

## On the van der Waals Theory of the Vapor-Liquid Equilibrium. III. Discussion of the Critical Region

P. C. HEMMER,\* M. KAC, AND G. E. UHLENBECK  
The Rockefeller Institute, New York, New York  
(Received 20 September 1963)

The discussion of the properties of the Kac one-dimensional fluid model presented in Parts I and II of this series of papers breaks down near the critical point. In Sec. II of the present paper we develop a new successive-approximation method for the eigenvalues and eigenfunctions of the Kac integral equation which is valid in the critical region and which connects smoothly with the developments in the one- and two-phase regions given in Part I. The perturbation parameter is  $(\gamma\delta)^{\frac{1}{2}}$  where  $\gamma\delta$  is the ratio of the ranges of the repulsive and attractive forces. The main physical consequence is that in the critical region the long-range behavior of the two-point distribution function is represented by an infinite series of decreasing exponentials with ranges all of order  $1/\gamma(\gamma\delta)^{\frac{1}{2}}$ , and with amplitudes of order  $(\gamma\delta)^{\frac{1}{2}}$ . This leads to deviations from the Ornstein-Zernike theory and to a specific heat anomaly which are discussed in Sec. V. We conclude with some comments on the possible relevance of our results for the three-dimensional problem.

### I. INTRODUCTION

AS we noted already in the first two parts of this series of papers,<sup>1</sup> the discussion of the approach to the van der Waals limit which was given there breaks down near the critical point. This is evident from the way the quantity  $B^2$ , which is proportional to  $\partial p/\partial l$ , enters into the expansions for the eigenvalues and eigenfunctions of the Kac equation and into the expansions for the short- and long-range behavior of the two-point distribution function. For  $B = 0$  all these expansions blow up. It is therefore necessary to develop a new asymptotic treatment of the Kac equation in the critical region and this is presented in this paper.

It turns out that the critical region should be defined by the ranges in temperature and specific volume given by

$$(T - T_c)/T_c \approx (\gamma\delta)^{\frac{1}{2}}, \quad (l - l_c)/l_c \approx (\gamma\delta)^{\frac{1}{2}}, \quad (1)$$

where  $T_c$  and  $l_c$  are the van der Waals critical values and where  $\gamma\delta$  is again the ratio of the ranges of the repulsive and attractive forces. In Sec. II we will show that in this region one can again "tame" the Kac equation by an appropriate change of variables, and that this leads to a consistent successive-approximation method for the eigenfunctions and eigenvalues. In contrast to the one- and two-phase regions, the expansion parameter is no longer  $\gamma\delta$  but  $(\gamma\delta)^{\frac{1}{2}}$ , and also the zeroth-order eigenfunctions are no longer the harmonic oscillator eigenfunctions ( $\equiv$  Weber functions), but correspond

to the eigenfunctions of an oscillator for which the potential energy is a fourth-degree polynomial in the deflection. As a result, the eigenfunctions and eigenvalues can no longer be determined explicitly. However, it is possible to discuss qualitatively how the eigenfunctions change when one goes away from the critical region, and it is of special interest to note the difference in behavior when one goes towards the one-phase region or towards the two-phase region. In the first case, the eigenfunctions become again the Weber functions with only slight distortions, but in the second case (two-phase region) they approach the eigenfunctions for a potential which has two equal or almost equal minima. It is well known that for such a two-minimum potential, the lowest eigenvalue is almost doubly degenerate, and this corresponds to the beginning of the degeneracy which is characteristic for the two-phase region.

In Sec. III the consequences are discussed with respect to the form of the isotherms in the critical region. In I we have already pointed out that, to any order in  $\gamma\delta$ , the successive-approximation method always gives a phase transition and a van der Waals-like equation of state. We now find that in the critical region (i.e., for finite  $\gamma\delta$ ), there is a *qualitative* difference of the isotherm net from the prediction of the simple van der Waals theory, (i.e., for  $\gamma\delta = 0$ ). For finite  $\gamma\delta$ , the transition from the one-phase to the two-phase regime occurs continuously in the critical region.<sup>2</sup> Strictly speaking,

\* Present address: Institute for Theoretical Physics, N.T.H. Trondheim, Norway.

<sup>1</sup> J. Math. Phys. 4, 216, 229 (1963), hereafter referred to as I and II, respectively.

<sup>2</sup> The concept of a critical *region* in contrast to a critical *point* has often been discussed especially in order to explain various anomalous critical phenomena which apparently were in conflict with the van der Waals equation. For a review

for  $T < T_c$  the isotherms do *not* have a horizontal portion, and as a result the densities of the two coexistent phases cannot be defined unambiguously. However, although it is difficult to make precise statements because of the uncertainty one always encounters when one tries to join two different asymptotic developments of the same function, it is possible to make a reasonable extrapolation of the locus of the coexistent points from the two-phase region into the critical region. We then find that, for finite  $\gamma\delta$ , the critical density remains at the van der Waals value, but the critical temperature is lowered by  $\Delta T_c$  with  $\Delta T_c/T_c \cong 0.702(\gamma\delta)^{\frac{1}{2}}$ . At the new critical point, the locus of the coexistent points is still parabolic but it is much flatter than the van der Waals theory predicts.<sup>3</sup>

In Sec. IV and V the consequences are discussed with respect to the two-point distribution function. The main result is that in the critical region the long-range behavior of this distribution function is represented by an infinite series of decreasing exponentials. The ranges of these exponentials are all of order  $1/\gamma(\gamma\delta)^{\frac{1}{2}}$ , and also the amplitudes are all

of the older literature, see for instance J. P. Kuenen, *Die Zustandsgleichung* (Vieweg, Braunschweig, 1907), Chap. 5, especially for the effects of gravity and of impurities on the critical phenomena. The only attempt we know of to deduce a critical region from the ideas of van der Waals is by G. Bakker [Z. Physik. Chem. 49, 609 (1904)]. He pointed out that there may be a range in temperature where the thickness of the capillary layer is of the same order as  $v_1^{\frac{1}{2}} - v_2^{\frac{1}{2}}$ . In this region one would not see a meniscus, although the two phases are still present. This is also suggested by Mayer. For a review of his arguments, which are partially formal and partially physical, and are based on the fugacity and virial expansions, see the book by J. E. Mayer and M. G. Mayer [*Statistical Mechanics*, (John Wiley & Sons, Inc., New York, 1940), Chap. 14]. Mayer's conclusion is that there may be a temperature  $T_m < T_c$  where the meniscus would disappear, although there are still horizontal parts in the isotherms for temperatures between  $T_m$  and  $T_c$ . In this temperature range, the isotherms enter the two-phase region with a horizontal tangent. Because of the resulting shape of the coexistence curve near the critical point, this region is often referred to as Mayer's derby hat.

From the experimental point of view the existence of such a critical region is still controversial. For a review of recent experimental results see the book by T. O. Hirschfelder, Ch. F. Curtiss, and R. B. Bird [*Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 5, Sec. 2]. See also the work by H. W. Habgood and W. G. Schneider on Xenon [Can. J. Chem. 32, 98, 164 (1954)].

<sup>3</sup> The question of the shape of the coexistence curve near the critical point has been much discussed. Guggenheim [J. Chem. Phys. 13, 253 (1945)], pointed out that the data are better represented by the law  $(v_1 - v_2) \sim (T_c - T)^{\frac{1}{2}}$  than by the van der Waals result  $(v_1 - v_2) \sim (T_c - T)^{\frac{1}{3}}$  which follows from the parabolic form of the coexistence curve near the critical point. Compare also M. A. Weinberger and W. G. Schneider, Can. J. Chem. 30, 422 (1952), and the more recent discussion by B. Widom and O. K. Rice, J. Chem. Phys. 23, 1250 (1955). The Guggenheim result would imply that at the critical point also  $(\partial^3 p/\partial v^3)_T$  would be zero, and B. H. Zimm [J. Chem. Phys. 19, 1019 (1951)] has given a plausibility argument for the vanishing of *all* derivatives at the critical point. However, also in this respect, there are no results which are generally accepted.

of the same order of magnitude, namely  $(\gamma\delta)^{\frac{1}{2}}$ . The Ornstein-Zernike theory is therefore *not* valid in the critical region. However, we can show that if one goes away from the critical region towards the one-phase region, our results go over into the expansions of the long-range behavior of the correlation function derived in II, of which the Ornstein-Zernike exponential was the first term. The situation seems to be that, if one approaches the critical point, more and more exponential terms become excited, so to say. *Outside* the critical region these terms are of decreasing order of magnitude, but *in* the critical region they all contribute.

It seems to us that this picture of how the deviations from the Ornstein-Zernike theory develop if one approaches the critical point, is probably also valid in three dimensions, and that it is independent of our assumption of an exponential attractive potential. In fact, we show in Sec. VI that the whole discussion of Sec. IV can be generalized to the case where the attractive potential consists of a sum of  $m$  exponentials, and that this does not change the qualitative picture.

In Sec. VII we conclude with a few comments on some recent experimental results on the critical opalescence and on the so-called specific-heat anomaly in order to see whether there are some experimental indications for the existence of a critical region.

## II. THE EIGENFUNCTIONS AND EIGENVALUES IN THE CRITICAL REGION

We will develop all quantities around the critical point of the zeroth-order equation of state, that is the van der Waals equation

$$s = 1/(l - \delta) - \nu_0/l^2,$$

in the notation used in I and II. The critical quantities are given by:

$$s_c = 1/8\delta; \quad l_c = 3\delta; \quad \nu_{0c} = \frac{2}{3}\delta. \quad (2)$$

Instead of I, Eq. (33), it turns out that around the critical point one can "tame" the basic Kac integral equation [I, Eq. (10)] by the substitution

$$z = (\gamma\delta)^{\frac{1}{2}}[x - \eta_c(2/\gamma)^{\frac{1}{2}}], \quad (3)$$

where  $\eta_c \equiv \eta(s_c) = (2\nu_{0c})^{\frac{1}{2}}/l_c$ . This is motivated by the fact that in the one-phase region the "tamed" eigenfunctions depend on the variable [see I, Eq. (38)]

$$z = (B/l)^{\frac{1}{2}}[x - \eta(2/\gamma)^{\frac{1}{2}}]. \quad (4)$$

If one now *defines* the critical region in temperature and specific volume by the equations corresponding

to (1),

$$\nu_0 = \nu_{0c}[1 + \nu_1(\gamma\delta)^{\frac{1}{3}}], \tag{5}$$

$$l = l_c[1 + l_1(\gamma\delta)^{\frac{1}{3}}], \tag{6}$$

then one finds that  $B/l$  is of order  $(\gamma\delta)^{\frac{1}{3}}$ , so that (4) goes over into (3). However, one must of course still show that the substitution (3) works! We proceed in the same way as in I. For the variable  $y$  in the Kac equation, one makes the analogous substitution

$$z' = (\gamma\delta)^{\frac{1}{3}}[y - \eta_c(2/\gamma)^{\frac{1}{3}}],$$

and we put

$$z' = ze^{-\gamma\tau} + (\gamma\delta)^{\frac{1}{3}}\zeta(1 - e^{-2\gamma\tau})^{\frac{1}{2}},$$

$$\psi(x) = \psi[(\gamma\delta)^{-1/6}z + \eta_c(2/\gamma)^{1/2}] \equiv (\gamma\delta)^{1/12}H(z),$$

where the factor  $(\gamma\delta)^{1/12}$  is introduced in order to keep  $H(z)$  normalized to one. Finally we put for  $s$  the expansion<sup>4</sup>

$$s = s_c[1 - 3\nu_1(\gamma\delta)^{2/3} + s_1(\gamma\delta) + s_2(\gamma\delta)^{4/3} + \dots], \tag{7}$$

where the numbers  $s_1, s_2, \dots$  will depend on the given numbers  $\nu_1$  and  $l_1$  through the equation of state, which is still given by [see I, Eq. (20)]

$$l = -\lambda'_0(s)/\lambda_0(s), \tag{8}$$

in terms of the maximum eigenvalue  $\lambda_0(s)$  of the Kac equation.

