$$\lambda = \tfrac{2}{3}\pi\rho\int_0^\infty r^4 c(r)\ dr \tag{38}$$
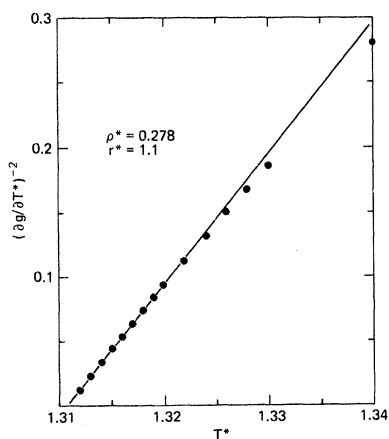
varies slowly and

FIG. 10. $\partial g/\partial T$ at constant density of a 6:12 fluid for $\rho = \rho_c$ and $r = 1.1\sigma$. The points give the results of our calculations and the curve is a linear fit of these results for $T \sim T_c$.
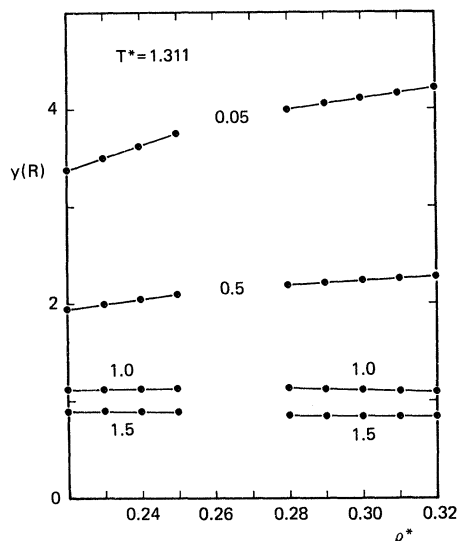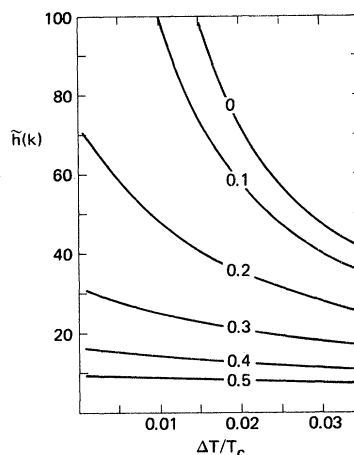

FIG. 12. $\tilde{h}(k)$ of a 6:12 fluid for $\rho = \rho_c$. The quantity $\Delta T = T - T_c$. The curves are labeled with the appropriate value of $k\sigma$.
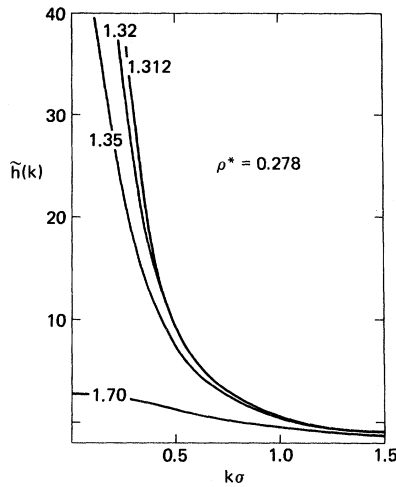
FIG. 13. $\bar{h}(k)$ of a 6:12 fluid for $\rho = \rho_c$. The curves are isotherms labeled with the appropriate reduced temperature.

$$\kappa = \left[\frac{1}{\lambda k_B T} \left(\frac{\partial p}{\partial \rho} \right) \right]^{1/2} \tag{39}$$

tends to zero at the critical point. From Fig. 8, we see that near the critical point $h(r)$ is of this form for large r. We have not examined $h(r)$ away from the critical point because away from the critical point $h(r)$ is very small for large r and our numerical values are less accurate.

In Fig. 9, we have plotted $\partial g/\partial T$ as a function of T for $\rho = \rho_c$. We see that $\partial g/\partial T$ diverges at the compressibility critical temperature T_c for all values of r. For r large, where (37) is valid,

$$\frac{\partial g(r)}{\partial T} = - \frac{1}{4\pi\rho\lambda} e^{-\kappa r} \frac{\partial \kappa}{\partial T} . \tag{40}$$

Since $\gamma = 1$ we have, from (39), $\kappa \propto |T - T_c|^{1/2}$. Thus, $\partial g/\partial T \propto |T - T_c|^{-1/2}$ at large r. We have plotted $(\partial g/\partial T)^{-2}$ for $r = 1.1\sigma$ as a function of T for $\rho = \rho_c$ in Fig. 10. For T near T_c we see that $(\partial g/\partial T)^{-2}$ varies linearly with T. We have found similar behavior for other values of r. Thus, we conclude that for T near T_c and $\rho = \rho_c$,

$$\frac{\partial g}{\partial T} \propto |T - T_c|^{-1/2} \tag{41}$$

for all r.

We have examined $y(r)$, and thus $c(r)$ and $g(r)$, for $T = T_c$. Some of our results are plotted in Fig. 11. We see that, at least for small r, $y(r)$ is a linear function of ρ. For large r, $\partial y(r)/\partial \rho$ is small. However, to within the numerical accuracy of our calculations $y(r)$ is a linear function of ρ at large r. Thus, we conclude that $y(r)$ is a linear function of ρ for $\rho \sim \rho_c$ for all r. This is consistent with $\delta = 3$.