Making all these substitutions, introducing the expansions (5) and (7), and developing the kernel in powers of  $(\gamma\delta)^{1/3}$  up to order  $(\gamma\delta)^{5/3}$ , one finds, after carrying out the integrations over  $\zeta$  and  $\tau$  and using (2),

$$\begin{aligned} \frac{d^2H}{dz^2} [3(\gamma\delta)^{4/3} - (6)^{1/2}z(\gamma\delta)^{5/3}] - (6)^{1/2}(\gamma\delta)^{5/3} \frac{dH}{dz} \\ + H(z) \left[ 3\Lambda + \left(\frac{3}{2}\right)^{1/2} z \left\{ \left(\frac{s_1}{4} - 1\right) (\gamma\delta)^{4/3} \right. \right. \\ + \left. \left. \left(\frac{s_2}{4} - \frac{39}{16} \nu_1^2\right) (\gamma\delta)^{5/3} \right\} + z^2 \left\{ \frac{3\nu_1}{4} (\gamma\delta)^{4/3} \right. \right. \\ + \left. \left. \left(1 - \frac{s_1}{4}\right) (\gamma\delta)^{5/3} \right\} - \frac{3}{8} \left(\frac{3}{2}\right)^{1/2} \nu_1 (\gamma\delta)^{5/3} z^3 \right. \\ \left. - \frac{1}{16} (\gamma\delta)^{4/3} z^4 + \frac{1}{20} \left(\frac{3}{2}\right)^{1/2} (\gamma\delta)^{5/3} z^5 \right] = 0 \tag{9} \end{aligned}$$

where the new eigenvalue parameter  $\Lambda$  is related to the original  $\lambda$  by the equation

<sup>4</sup> It follows from the van der Waals equation and Eqs. (5) and (6), that in (7) the coefficient of the term of order  $(\gamma\delta)^{\frac{1}{3}}$  must be  $(-3\nu_1)$ . It is also not difficult to show that only in this way one obtains a consistent approximation procedure for the Kac equation.

$$\begin{aligned} \frac{\lambda}{\omega(s_c)} = 1 + \frac{9\nu_1}{4} (\gamma\delta)^{2/3} + \frac{3}{2} \left(1 - \frac{s_1}{4}\right) \gamma\delta \\ + \frac{3}{8} \left(-s_2 + \frac{27}{4} \nu_1^2\right) (\gamma\delta)^{4/3} + \dots - 3\Lambda. \tag{10} \end{aligned}$$

From (9) one sees that one obtains a consistent approximation procedure by putting

$$\begin{aligned} H(z) = H^{(0)}(z) + (\gamma\delta)^{\frac{1}{3}}H^{(1)}(z) \\ + (\gamma\delta)^{\frac{2}{3}}H^{(2)}(z) + \dots, \\ \Lambda = \Theta(\gamma\delta)^{4/3} + \Omega(\gamma\delta)^{5/3} + \Xi(\gamma\delta)^2 + \dots \tag{11} \end{aligned}$$

In lowest order [i.e.,  $(\gamma\delta)^{4/3}$ ] one gets

$$\begin{aligned} \left[ \frac{d^2}{dz^2} - \frac{z^4}{48} + \frac{\nu_1}{4} z^2 \right. \\ \left. + (6)^{-\frac{1}{2}} \left(\frac{s_1}{4} - 1\right) z + \Theta \right] H^{(0)}(z) = 0, \tag{12} \end{aligned}$$

and in next order [i.e.,  $(\gamma\delta)^{5/3}$ ],

$$\begin{aligned} \left[ \frac{d^2}{dz^2} - \frac{z^4}{48} + \frac{\nu_1}{4} z^2 + (6)^{-\frac{1}{2}} \left(\frac{s_1}{4} - 1\right) z + \Theta \right] H^{(1)}(z) \\ = \left[ \left(\frac{2}{3}\right)^{\frac{1}{2}} \frac{d}{dz} z \frac{d}{dz} - \frac{z^5}{20(6)^{\frac{1}{2}}} + \frac{\nu_1}{8} \left(\frac{3}{2}\right)^{\frac{1}{2}} z^3 \right. \\ \left. + \frac{s_1 - 4}{12} z^2 - \left(\frac{2}{3}\right)^{\frac{1}{2}} \left(\frac{s_2}{8} - \frac{39}{32} \nu_1^2\right) z - \Omega \right] H^{(0)}(z). \tag{13} \end{aligned}$$

These equations determine, in principle, the eigenfunctions  $H_n^{(0)}(z), H_n^{(1)}(z)$  and the corresponding eigenvalues  $\Theta_n, \Omega_n$  as functions of the constants  $\nu_1, s_1,$  and  $s_2$ .

Turning now to the equation of state, we start from the general expression

$$\begin{aligned} -\lambda'_0(s) = \iint_{-\infty}^{+\infty} dx dy \psi_0(x) \psi_0(y) \left[ \frac{W(x)}{W(y)} \right]^{\frac{1}{2}} \\ \exp \left\{ \frac{(\nu_0\gamma)^{\frac{1}{2}}}{2} (x + y) \right\} \int_0^{\infty} d\tau \tau e^{-\tau} P_{\gamma}(x | y, \tau). \end{aligned}$$

By expanding  $\nu_0$  and  $s$  around the critical values, and by using the same taming substitutions for  $x$  and  $y$ , one obtains:

$$\begin{aligned} -\lambda'_0(s) = \omega(s_c) \left[ 3\delta - \delta(6)^{\frac{1}{2}} (\gamma\delta)^{\frac{1}{3}} \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z)^2 \right. \\ + (\gamma\delta)^{\frac{1}{3}} \left\{ -2\delta(6)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z) H_0^{(1)}(z) \right. \\ \left. + 2\delta \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)}(z)^2 + \frac{33}{4} \delta\nu_1 \right\} + \dots \tag{14} \end{aligned}$$

From (10) and the equation of state (8), one then finds that one must have, by comparing the result for  $l$  with the defining equation (6),

$$\int_{-\infty}^{+\infty} dz z H_0^{(0)}(z)^2 = -l_1 \left(\frac{2}{3}\right)^{\frac{1}{2}} \quad (15)$$

$$-2\left(\frac{2}{3}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z) H_0^{(1)}(z) + \frac{2}{3} \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)}(z)^2 + \frac{1}{2} \nu_1 = 0, \quad (16)$$

and these equations determine, in principle, the dependence of  $s_1$  and  $s_2$  on  $\nu_1$  and  $l_1$ .

III. ISOTHERM NET IN THE CRITICAL REGION

Since the equation of state is expressed in such an implicit fashion in terms of the lowest eigenvalue and eigenfunction of Eq. (12) which can not be determined in closed form, it is convenient for the discussion to make use of the following physical analogy. Writing Eq. (12) in the form

$$d^2 H^{(0)} / dz^2 + [\Theta - V(z) + Fz] H^{(0)} = 0, \quad (17)$$

with

$$V(z) = \frac{1}{4} z^4 - \left(\frac{1}{2} \nu_1\right) z^2, \quad F = (s_1 - 4) / 4(6)^{\frac{1}{2}}, \quad (18)$$

one sees that Eq. (12) can be looked upon as a Schrödinger equation for a particle moving in the potential  $V(z)$  and under the influence of a quasi-“electric” field of strength  $F$ . Furthermore it is easy to show that from Eq. (15) it follows that

$$l_1 = \left(\frac{2}{3}\right)^{\frac{1}{2}} \partial \Theta_0 / \partial F. \quad (19)$$

Hence  $l_1$  is proportional to the “electric moment” produced by  $F$ , and the discussion of the isotherm becomes equivalent to the discussion of the Stark effect for the lowest state of the motion of the particle in the potential  $V(z)$ .

Consider first the case when  $F$  is small. Since  $V(z) = V(-z)$ , the lowest eigenfunction  $H_0^{(0)}(z)$  is also symmetric in  $z$  when  $F = 0$ . Hence one has a quadratic Stark effect, so that  $l_1 = 0$  for  $F = 0$ , which follows also immediately from (15). By the usual perturbation theory one finds

$$\Theta_0(F) = \Theta_0 - F^2 \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \times \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 + O(F^4), \quad (20)$$

where the  $\Theta_n$  and  $H_n^{(0)}$  are the eigenvalues and eigenfunctions of the unperturbed equation. Therefore for  $F = 0$ ,  $\partial^2 \Theta_0 / \partial F^2 < 0$ , and not only  $\partial \Theta_0 / \partial F = 0$ , but also  $\partial^3 \Theta_0 / \partial F^3 = 0$ . This implies that at the critical density, that is for  $l_1 = 0$ , all isotherms have an inflection point with a negative slope. In fact one obtains from (19) and (20)

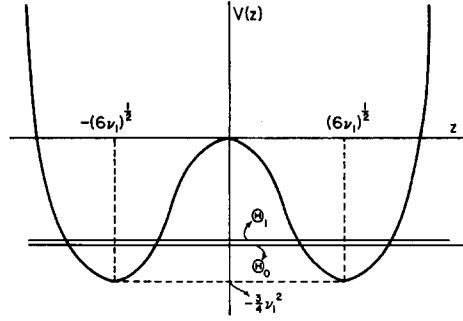


FIG. 1. The potential  $V(z)$  of Eq. (17) for a temperature much below the critical temperature.

$$\left(\frac{\partial s}{\partial l}\right)_{l_1=0} = -\frac{(\gamma \delta)^{\frac{1}{2}}}{4 \delta^2} / \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \times \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2, \quad (21)$$

which is always negative. The isotherms have therefore *no* horizontal part in the critical region. However the behavior of the slope (21) as function of the temperature is quite different for positive or negative  $\nu_1$ , that is, for  $T < T_c$  or  $T > T_c$ . Clearly, for negative  $\nu_1$  ( $T > T_c$ ), the potential  $V(z)$  has only a minimum at  $z = 0$ , and for  $\nu_1 \ll -1$ ,  $V(z)$  becomes a parabola and the eigenfunctions become the Weber functions. For  $\nu_1 \ll -1$ , it is simple to develop a perturbation method for the  $\Theta_n$  and  $H_n^{(0)}(z)$  and hence for the slope (21). One finds for  $\nu_1 \ll -1$

$$\left(\frac{\partial s}{\partial l}\right)_{l_1=0} = \frac{(\gamma \delta)^{\frac{1}{2}}}{4 \delta^2} \nu_1 \left[ 1 + \frac{1}{2(-\nu_1)^{\frac{1}{2}}} + O(-\nu_1)^{-3} \right]. \quad (22)$$

It is also easy to see that this is in agreement with the equation of state in the one-phase region,

$$s = \frac{1}{l - \delta} - \frac{\nu_0}{l^2} + \frac{\gamma}{2} \left[ 1 - \frac{l}{B} \left\{ 1 - \frac{\nu_0(l^2 - \delta^2)}{l^3} \right\} \right], \quad (23)$$

with

$$B^2 / l^2 = 1 - 2\nu_0(l - \delta)^2 / l^2,$$

which was given in I, Sec. IV. Using (5) and (6) one obtains from (23) the expansion (7) for  $s$  with

$$s_1 = 6\nu_1 l_1 - \frac{2}{3} l_1^2 + 4 - 6l_1(3l_1^2 - 4\nu_1)^{-\frac{1}{2}}, \quad (24)$$

from which (22) follows.

The discussion is quite different for the case  $\nu_1 > 0$ , that is  $T < T_c$ . The potential  $V(z)$  now has *two* minima (see Fig. 1), and for  $\nu_1 \gg 1$ , this leads to the well-known near degeneracy of the lowest energy level corresponding to the symmetric

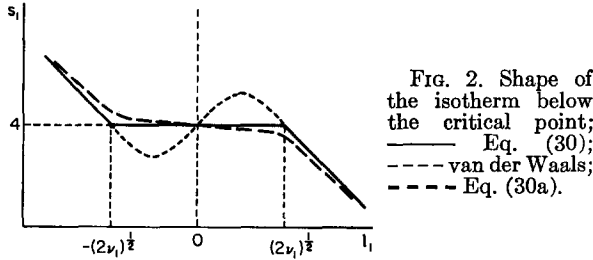


FIG. 2. Shape of the isotherm below the critical point; — Eq. (30); - - - van der Waals; - · - Eq. (30a).

and antisymmetric combination of the two lowest harmonic-oscillator eigenfunctions around the two minima. Using the WKB method<sup>5</sup> one finds

$$\Theta_1 - \Theta_0 \cong [(2\nu_1)^{1/2}/\pi] \exp[-(2\nu_1)^{1/2}],$$

$$\int_{-\infty}^{+\infty} dz z H_0^{(0)} H_1^{(0)} \cong (6\nu_1)^{1/2}.$$

Only the first term in the sum in (21) contributes, so that for  $\nu_1 \gg 1$ ,

$$\left(\frac{\partial s}{\partial l}\right)_{l_1=0} \cong -\frac{(\gamma\delta)^{1/2}}{12\pi\delta^2(2\nu_1)^{1/2}} \exp[-(2\nu_1)^{1/2}]. \quad (25)$$

The slope of the isotherm drops therefore very fast to zero if  $\nu_1$  increases.

Consider next the case when  $F$  and therefore  $l_1$  are not small. Again, to discuss  $s_1(l_1, \nu_1)$ , one must distinguish between the cases  $\nu_1 \ll -1$  and  $\nu_1 \gg 1$ . For temperatures *above*  $T_c$  ( $\nu_1 \ll -1$ ), the "potential" function  $V(z) - Fz$  has still only one minimum at  $z = z_0$ , determined by

$$\frac{1}{2}z_0^3 - (\frac{1}{2}\nu_1)z_0 - F = 0. \quad (26)$$

The "energy"  $\Theta_0$  is then given approximately by

$$\Theta_0 = V(z_0) - Fz_0 + 2^{-1/2}(z_0^2 - 2\nu_1)^{1/2}, \quad (27)$$

where the last term represents the "zero-point energy"  $\frac{1}{2}\hbar\omega$  of the oscillation around  $z_0$  [with  $\hbar = 1$ ,  $m = \frac{1}{2}$ , potential energy  $\frac{1}{4}\omega^2(z - z_0)^2 = \frac{1}{2}(d^2V/dz^2)_0(z - z_0)^2$ , so that  $\omega = 2^{1/2}(d^2V/dz^2)_0^{1/2} = 2^{-1/2}(z_0^2 - 2\nu_1)^{1/2}$ ]. From (19) and (27) one gets

$$\begin{aligned} (\frac{3}{2})^{1/2}l_1 &= -z_0 + 2^{-1/2}z_0(z_0^2 - 2\nu_1)^{-1/2} \partial z_0 / \partial F \\ &= -z_0 + 2^{1/2}z_0 / (z_0^2 - 2\nu_1)^{1/2}, \end{aligned}$$

using (26). In *zeroth* approximation, the minimum  $z_0 = -(\frac{3}{2})^{1/2}l_1$ , and substituting this in (26), and expressing  $F$  in  $s_1$  by (18), one obtains the first three terms of the equation of state (24) which also follow from the van der Waals equation. One can say that these van der Waals terms correspond to the "classical" approximation of the Stark effect.

In *first* approximation,  $z_0$  becomes

<sup>5</sup> Compare D. M. Dennison and G. E. Uhlenbeck, Phys. Rev. 41, 313 (1932).

$$z_0 = -(\frac{3}{2})^{1/2}l_1[1 - 2(6)^{1/2}l_1/(3l_1^2 - 4\nu_1)^{1/2}]$$

and this leads to the last term in the equation of state (24), which represents therefore, so to say, the first "quantum" correction to the van der Waals equation. Note that the corresponding result for the energy levels  $\Theta_n$  is given by

$$\begin{aligned} \Theta_n &= -\frac{9}{8}l_1^4 + \frac{3}{8}l_1\nu_1 - \nu_1/(3l_1^2 - 4\nu_1)^{1/2} \\ &\quad + \frac{1}{2}n(3l_1^2 - 4\nu_1)^{1/2}, \quad (28) \end{aligned}$$

and that in this approximation the eigenfunctions are the Weber functions  $D_n(y)$ , where

$$y = 2^{-1/2}(3l_1^2 - 4\nu_1)^{1/2}\{z + (3/2)^{1/2}l_1\}. \quad (29)$$

It is also not difficult to find the higher approximations. The results are collected in Appendix I, since they are needed in Sec. IV.

For temperatures *below*  $T_c$  ( $\nu_1 \gg 1$ ), the potential function  $V(z) - Fz$  can have *two* minima which will be of unequal depth and the sign of  $F$  [or of  $(s_1 - 4)$ ] determines which minimum is deeper. If in zeroth approximation we assume again that the energy  $\Theta_0$  is given by the value of the potential function at the deeper minimum, then one finds (in exactly the same way as above) for the equation of state

$$\begin{aligned} l_1 &= -2\nu_1^{1/2} \text{sign}(s_1 - 4) \\ &\quad - (s_1 - 4)/12\nu_1 + O(\nu_1^{-3/2}), \quad (30) \end{aligned}$$

and this follows also from the van der Waals equation [first three terms in (24)] plus the Maxwell rule (see Fig. 2). Again one can say that the van der Waals equation is the "classical" approximation of the corresponding Stark-effect problem. Especially the horizontal portion of the isotherm at  $s_1 = 4$  is due to the fact that the deeper minimum switches from the right to the left when  $F$  changes sign. Adding to the minimum energy, the zero-point energy does *not* change the qualitative picture; the horizontal portion remains. The finite slope of the isotherm, which we discussed before [see Eq. (25)] is due to a second "quantum mechanical" effect, namely the penetration of the barrier between the two minima if they become of almost equal depth. By using the WKB method one can show that this penetration effect changes Eq. (30) to

$$\begin{aligned} l_1 &= -2\nu_1^{1/2}(s_1 - 4)/[(s_1 - 4)^2 + \epsilon^2]^{1/2} \\ &\quad - (s_1 - 4)/12\nu_1, \quad (30a) \end{aligned}$$

where

$$\epsilon = (2^{1/2}/\pi) \exp[-(2\nu_1)^{1/2}]$$

and this agrees with Eq. (25).

So far we have discussed the isotherm net mainly for  $\nu_i \ll -1$  and  $\nu_i \gg 1$ . Although it is qualitatively clear how the isotherms change going through the critical region, it is difficult to make precise statements if  $\nu_i$  is of order one, and it is clearly *not* possible to answer unambiguously the question of what the shape of the coexistence curve is in the critical region. However, it seems reasonable to say that, because of the symmetry of the function  $V(z)$ , the critical density is not changed if  $\gamma\delta$  is finite, but that the critical temperature is lowered because for  $\nu_i > 0$ ,  $V(z)$  will have two minima, which is somehow an indication for the separation of the two phases. One can then define the new critical temperature as that value of  $\nu_i$  for which the lowest energy level is just at zero, which is the value of  $V(z)$  at the maximum. To determine this value one can use the variant of the WKB method which was developed by Kramers and Ittmann.<sup>6</sup> With this method one finds that the relation between  $\nu_i$  and  $\Theta_0$ , for  $l_1 = 0$  and  $\Theta_0$  close to zero, is given by

$$\nu_i = \left(\frac{3\pi}{16}\right)^{\frac{1}{2}} + \frac{|\lambda|}{6} \left(\frac{2}{3\pi}\right)^{\frac{1}{2}} \left[ \ln(36\pi) + C + \frac{\pi}{2} \right], \quad (31)$$

where  $\lambda = 2\Theta_0\nu_i^{-\frac{1}{2}}$  and  $C$  is the Euler constant. Hence  $\nu_i = \left(\frac{3}{16\pi}\right)^{\frac{1}{2}} = 0.702$  if  $\Theta_0 = 0$ , so that the critical temperature changes by  $\Delta T_c$  with  $\Delta T_c/T_c = 0.702(\gamma\delta)^{\frac{1}{2}}$ . For still lower temperatures, that is, for  $\nu_i > 0.702$ , the lowest eigenfunction will have two maxima. It is tempting to identify the positions of these maxima with the value of  $l_1\left(\frac{3}{2}\right)^{\frac{1}{2}}$  for the incipient "gas" and "liquid" phase. Doing this one obtains

$$l_1^2 = 4\nu_i^{-\frac{1}{2}} |\lambda|. \quad (32)$$

Eliminating  $|\lambda|$  between (31) and (32) then gives for the extrapolated coexistence curve<sup>7</sup> the equation

$$\begin{aligned} \nu_i &= \left(\frac{3\pi}{16}\right)^{\frac{1}{2}} + \frac{1}{48} \left[ \ln(36\pi) + C + \frac{\pi}{2} \right] l_1^2 \\ &= 0.702 + 0.143 l_1^2. \end{aligned} \quad (33)$$

This is still a parabola, but it is appreciably flatter than the van der Waals result  $\nu_i = \frac{1}{4} l_1^2$  (see Fig. 3).