We have plotted $\bar{h}(k)$ as a function of T and k for $\rho = \rho_c$ in Figs. 12 and 13. Fisher and Burford[14] have suggested that for real systems $\bar{h}(k)$ exhibits a maximum for fixed k at a temperature above T_c. The PY $\bar{h}(k)$ does not appear to exhibit such a maximum and is like the Ornstein–Zernike and random-phase approximations. However, the possibility that such maxima occur at smaller values of $\Delta T = T - T_c$ than we have considered is not ruled out.

VI. SUMMARY

We have shown that, at least for the systems we have considered, in the PY theory $\alpha = 0$ and $\beta = \frac{1}{2}$ for the energy equation of state and $\gamma = 1$ and $\delta = 3$ for the compressibility equation of state. It is our conjecture that these values are valid for any potential (except for a purely repulsive potential for which there is no critical point).

In addition, we have shown that for the 6:12 fluid $\partial g/\partial T$ diverges in the PY theory for all values of r and with a critical exponent of $\frac{1}{2}$ which is independent of r. An examination of the density dependence of the correlation functions shows them to be, for $T = T_c$, linear functions of ρ for all r.

The PY values of γ and δ for the energy equation and of α and β for the compressibility equation are not known. Also none of the critical exponents for the related hypernetted chain equation are known. Both problems are of considerable interest.

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Retarded van der Waals Potential between Pairs of Spinless Atoms[*][†]

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The retarded van der Waals potential between pairs of spinless atoms, H-H, H-He, He-He, Ne-Ne, Ne-Ar, and Ar-Ar, was computed with covariant formulas of Feinberg and Sucher. Electric and magnetic effects were treated on equal footing. For hydrogen, which posses-a large magnetic polarizability, magnetic effects dominate for large distance of separation, and for small distances, an additional contribution to the London constant for a pair of hydrogen atoms from the magnetic effects is found to be $0.0155 \alpha_a^5$, about 0.24% of the currently accepted value.

I. INTRODUCTION

Recently, using a model-independent approach, Feinberg and Sucher[1] have obtained a covariant formula (hereafter, the FS formula) for the retarded long-range electromagnetic interaction potential (the retarded van der Waals potential) between a pair of spinless and neutral particles, separated at a distance R on the assumption that the long-range force is due to two-photon exchange. This potential is written as

$$V_{2\gamma}^{A,B}(R) = \sum_{X,Y} V_{XY}(R) , \qquad (1)$$

where X, $Y = E$ or M corresponding to electric or magnetic effects, and

$$V_{X,Y} = \frac{-1}{(4\pi)^4/R} \int_0^\infty dt\, e^{-\sqrt{t}R}$$

$$\times \int_{m_A^2}^\infty \int_{m_B^2}^\infty \frac{d\sigma_A'}{\pi} \frac{d\sigma_B'}{\pi} \rho_X^A(\sigma_A', t) \rho_Y^B(\sigma_B', t)\, \Phi_{XY}^0 , \qquad (2)$$

where Φ_{XY}^0[1] is a phase-space factor, the ρ's the spectral functions of the corresponding form factors in the atomic Compton amplitude, and σ' and t denote, respectively, the invariant c.m. energy square and momentum transfer square of the Compton process. To a first approximation, we can put[1,2]

$$\rho_X(\sigma, t) \text{ as } \rho_X(\sigma) \equiv \rho_X(\sigma, t = 0) . \qquad (3)$$

Then V_{XY} in (2) simplifies to

$$V_{XY} = - C_{XY}(R)/R^6 , \qquad (4)$$

with

$$C_{XY} = \frac{1}{4\pi^5} \int_0^\infty dk_A \int_0^\infty dk_B\, k_A k_B \rho_X^A(k_A) \rho_Y^B(k_B)$$

$$\times \int_0^\infty d\xi\, \frac{e^{-2\xi R} P_{XY}(\xi R)}{(k_A^2 + \xi^2)(k_B^2 + \xi^2)} , \qquad (5)$$

where

$$P_{EE}(\eta) = P_{MM}(\eta) = \eta^4 + 2\eta^3 + 5\eta^2 + 6\eta + 3 , \qquad (6)$$

$$P_{EM}(\eta) = P_{ME}(\eta) = -(\eta^4 + 2\eta^3 + \eta^2) . \qquad (7)$$

The expression in (5) can be transformed to the familiar integral over imaginary frequency and to a one-dimensional integral over the real and imaginary parts of the Compton amplitude at real frequencies,[1] namely,

$$C_{XY} = (1/8\pi^4) P_{XY}^{op} \int_0^\infty d\omega\, f(z\,\omega R)$$

$$\times [\operatorname{Re} F_X^A(\omega) \operatorname{Im} F_Y^B(\omega) + \operatorname{Im} F_X^A(\omega) \operatorname{Re} F_Y^B(\omega)] , \qquad (8)$$

where

$$f(x) = \cos x \operatorname{si} x - \sin x \operatorname{ci} x , \qquad (9)$$

$$P_{EE}^{op} = P_{MM}^{op} = \tfrac{1}{16} R^4 \partial_R^4 - \tfrac{1}{4} R^3 \partial_R^3 + \tfrac{5}{4} R^2 \partial_R^2 - 3R\partial_R + 3 , \qquad (10)$$

$$P_{EM}^{op} = P_{ME}^{op} = -\tfrac{1}{16} R^4 \partial_R^4 + \tfrac{1}{4} R^3 \partial_R^3 - \tfrac{1}{4} R^2 \partial_R^2 . \qquad (11)$$

It has also been shown by Sucher and O'Car-