#### IV. THE TWO-POINT DISTRIBUTION FUNCTION IN THE CRITICAL REGION

To determine the long-range behavior of the two-point distribution function in the critical region

<sup>6</sup> H. A. Kramers and G. P. Ittmann, Z. Physik 58, 217 (1929). See especially Sec. 6.

<sup>7</sup> Note that the equation for the coexistence curve as derived from the van der Waals equation plus the corrections of  $O(\gamma)$  (see I, Sec. 4) diverges at the critical point, so that a direct extrapolation is not possible.

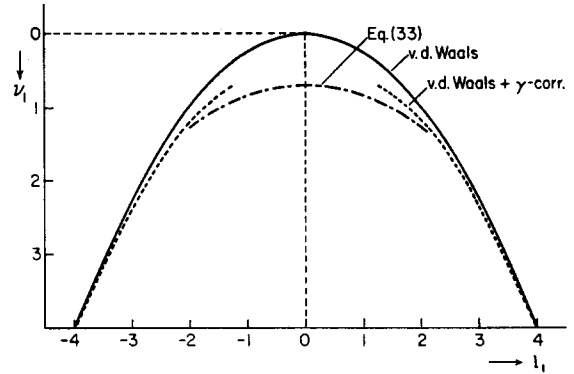


FIG. 3. Shape of the coexistence curve near the critical point; ——— van der Waals; - - - - van der Waals +  $\gamma$  corrections [Eq. (23)]; ·-·-· Eq. (33).

we will follow the same method as used in II, Sec. V for the one-phase region. However, since in the latter region  $\bar{n}_2(x; l)$  decays to  $1/l^2$  according to the Ornstein-Zernike exponential  $\exp(-B\gamma x/l)$  [II, Eq. (54)], and since in the critical region  $B/l$  is of order  $(\gamma\delta)^{\frac{1}{2}}$ , one should expect that in the critical region the range in  $x$  is of order  $1/(\gamma\delta)^{\frac{1}{2}}$ . We therefore replace, in the basic formula [II, Eq. (9a)] for the Laplace transform of  $\bar{n}_2(x; l)$ , the variable  $\sigma$  by  $\sigma\gamma(\gamma\delta)^{\frac{1}{2}}$  and we start from

$$\begin{aligned} l \int_0^\infty dx \bar{n}_2(x; l) \exp[-\sigma\gamma(\gamma\delta)^{\frac{1}{2}}x] \\ = -1 + \sum_{n=0}^\infty \frac{\lambda_0(s)}{\lambda_0(s) - \lambda_n(s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}})} b_n^2, \end{aligned} \quad (34)$$

with

$$b_n = \int_{-\infty}^{+\infty} dx \psi_0(x; s) \psi_n(x; s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}).$$

We first compute  $b_n^2$  up to order  $(\gamma\delta)^{\frac{1}{2}}$ . Introduce the variable  $z$  of Eq. (3) and the expansion (11) for the eigenfunctions. Notice that  $s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$  is obtained from the expansion (7) for  $s$  by adding  $8\sigma$  to  $s_2$ , so that the equation (12) for  $H^{(0)}$  is *not* affected by the change of  $s$  to  $s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$ . Using the orthogonality and normalization relations, one obtains

$$\begin{aligned} b_n^2 &= \delta_{n0} + (\gamma\delta)^{\frac{1}{2}} \left\{ \int_{-\infty}^{+\infty} dz H_0^{(0)}(z, s) \right. \\ &\quad \times [H_n^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_n^{(1)}(z, s)] \left. \right\}^2 \\ &\quad + 2(\gamma\delta)^{\frac{1}{2}} \delta_{n0} \int_{-\infty}^{+\infty} dz \{ H_0^{(0)}(z, s) \\ &\quad \times [H_0^{(2)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(2)}(z, s)] \\ &\quad + H_0^{(1)}(z, s) [H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)}(z, s)] \}. \end{aligned} \quad (35)$$

The second term can be calculated as follows. From Eq. (13) for  $H^{(1)}$  and the fact that  $H_n^{(0)}$  and  $\Theta_n$  are not affected by the change  $s \rightarrow s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}}$ , one shows that

$$\left[ \frac{d^2}{dz^2} - \frac{z^4}{48} + \frac{\nu_1 z^2}{4} + \frac{s_1 - 4}{4(6)^{\frac{1}{3}}} z + \Theta_n \right] \times [H_n^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}}) - H_n^{(1)}(z, s)] = [-(\frac{2}{3})^{\frac{1}{3}} \sigma z - \Omega_n(\sigma) + \Omega_n(0)] H_n^{(0)}(z, s), \tag{36}$$

where  $\Omega_n(\sigma) \equiv \Omega_n(s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}})$ . Multiplying (36) with  $H_0^{(0)}(z, s)$  and integrating gives for  $n \neq 0$

$$\int_{-\infty}^{+\infty} dz H_0^{(0)}(z, s) \{ H_n^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}}) - H_n^{(1)}(z, s) \} = -(\frac{2}{3})^{\frac{1}{3}} \frac{\sigma}{\Theta_n - \Theta_0} \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z, s) H_n^{(0)}(z, s). \tag{37}$$

To calculate next the terms in (34) containing the eigenvalues, it turns out that we need to extend the expansion (10) up to order  $(\gamma\delta)^2$ . This leads to

$$\lambda_0(s) - \lambda_n(s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}}) = \omega(s_c) \times \left\{ 3(\Theta_n - \Theta_0 + \sigma)(\gamma\delta)^{4/3} + 3[\Omega_n(\sigma) - \Omega_0(0)](\gamma\delta)^{5/3} + 3\left[ \Xi_n(\sigma) - \Xi_0(0) + \frac{11}{4} \nu_1 \sigma \right] (\gamma\delta)^2 + \dots \right\},$$

which gives

$$3(\gamma\delta)^{4/3} \sigma \frac{\lambda_0(s)}{\lambda_0(s) - \lambda_n(s + \sigma\gamma(\gamma\delta)^{\frac{1}{3}})} = \frac{\sigma}{\sigma + \Theta_n - \Theta_0} - \frac{(\gamma\delta)^{\frac{1}{3}} \sigma}{(\sigma + \Theta_n - \Theta_0)^2} \times [\Omega_n(\sigma) - \Omega_0(0)] + \frac{(\gamma\delta)^{\frac{1}{3}} \sigma^2}{(\sigma + \Theta_n - \Theta_0)^2} \times \left\{ +\frac{11\nu_1}{4} + \frac{9\nu_1}{4} \left( 1 + \frac{\Theta_n - \Theta_0}{\sigma} \right) + \frac{[\Omega_n(\sigma) - \Omega_0(0)]^2}{\sigma[\sigma + \Theta_n - \Theta_0]} - \frac{\Xi_n(\sigma) - \Xi_0(0)}{\sigma} \right\}. \tag{38}$$

Notice also that from (36) for  $n = 0$  one gets, by multiplying with  $H_0^{(0)}(z, s)$  and integrating,

$$\Omega_0(\sigma) - \Omega_0(0) = -(\frac{2}{3})^{\frac{1}{3}} \sigma \int_{-\infty}^{+\infty} dz z H_0^{(0)}(z, s)^2 = \sigma l_1, \tag{39}$$

where we have used the equation of state (15).

Substituting all these partial results in (34) one finds after some simple rearrangements

$$l_c^2 \sigma \gamma (\gamma\delta)^{\frac{1}{3}} \int_0^{\infty} dx \exp[-\sigma\gamma(\gamma\delta)^{\frac{1}{3}} x] \left[ \bar{n}_2(x; l) - \frac{1}{l^2} \right]$$

$$= (\gamma\delta)^{\frac{1}{3}} \frac{2}{3} \sum_{n=1}^{\infty} \frac{\sigma}{\sigma + \Theta_n - \Theta_0} \times \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 + (\gamma\delta)^{\frac{1}{3}} R. \tag{40}$$

Here  $R$  is a collection of terms for which we refer to Appendix II, where it will be proved that in fact  $R = 0$ . Of course Eq. (40) is valid only in the critical region, so that  $l$  is always given by Eq. (6), and the eigenvalues  $\Theta_n$  and eigenfunctions  $H_n^{(0)}$  must be determined from Eq. (12). With  $R = 0$  one can invert the Laplace transform, and one finds

$$\bar{n}_2(x, l) = \frac{1}{l^2} + \frac{2}{3} \frac{(\gamma\delta)^{\frac{1}{3}}}{l_c^2} \sum_{n=1}^{\infty} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 \times \exp[-(\Theta_n - \Theta_0)\gamma x (\gamma\delta)^{\frac{1}{3}}]. \tag{41}$$

This is the final result. It shows that in the critical region the decay of  $\bar{n}_2(x, l)$  to the uncorrelated value  $1/l^2$  is represented by an infinite series of decreasing exponentials which are all of order  $(\gamma\delta)^{\frac{1}{3}}$  and have ranges of order  $1/\gamma(\gamma\delta)^{\frac{1}{3}}$ .

Before starting a detailed discussion of Eq. (41) we conclude with some remarks.

(a) The fluctuation theorem [see II, Eq. (34a)] can be checked as follows. From (41) one gets:

$$\int_0^{\infty} dx \left[ \bar{n}_2(x, l) - \frac{1}{l^2} \right] = \frac{2}{3} \frac{\delta}{l_c^2} (\gamma\delta)^{-\frac{1}{3}} \times \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2,$$

and from (21) one sees that to order  $(\gamma\delta)^{-\frac{1}{3}}$ , the right-hand side is equal to  $(-\frac{1}{2}l^3)/(\partial s/\partial l)$  and this is also the leading term of the fluctuation integral.

(b) In the range  $x \sim 1/\gamma$ , Eq. (41) gives, to lowest order,

$$\bar{n}_2(x, l) = \frac{1}{l^2} + \frac{2}{3l_c^2} (\gamma\delta)^{\frac{1}{3}} \times \sum_{n=0}^{\infty} \left\{ \int_{-\infty}^{+\infty} dz [z + (\frac{2}{3})^{\frac{1}{3}} l_1] H_0^{(0)} H_n^{(0)} \right\}^2 = \frac{1}{l^2} + \frac{2}{3l_c^2} (\gamma\delta)^{\frac{1}{3}} \int_{-\infty}^{+\infty} dz [z + (\frac{2}{3})^{\frac{1}{3}} l_1]^2 H_0^{(0)}(z)^2, \tag{42}$$

where the equation of state (15) has been used to extend the summation from zero to infinity which then allows the application of Parseval's theorem. One can derive (42) also directly from the basic formula [II, Eq. (9a)] replacing  $\sigma$  by  $\sigma\gamma$  and expanding to order  $(\gamma\delta)^{\frac{1}{3}}$ , but we will leave this to the reader. Eq. (42) clearly shows that in the critical region  $1/\gamma$  is *not* the ultimate range, since in this

range  $\bar{n}_2(x, l)$  still differs from  $1/l^2$  by a constant of order  $(\gamma\delta)^{\frac{1}{2}}$ .

(c) To check the virial theorem [see II, Eq. (40a)]

$$s = \frac{1}{l} + \delta\bar{n}_2(\delta^+, l) - \nu_0\gamma^2 \int_0^\infty dx xe^{-\gamma x} \bar{n}_2(x; l)$$

in the critical region, one still needs the correction of order  $(\gamma\delta)^{\frac{1}{2}}$  in the short-range behavior of  $\bar{n}_2(x; l)$ . In Appendix III we prove that

$$\bar{n}_2(\delta^+, l) = \frac{1}{l(l-\delta)} + \frac{9}{4l_c^2} (\gamma\delta)^{\frac{1}{2}} \times \int_{-\infty}^{+\infty} dz [z + (\frac{3}{2})^{\frac{1}{2}} l_1]^2 H_0^{(0)}(z)^2. \quad (43)$$

Using (42) and the expansions (5), (6), and (7) for  $\nu_0$ ,  $l$ , and  $s$ , it is then easy to check the virial theorem up to order  $(\gamma\delta)^{\frac{1}{2}}$ .

V. DISCUSSION OF EQ. (41)

We will show that Eq. (41) goes over into the results obtained in II for the long-range behavior of  $\bar{n}_2(x; l)$  in the one- and two-phase region.

Consider first the two-phase region. We found (see II, Sec. VI) that there, in the range  $x \sim 1/\gamma$  and up to order  $\gamma$ ,

$$\bar{n}_2(x, l) = \frac{\xi_l l_l}{l} \left[ \frac{1}{l_l^2} + \frac{\nu_0(l_l - \delta)^4 \gamma}{l_l^5 B_l} \exp\left(-\frac{B_l}{l_l} \gamma x\right) \right] + \frac{\xi_g l_g}{l} \left[ \frac{1}{l_g^2} + \frac{\nu_0(l_g - \delta)^4 \gamma}{l_g^5 B_g} \exp\left(-\frac{B_g}{l_g} \gamma x\right) \right], \quad (44)$$

where  $\xi_l$ ,  $\xi_g$  are the mole fractions of the liquid and vapor phase which have the specific volumes  $l_l$  and  $l_g$ , so that

$$\xi_l + \xi_g = 1, \quad \xi_l l_l + \xi_g l_g = l.$$

Using the expansion (5) for  $\nu_0$  and the expansion (6) both for  $l_l$  and  $l_g$ , one finds

$$B_i/l_i = (\gamma\delta)^{\frac{1}{2}} (\frac{3}{4} l_i^2 - \nu_1)^{\frac{1}{2}}, \text{ with } i = l \text{ or } g, \quad (45) \frac{1}{l} \left( \frac{\xi_l}{l_l} + \frac{\xi_g}{l_g} \right) = \frac{1}{l^2} + \frac{\xi_l \xi_g (l_{1g} - l_{1l})^2}{l_c^2} (\gamma\delta)^{\frac{1}{2}} + O(\gamma\delta).$$

Furthermore, near the critical point,  $l_{1l} = -2\nu_1^{\frac{1}{2}}$  and  $l_{1g} = +2\nu_1^{\frac{1}{2}}$ , since the van der Waals coexistence curve is given by  $l_1^2 = 4\nu_1$ . Hence  $B/l = (\gamma\delta)^{\frac{1}{2}} (2\nu_1)^{\frac{1}{2}}$  both for the liquid and the vapor, so that the two exponentials in (44) become identical. Finally one has

$$l_1 = \xi_l l_{1l} + \xi_g l_{1g} = 2\nu_1^{\frac{1}{2}} (\xi_g - \xi_l),$$

which gives

$$\left. \begin{matrix} \xi_l \\ \xi_g \end{matrix} \right\} = \frac{1}{2} \left[ 1 \mp \frac{l_1}{2\nu_1^{\frac{1}{2}}} \right].$$

Substituting all this in (44) one obtains

$$\bar{n}_2(x, l) = \frac{1}{l^2} + \frac{2}{3} \frac{(\gamma\delta)^{\frac{1}{2}}}{l_c^2} \left\{ 6\nu_1 - \frac{3}{2} l_1^2 + \frac{1}{(2\nu_1)^{\frac{1}{2}}} \times \exp[-(2\nu_1)^{\frac{1}{2}} \gamma (\gamma\delta)^{\frac{1}{2}} x] \right\}. \quad (46)$$

This follows also from Eq. (41) when  $\nu_1 \gg 1$ . Let us verify it only in the symmetric case ( $l_1 = 0$ ). We saw in Sec. III that then the energy levels  $\Theta_n$  are a series of narrow doublets corresponding to the symmetric and antisymmetric combinations of the oscillator eigenfunctions around the two minima. In the series (41) only the odd values of  $n$  contribute, and in first approximation only  $n = 1$  and  $n = 3$  need to be considered. One finds

$$\Theta_1 - \Theta_0 \cong 0, \quad \Theta_3 - \Theta_0 \cong (2\nu_1)^{\frac{1}{2}}; \int dz z H_0^{(0)} H_1^{(0)} \cong (6\nu_1)^{\frac{1}{2}}, \quad \int dz z H_0^{(0)} H_3^{(0)} \cong (2\nu_1)^{-\frac{1}{2}};$$

so that Eq. (41) becomes equal to (46) with  $l_1 = 0$ .

Consider next the transition to the one-phase region, which is of greater interest since more detailed results are available [see II, Sec. V, Eqs. (54) and (55)]. For  $\nu_1 \ll -1$ , or better, for  $(3l_1^2 - 4\nu_1) \gg 1$ , we found in Sec. III that in first approximation [see Eq. (28)]

$$\Theta_n - \Theta_0 = \frac{1}{2} n (3l_1^2 - 4\nu_1)^{\frac{1}{2}},$$

and that the eigenfunctions are just the Weber functions  $D_n(y)$ , where  $y$  is given by Eq. (29). It is then easy to verify that the first term of the sum in Eq. (41) becomes

$$\frac{4}{3l_c^2} \frac{(\gamma\delta)^{\frac{1}{2}}}{(3l_1^2 - 4\nu_1)^{\frac{1}{2}}} \exp[-\frac{1}{2} (3l_1^2 - 4\nu_1)^{\frac{1}{2}} \gamma x (\gamma\delta)^{\frac{1}{2}}],$$

and that this is also precisely what the Ornstein-Zernike term [see II, Eq. (54)]

$$[\gamma\nu_0(l-\delta)^4/l^5 B] \exp[-(B/l)\gamma x]$$

becomes in the critical region up to order  $(\gamma\delta)^{\frac{1}{2}}$ . One only has to use (45) for  $B/l$ , and replace  $\nu_0$  and  $l$  by their critical values.

In the next approximation, using the results derived in Appendix I, one finds

$$\Theta_n - \Theta_0 = \frac{1}{2} n (3l_1^2 - 4\nu_1)^{\frac{1}{2}} + \frac{1}{2(3l_1^2 - 4\nu_1)} \left[ n^2 + n - \frac{2l_1^2}{3l_1^2 - 4\nu_1} (5n^2 - n) \right],$$

and up to order  $\epsilon^2$ ,

$$\int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} = (\frac{3}{4} l_1^2 - 4\nu_1)^{-\frac{1}{2}} \times \left\{ \delta_{n1} \left[ 1 + \frac{\epsilon^2}{3} \frac{12\nu_1 - 5l_1^2}{3l_1^2 - 4\nu_1} \right] - 2(\frac{3}{2})^{\frac{1}{2}} \frac{\epsilon l_1}{(3l_1^2 - 4\nu_1)} \delta_{n2} \right\},$$



omitting terms which do not contribute after squaring. In this order, therefore, the first and second term of the sum in Eq. (41) contribute. One obtains

$$\begin{aligned} \bar{n}_2(x; l) - \frac{1}{l^2} &= \frac{(\gamma\delta)^{\frac{1}{2}}}{l_c^2} \left[ \frac{4}{3} \frac{1}{(3l_1^2 - 4\nu_1)^{1/2}} \right. \\ &+ \frac{4}{3} \frac{l_1^2 + 4\nu_1}{(3l_1^2 - 4\nu_1)^{5/2}} \gamma x (\gamma\delta)^{1/3} - \frac{8}{9} \frac{5l_1^2 - 12\nu_1}{(3l_1^2 - 4\nu_1)^3} \left. \right] \\ &\times \exp \left[ -\frac{1}{2}(3l_1^2 - 4\nu_1)^{1/2} \gamma x (\gamma\delta)^{1/3} \right] \\ &+ \frac{(\gamma\delta)^{2/3}}{l_c^2} \frac{32}{9} \frac{l_1^2}{(3l_1^2 - 4\nu_1)^3} \\ &\times \exp \left[ -(3l_1^2 - 4\nu_1)^{1/2} \gamma x (\gamma\delta)^{1/3} \right] + \dots, \quad (47) \end{aligned}$$

and one can verify that the last three terms in (47) correspond precisely to the three corrections of order  $\gamma^2$  to the Ornstein-Zernike result in the one-phase region [see II, Eq. (55)] if these corrections are computed in the critical region up to order  $(\gamma\delta)^{\frac{1}{2}}$ . This confirms the general picture mentioned in the introduction, and it shows again that the Ornstein-Zernike exponential is the leading term only *outside* the critical region.

Since in the experimental investigation of the critical opalescence one observes the Fourier transform of the two-point distribution function, it is of interest to discuss also for our model the function

$$\begin{aligned} \tilde{g}(k) &= \int_{-\infty}^{+\infty} dx e^{ikx} g(x) \\ &= l \int_{-\infty}^{+\infty} dx e^{ikx} \left[ \bar{n}_2(x, l) - \frac{1}{l^2} \right]. \end{aligned}$$

For the Ornstein-Zernike exponential (in any number of dimensions),  $\tilde{g}(k) \sim 1/(k^2 + b^2)$ , where  $b^2$  is proportional to the compressibility, and it is therefore customary to plot  $1/\tilde{g}(k) \equiv f(k)$  vs  $k^2$ , since this should be a straight line intersecting the  $f(k)$  axis at a point which goes to zero at the critical point if the Ornstein-Zernike theory is correct. Since Eq. (41) is of the form

$$g(x) = \sum_{n=0}^{\infty} a_n e^{-b_n x},$$

where the  $a_n$  and  $b_n$  are positive, we obtain for our model, in the critical region,

$$\frac{1}{f(k)} \equiv \tilde{g}(k) = \sum_0^{\infty} \frac{2a_n b_n}{b_n^2 + k^2}.$$

For  $k^2$  large compared to the  $b_n^2$ ,  $f(k)$  is almost linear in  $k^2$ . In fact,

$$f(k) = \frac{k^2}{2 \sum a_n b_n} + \frac{\sum a_n b_n^3}{2(\sum a_n b_n)^2} + O\left(\frac{1}{k^2}\right). \quad (48)$$

To study the curvature for smaller  $k^2$ , note that one can write

$$\begin{aligned} \frac{f''}{2f^3} &= \left[ \sum_n \frac{a_n b_n}{(b_n^2 + k^2)^2} \right]^2 \\ &- \left( \sum_n \frac{a_n b_n}{b_n^2 + k^2} \right) \left[ \sum_n \frac{a_n b_n}{(b_n^2 + k^2)^3} \right], \end{aligned}$$

where the primes denote differentiations after  $k^2$ . Hence, by Schwartz's inequality, one concludes that  $f'' \leq 0$ , so that the curve is convex towards the  $k^2$  axis.

For the discussion of the temperature dependence of the Ornstein-Zernike plot, we will restrict ourselves to the case that  $l_1 = 0$  (critical density) and that  $\nu_1 \ll -1$ . One then can use Eq. (47); since the last term vanishes, one can write  $g(x)$  as one exponential by putting the second term back in the exponent, and one obtains

$$g(x) = a_1 e^{-b_1 x},$$

with

$$\begin{aligned} a_1 &= \frac{2}{3l_c} \frac{(\gamma\delta)^{\frac{1}{2}}}{(-\nu_1)^{\frac{1}{2}}} \left[ 1 - \frac{1}{4(-\nu_1)^{\frac{1}{2}}} + \dots \right], \\ b_1 &= (\gamma\delta)^{4/3} \frac{(-\nu_1)^{\frac{1}{2}}}{\delta} \left[ 1 + \frac{1}{4(-\nu_1)^{\frac{1}{2}}} + \dots \right]. \end{aligned}$$

Since the slope of the Ornstein-Zernike plot is  $\frac{1}{2} a_1 b_1$ , one sees that the temperature dependence drops out up to order  $(-\nu_1)^{\frac{1}{2}}$ , so that the straight parts of the plot are very nearly parallel. From (48) one further sees that the intersection with the  $f(k)$  axis is  $b_1/2a_1$ , or

$$f(0) = \frac{3}{4} (\gamma\delta)^{\frac{1}{2}} (-\nu_1) \left[ 1 + 1/2(-\nu_1)^{\frac{1}{2}} + \dots \right].$$

Since  $-(\gamma\delta)^{\frac{1}{2}} \nu_1 = (T - T_c)/T_c$  to this order in  $(\gamma\delta)$  one sees that, in first approximation,  $f(0) \sim (T - T_c)$  which is the Ornstein-Zernike result. However, closer to the critical point,  $f(0)$  bends upwards and one can show [using the exact Eq. (41)] that  $f(0)$  is finite for  $T = T_c$ . The deviations from the Ornstein-Zernike theory which follow from our model, look therefore about as shown in Fig. 4.

Finally we will discuss briefly the so-called *specific heat anomaly*.<sup>8</sup> It is well known that according to the van der Waals theory the specific heat at constant volume is constant ( $= \frac{3}{2}k$ ) in the one-phase region and increases suddenly if one crosses at a fixed density into the two-phase region. Especially at the critical density one finds

<sup>8</sup> We are indebted to Dr. J. V. Sengers for pointing out to us the interest of discussing this anomaly for our model.

$$\Delta c_s = 0 \text{ for } T > T_c, \tag{49}$$

$$\frac{3}{2}k[1 - \frac{2}{3}(T_c - T)/T_c + \dots]$$

for  $T < T_c$ .

Since the experimental results are quite different (this is the anomaly), it is of interest to see what the implications are of Eq. (41) for the specific heat. We start from the equation

$$\epsilon = \frac{kT}{2} - \frac{\alpha_0}{l_c} - \frac{2}{3} \frac{\alpha_0}{l_c} (\gamma\delta)^{\frac{1}{2}}$$

$$\times \int_{-\infty}^{+\infty} dz [z + l_1(\frac{3}{2})^{\frac{1}{2}}]^2 H_0^{(0)}(z)^2, \tag{50}$$

which follows from the general result [II, Eq. (41)] by introducing the expression (42) for  $n_2(x; l)$ . Since in the critical region

$$\frac{\partial}{\partial T} = -\frac{\alpha_0}{kT_c^2 \nu_{0c}(\gamma\delta)^{\frac{1}{2}}} \frac{\partial}{\partial \nu_1},$$

one obtains

$$\Delta c_s \equiv \left(\frac{\partial \epsilon}{\partial T}\right)_l - \frac{k}{2} = \frac{3}{4} k \frac{\partial}{\partial \nu_1} \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)2}(z, \nu_1, l_1)$$

$$= -3k \left(\frac{\partial^2 \Theta_0}{\partial \nu_1^2}\right)_{l_1} + \frac{3k}{8} l_1 \left(\frac{\partial^2 s_1}{\partial \nu_1^2}\right)_{l_1}, \tag{51}$$

by differentiating Eq. (12) for  $H_0^{(0)}(z)$  after  $\nu_1$  at constant  $l_1$ , and by using the equation of state (15). This shows that our model gives corrections to the specific heat which are of order  $k$  in the critical region, so that in this sense our model gives an anomalous behavior of  $c_s$ . To discuss Eq. (51) further, consider first the case  $l_1 = 0$ . It is easy to show that then

$$\Delta c_s = -3k \left(\frac{\partial^2 \Theta_0}{\partial \nu_1^2}\right)_{l_1}$$

$$= \frac{3k}{8} \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \left[ \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)} H_n^{(0)} \right]^2,$$

and by using the results of Sec. III one finds for  $\nu_1 \ll -1$

$$\Delta c_s = \frac{3}{8}k[1/(-\nu_1)^{\frac{1}{2}}] + \dots,$$

and for  $\nu_1 \gg 1^{\circ}$

$$\Delta c_s = \frac{3}{2}k - \frac{3}{4}k[1/(2\nu_1)^{\frac{1}{2}}] + \dots$$

At the critical density our model therefore smooths out the discontinuity (49) in  $c_s$  which follows from the van der Waals equation. Next, consider the

<sup>9</sup> To derive this result it is simpler not to use (51), but to go back to the general result [See II, Eq. (41)] and then use Eq. (46) for  $\bar{n}_2(x; l)$ .

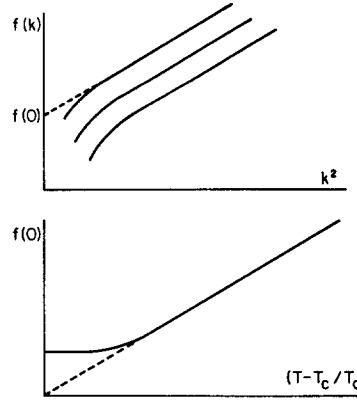


FIG. 4. Ornstein-Zernike plot according to Eq. (47).

dependence of  $\Delta c_s$  on  $l_1$  at fixed  $\nu_1$ . From (51) follows

$$[\partial(\Delta c_s)/\partial l_1]_{\nu_1} = \frac{3}{8}k(\partial^2 s_1/\partial \nu_1^2)_{l_1}, \tag{52}$$

using

$$8(\partial \Theta_0/\partial l_1)_{\nu_1} = l_1(\partial s_1/\partial l_1)_{\nu_1},$$

which is a consequence of (19). Eq. (52) is just a transcription of the thermodynamic formula

$$(\partial c_s/\partial \nu)_T = T(\partial^2 p/\partial T^2)_\nu,$$

and it shows that, at the critical density,  $\Delta c_s$  has always an extremum, because  $(s_1 - 4)$  is an odd function of  $l_1$  so that  $\partial^2 s_1/\partial \nu_1^2$  is zero for  $l_1 = 0$ . Furthermore, for small  $l_1$ ,

$$\Delta c_s = \Delta c_s(l_1 = 0) + l_1^2 \frac{3}{8}k(\partial^3 s_1/\partial \nu_1^2 \partial l_1)_{l_1=0} + \dots,$$

which gives for  $\nu_1 \ll -1$

$$\Delta c_s = \Delta c_s(l_1 = 0) - \frac{27}{8}k[l_1^2/(-\nu_1)^{5/2}] + \dots,$$

and for  $\nu_1 \gg 1$

$$\Delta c_s = \Delta c_s(l_1 = 0) - (27k/8\pi)(2\nu_1)^{\frac{1}{2}}$$

$$\times \exp[-(2\nu_1)^{\frac{1}{2}}]l_1^2 + \dots,$$

so that the extremum is probably always a maximum. The maximum becomes sharper when one approaches the critical point from the one-phase region, and then becomes rapidly very flat in the two-phase region. Presumably, the width of the maximum is smallest for  $\nu_1$  of order one.

### VI. GENERALIZATION OF EQ. (41)

In order to show that qualitatively the behavior of the two-point distribution function in the critical region does not depend sensitively on the form of the attractive potential (provided it has a long range), we will generalize the discussion of Sec. IV to the case where the attractive potential consists of a sum of  $m$  exponentials. Since the formulas are very long, we will only present an outline of the

calculations. As in II, Sec. VII, we write the attractive potential in the form

$$\varphi_{n+1}/kT = -\gamma \sum_{i=1}^m \nu_i \exp(-\gamma \sigma_i x),$$

where  $\nu_i = \alpha_i/kT$ , and we start to tame the Kac integral equation in the same way as in II, except that we replace  $\eta$  by  $\eta_c \equiv \eta(s_c)$ . One expands the van der Waals  $\nu_0 = \sum_i (\nu_i/\sigma_i)$  [see II, Eq. (79)] and  $s$  as in (5) and (7), and one then introduces new variables  $y_m$  by an orthogonal transformation which diagonalizes, just as in II, Eq. (75), the matrix

$$M_{ij} = \sigma_i^2 \delta_{ij} - \sigma_i \sigma_j (c_i c_j)^{\frac{1}{2}},$$

except that now,

$$c_i = \frac{2\nu_{ic}(l_c - \delta)^2}{\sigma_i l_c^3} = \frac{8\nu_{ic}}{27\sigma_i \delta} = \frac{\nu_{ic}}{\sigma_i \nu_{0c}} = \frac{\nu_i}{\sigma_i \nu_0},$$

where  $\nu_{ic} = \alpha_i/kT_c$ . It follows that  $\sum c_i = 1$ , in agreement with II, Eq. (80), since  $B = 0$ , and from the discussion given in II, this implies that the smallest eigenvalue  $A_m = 0$ , so that

$$\sum_{i,j} M_{i,j} y_i y_j = \sum_{k=1}^{m-1} A_k y_k^2.$$

The variable  $y_m$  plays a special role; *only* in this variable one must make the second, or critical-region “taming”,

$$y_m = z/(\gamma \delta)^{\frac{1}{3}},$$

and one then gets a consistent successive-approximation scheme with the parameter  $(\gamma \delta)^{1/3}$ . Up to order  $(\gamma \delta)^{4/3}$  one obtains<sup>10</sup>

$$\begin{aligned} \gamma \delta \sum_{k=1}^{m-1} \left( \frac{\partial^2 h}{\partial y_k^2} - \frac{A_k}{4} y_k^2 h \right) + (\gamma \delta)^{4/3} \left[ \frac{\partial^2 h}{\partial z^2} - \frac{(\mu z)^4}{48} h \right. \\ \left. + \frac{\nu_1 (\mu z)^2}{4} h + \frac{\mu z}{6^{\frac{1}{3}}} \left( \frac{s_1}{4} - \sum_{i=1}^m \sigma_i \right) h \right] \\ + (\gamma \delta)^{4/3} \frac{\mu z h}{2(6)^{\frac{1}{3}}} \sum_{k=1}^{m-1} A_k y_k^2 + \Lambda h = 0, \end{aligned} \quad (53)$$

which replaces Eq. (9) up to this order. In (53),  $h$  is a function of  $y_1, y_2, \dots, y_{m-1}, z$ , and the new eigenvalue  $\Lambda$  is defined by

$$\begin{aligned} 3\Lambda = 1 + \frac{9\nu_1}{4} (\gamma \delta)^{2/3} + \frac{3}{2} (\gamma \delta) \left( \sum_{i=1}^m \sigma_i - \frac{s_1}{4} \right) \\ + (\gamma \delta)^{4/3} \left( -\frac{3}{8} s_2 + \frac{81}{32} \nu_1^2 \right) - \frac{\lambda}{\omega(s_c)}, \end{aligned} \quad (54)$$

<sup>10</sup> In this equation,  $\nu_1$  should not be confused with  $\nu_1 = \alpha_1/kT$ . From now on, only the critical quantities  $\nu_{ic}$  will appear and  $\nu_1$  will always mean the number defined by Eq. (5).

which replaces Eq. (10). Finally the quantity  $\mu$  is defined by

$$\sum_{i=1}^m \sigma_i^2 a_{im}^2 = \left( \sum_{i=1}^m \sigma_i c_i^{\frac{1}{2}} a_{im} \right)^2 \equiv \mu^2,$$

where  $a_{ik}$  is the orthogonal matrix, which diagonalizes  $M_{ij}$ . By introducing instead of the  $y_k$  the new variables  $w_k$  by

$$y_k = w_k \{ 1 + [\mu z/2(6)^{\frac{1}{3}}] (\gamma \delta)^{\frac{1}{3}} \},$$

Eq. (53) can be written (always up to order  $(\gamma \delta)^{4/3}$ ) in the form

$$\begin{aligned} \gamma \delta \left[ 1 - \frac{\mu z}{6^{\frac{1}{3}}} (\gamma \delta)^{\frac{1}{3}} \right] \sum_{k=1}^{m-1} \left[ \frac{\partial^2 h}{\partial w_k^2} - \frac{A_k}{4} w_k^2 h \right] \\ + (\gamma \delta)^{4/3} \left[ \frac{\partial^2 h}{\partial z^2} - \frac{(\mu z)^4}{48} h + \frac{\nu_1 (\mu z)^2}{4} h \right. \\ \left. + \frac{\mu z}{6^{\frac{1}{3}}} \left( \frac{s_1}{4} - \sum_i \sigma_i \right) h \right] + \Lambda h = 0, \end{aligned} \quad (55)$$

and hence it becomes separable. It is easy to verify that (55) is fulfilled by putting

$$\Lambda = \gamma \delta \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} (n_k + \frac{1}{2}) + \Theta (\gamma \delta)^{4/3}, \quad (56)$$

$$h(w_1 \cdots w_{m-1}, z) = \prod_{k=1}^{m-1} N_{n_k} D_{n_k} (A_k^{\frac{1}{2}} w_k) H^{(0)}(z),$$

if  $H^{(0)}(z)$  and  $\Theta$  satisfy the equation

$$\begin{aligned} \left\{ \frac{d^2}{dz^2} - \frac{(\mu z)^4}{48} + \frac{\nu_1 (\mu z)^2}{4} + \frac{\mu z}{6^{\frac{1}{3}}} \left[ \frac{s_1}{4} - \sum_{i=1}^m \sigma_i \right. \right. \\ \left. \left. + \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} (n_k + \frac{1}{2}) \right] + \Theta \right\} H^{(0)} = 0, \end{aligned} \quad (57)$$

which is of the same form as (12). In fact by introducing the new variables

$$\hat{z} = z\mu^{2/3}, \quad \hat{\nu}_1 = \nu_1 \mu^{-2/3}, \quad \hat{\Theta} = \Theta \mu^{-4/3}, \quad (58)$$

$$\hat{s}_1 = 4 + \frac{1}{\mu} \left( s_1 - 4 \sum_{i=1}^m \sigma_i + 2 \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} \right),$$

and by putting  $H^{(0)}(z) \equiv \mu^{\frac{1}{2}} \hat{H}(\hat{z})$ , Eq. (57) becomes

$$\begin{aligned} \left[ \frac{d^2}{d\hat{z}^2} - \frac{\hat{z}^4}{48} + \frac{\hat{\nu}_1 \hat{z}^2}{4} + \frac{\hat{z}}{6^{\frac{1}{3}}} \left( \frac{\hat{s}_1}{4} - 1 \right) \right. \\ \left. + \frac{1}{\mu} \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} n_k \right] + \hat{\Theta}_n \hat{H}_n(\hat{z}) = 0, \end{aligned} \quad (59)$$

which is quite similar to (12). The only difference is that, because of the extra term containing the  $n_k$ , the eigenvalues  $\hat{\Theta}_n$  and eigenfunctions  $\hat{H}_n$  will depend on the whole set of “quantum” numbers  $\mathbf{n} \equiv n_1, n_2 \cdots n_m$ . Note still, that with the definitions (58) and with

$$\hat{\gamma} = \mu\gamma, \tag{60}$$

Eq. (5) for the critical temperature region can be written as

$$\nu_0 = \nu_{0c}[1 + \hat{\nu}_1(\hat{\gamma}\delta)^{\frac{1}{3}}],$$

while Eq. (7) for the pressure region becomes

$$s = s_c \left[ 1 - 3\hat{\nu}_1(\hat{\gamma}\delta)^{\frac{1}{3}} + \left( \hat{s}_1 - 4 + \frac{4}{\mu} \sum_{i=1}^m \sigma_i - \frac{2}{\mu} \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} \right) (\hat{\gamma}\delta) + \hat{s}_2(\hat{\gamma}\delta)^{4/3} + \dots \right],$$

with  $\hat{s}_2 = s_{2\mu}^{-4/3}$ . Finally, Eqs. (54) and (56) for the eigenvalue  $\lambda_n$  can be combined to

$$\begin{aligned} \frac{\lambda_n(s)}{\omega(s_c)} &= 1 + \frac{9}{4} \hat{\nu}_1(\hat{\gamma}\delta)^{\frac{1}{3}} + \frac{3}{2} \hat{\gamma}\delta \\ &\times \left[ 1 - \frac{\hat{s}_1}{4} - \frac{1}{\mu} \sum_{k=1}^{m-1} A_k^{\frac{1}{2}} (2n_k + \frac{1}{2}) \right] \\ &+ (\hat{\gamma}\delta)^{4/3} \left( -3\hat{\Theta}_n - \frac{3}{8} \hat{s}_2 + \frac{81}{32} \hat{\nu}_1^2 \right) + \dots \end{aligned}$$

Clearly it follows from (59) that the *maximum* eigenvalue and corresponding eigenfunction, for which the whole set  $\mathbf{n} = 0$ , obey in the capped variables exactly the same equation as before. Therefore the equation of state is still determined by

$$\int_{-\infty}^{+\infty} d\hat{z} \hat{z} \hat{H}_{0\dots 0}^2(\hat{z}) = -\left(\frac{3}{2}\right)^{\frac{1}{2}} \hat{l}_1, \tag{61}$$

where  $\hat{l}_1$  is defined by:

$$l = l_c [1 + \hat{l}_1(\hat{\gamma}\delta)^{\frac{1}{3}}],$$

similar to Eq. (6).

Turning now to the behavior of the two-point distribution function in the range of order  $1/\hat{\gamma}(\hat{\gamma}\delta)^{\frac{1}{3}}$  up to order  $(\hat{\gamma}\delta)^{\frac{1}{3}}$ , it is not difficult to prove that also in this case the calculation goes in the same way as before. The starting point is the obvious generalization of Eq. (34). One then shows that *only* the terms with  $n_1 = n_2 = \dots = n_{m-1} = 0$  contribute to order  $(\hat{\gamma}\delta)^{\frac{1}{3}}$ , and since in this case the equation for  $\hat{H}_{0\dots 0}$ ,  $n_m(\hat{z})$  is the same as Eq. (12) for  $H_n(z)$ , one obtains, in complete analogy with Eq. (41), that, in the general case,

$$\begin{aligned} \bar{n}_2(x; l) &= \frac{1}{l^2} + \frac{2}{3} \frac{(\hat{\gamma}\delta)^{\frac{1}{3}}}{l_c^2} \sum_{n=1}^{\infty} \left[ \int_{-\infty}^{+\infty} d\hat{z} \hat{z} \hat{H}_0 \hat{H}_n \right]^2 \\ &\times \exp [ -(\hat{\Theta}_n - \hat{\Theta}_0) x \hat{\gamma}(\hat{\gamma}\delta)^{\frac{1}{3}} ], \tag{62} \end{aligned}$$

where  $\hat{H}_n$  is the *same* function of  $\hat{z}$  as  $H_n^{(0)}$  is of  $z$  in (41), and  $\hat{\Theta}_n$  is equal to the  $\Theta_n$  occurring in (41).<sup>11</sup> The only essential change is therefore the

<sup>11</sup> These  $\Theta_n$  should not be confused with the  $\Theta$  occurring in Eq. (57), which is related to  $\hat{\Theta}$  by Eq. (58).

replacement of  $\gamma$  by  $\hat{\gamma} = \mu\gamma$ . Now we saw in II [see the equation following (85)] that, at the critical point,

$$a_{im} = (c_i^{\frac{1}{2}}/\sigma_i) / \left[ \sum_i (c_i/\sigma_i^2) \right]^{\frac{1}{2}}.$$

Hence,

$$\mu^2 = \sum_{i=1}^m \sigma_i^2 a_{im}^2 = \frac{\sum_i c_i}{\sum_i (c_i/\sigma_i^2)} = \frac{\sum_i (\alpha_i/\sigma_i)}{\sum_i (\alpha_i/\sigma_i^3)}$$

since  $c_i = (\alpha_i/\sigma_i)(1/\nu_0 kT)$ . Therefore we can write

$$\frac{1}{\hat{\gamma}^2} = \frac{1}{\mu^2 \gamma^2} = \frac{\frac{1}{2} \int_{-\infty}^{+\infty} dx x^2 \varphi_{\text{attr}}(|x|)}{\int_{-\infty}^{+\infty} dx \varphi_{\text{attr}}(|x|)}, \tag{63}$$

so that  $1/\hat{\gamma}$  is just the range  $R$  of the Ornstein-Zernike theory [see II, Eq. (72)]. The argument given in Sec. V, showing that the first term of the series (41) becomes the Ornstein-Zernike exponential in the one-phase region, can therefore be repeated in exactly the same way in the general case. We have not investigated in detail what happens in the higher approximations, but it seems very likely that qualitatively at least everything will remain the same.

### VII. CONCLUDING REMARKS

It is well known that the Fourier transform of the Ornstein-Zernike exponential [the function  $\tilde{g}(k)$  of Sec. V] is independent of the number of dimensions, and one may hope therefore that the deviations from the Ornstein-Zernike theory which follow from our model with regard to  $\tilde{g}(k)$  will at least qualitatively be the same in three dimensions. This is confirmed by the results of P. C. Hemmer, who has succeeded in generalizing to three dimensions the discussion of the long-range behavior of the correlation function reported in II.<sup>12</sup> It is therefore of interest to inquire whether there are any experimental indications of the deviations from the Ornstein-Zernike theory discussed in Sec. V [see especially Fig. 4].<sup>13</sup> Unfortunately, at present the experiments are still not decisive. The recent work

<sup>12</sup> This work will be reported in Part IV of this series.

<sup>13</sup> The question of the validity of the Ornstein-Zernike theory close to the critical point has been discussed especially by M. S. Green [J. Chem. Phys. 33, 1403 (1960)]. Although we do not agree with his theoretical arguments, we are very much indebted to Dr. Green for telling us about his work, and about the experimental results indicating deviations from the O-Z theory. Compare also the review by O. K. Rice in *Thermodynamics and Physics of Matter* (Princeton University Press, Princeton, New Jersey, 1955), Sec. E, where one finds a very complete bibliography.

by Thomas and Schmidt<sup>14</sup> on the critical opalescence in Argon does not show any deviation from the Ornstein-Zernike theory. On the other hand, deviations have been reported for various binary mixtures and these appear to point in the same direction as those shown in Figure 4.<sup>15</sup> It seems to us of great interest to see whether more refined experiments will show deviations from the Ornstein-Zernike theory, since such deviations *near* the critical point are perhaps the clearest indication of the existence of a critical *region*.

With regard to the specific-heat anomaly, the experiments<sup>16</sup> clearly show that  $c_v$  is *not* a constant in the one-phase region, and that it has a pronounced maximum as function of the density at constant temperature near the critical point. The maximum occurs close to the critical density, and this aspect of the anomaly agrees therefore qualitatively with the results for our model. However, the temperature dependence is quite different. Instead of smoothing out of the van der Waals discontinuity predicted by our model, recent experiments for Argon<sup>17</sup> show that at the critical density,  $c_v$  has as function of the temperature an asymmetric logarithmic singularity at the critical temperature. It seems therefore that in three dimensions, one has both a critical region *and* a critical point! Whether this is an universal phenomenon, more or less independent of the intermolecular forces, remains to be seen.

#### APPENDIX I. HIGHER APPROXIMATIONS OF THE EIGENFUNCTIONS NEAR THE ONE-PHASE REGION

For a systematic application of the perturbation theory to the basic equation (12) when  $\nu_1 \ll -1$ , it is best to replace  $z$  by the variable  $y$  of Eq. (29). Eq. (12) then becomes

$$\left[ \frac{d^2}{dy^2} - (3l_1^2 - 4\nu_1)^{-3/2} \frac{y^4}{6} + (3l_1^2 - 4\nu_1)^{-5/4} \right. \\ \left. \times \frac{l_1 y^3}{3^{1/2}} - \frac{y^2}{4} + \alpha y + \vartheta \right] K(y) = 0, \quad (\text{A1})$$

where

$$K(y) = \left( \frac{3}{4} l_1^2 - \nu_1 \right)^{-1/4} H^{(0)}(z),$$

<sup>14</sup> J. E. Thomas and P. W. Schmidt, J. Chem. Phys. (to be published).

<sup>15</sup> See especially D. McIntyre, A. Wims, and M. S. Green, J. Chem. Phys. **37**, 3019 (1962).

<sup>16</sup> The most complete data are for Argon, but other substances show the same behavior. See J. M. H. Levelt, Dissertation, University of Amsterdam, 1958.

<sup>17</sup> M. I. Bagatskii, A. V. Voronel, and V. G. Gusak, Zh. Eksperim. i Teor. Fiz. **43**, 728 (1962). We are indebted to Dr. M. Fisher for pointing out this reference to us.

$$\alpha = \frac{2}{3^{1/2}} (3l_1^2 - 4\nu_1)^{-1} \left( \frac{s_1}{4} - 1 + \frac{3}{8} l_1^3 - \frac{3}{2} \nu_1 l_1 \right), \quad (\text{A2}) \\ \vartheta = (3l_1^2 - 4\nu_1)^{-1/2} \\ \times \left( 2\Theta + l_1 - \frac{3}{32} l_1^4 + \frac{3}{4} l_1^2 \nu_1 - \frac{s_1}{4} l_1 \right).$$

For the small perturbation parameter, choose

$$\epsilon = (3l_1^2 - 4\nu_1)^{-1}$$

Note that  $l_1/(3l_1^2 - 4\nu_1)^{1/2}$  is always of order one. Write (A1) in the form

$$\left[ \frac{d^2}{dy^2} - \frac{\epsilon^2 y^4}{6} - \left( 1 - \frac{4\nu_1}{3l_1^2} \right)^{-1} \frac{\epsilon y^3}{3} - \frac{y^2}{4} \right. \\ \left. + \alpha(\epsilon)y + \vartheta(\epsilon) \right] K(y) = 0,$$

and expand

$$K(y) = K^{(0)}(y) + \epsilon K^{(1)}(y) + \epsilon^2 K^{(2)}(y) + \dots, \\ \alpha(\epsilon) = \alpha_0 + \epsilon \alpha_1 + \epsilon^2 \alpha_2 + \dots, \\ \vartheta(\epsilon) = \vartheta^{(0)} + \epsilon \vartheta^{(1)} + \epsilon^2 \vartheta^{(2)} + \dots.$$

In zeroth order, one gets

$$[d^2/dy^2 - \frac{1}{4}y^2 + \alpha_0 y + \vartheta^{(0)}] K^{(0)} = 0. \quad (\text{A3})$$

Since the equation of state (15) implies that for the ground state

$$\int_{-\infty}^{+\infty} dy y K_0(y)^2 = 0, \quad (\text{A4})$$

it follows that  $\alpha_0$  must be zero, and hence

$$K_n^{(0)}(y) = N_n D_n(y), \quad (\text{A5}) \\ \vartheta_n^{(0)} = n + \frac{1}{2}.$$

In first order one then gets

$$\left[ \frac{d^2}{dy^2} - \frac{y^2}{4} + n + \frac{1}{2} \right] K_n^{(1)}(y) \\ = \left[ - \left( 1 - \frac{4\nu_1}{3l_1^2} \right)^{-1} \frac{y^3}{3} - \alpha_1 y - \vartheta_n^{(1)} \right] K_n^{(0)}. \quad (\text{A6})$$

Since  $K_n^{(0)}(y)^2$  is symmetric in  $y$ , multiplication of (A6) with  $K_n^{(0)}$  and integration over  $y$  gives

$$\vartheta_n^{(1)} = 0. \quad (\text{A7})$$

For  $n = 0$ , one gets from (A6)

$$K_0^{(1)}(y) = \frac{1}{9} \left( 1 - \frac{4\nu_1}{3l_1^2} \right)^{-1} D_3(y) \\ + \left[ \left( 1 - \frac{4\nu_1}{3l_1^2} \right)^{-1} + \alpha_1 \right] D_1(y).$$

Since it follows from (A4) that

$$\int_{-\infty}^{+\infty} dy y K_0^{(0)} K_0^{(1)} = 0,$$

one concludes that

$$\alpha_1 = -[1 - \frac{4}{3}(\nu_1/l_1^2)]^{-1}. \tag{A8}$$

From (A2) together with (A5), (A7) and (A8) one obtains the results (24) and (28) for the equation of state and the energy  $\Theta_n$ . For the first-order correction to the eigenfunction, one then gets from (A6)

$$K_n^{(1)}(y) = N_n \left(1 - \frac{4\nu_1}{3l_1^2}\right)^{-1} \left[ \frac{1}{9} D_{n+3} + n D_{n+1} - n(n-1) D_{n-1} - \frac{n(n-1)(n-2)}{9} D_{n-3} \right].$$

In second order one obtains

$$\left[ \frac{d^2}{dy^2} - \frac{y^2}{4} + n + \frac{1}{2} \right] K_n^{(2)}(y) = - \left(1 - \frac{4\nu_1}{3l_1^2}\right)^{-1} \times \left( y - \frac{y^3}{3} \right) K_n^{(1)}(y) + \left( \frac{y^2}{6} - \alpha_2 y - \vartheta_n^{(2)} \right) K_n^{(0)}(y), \tag{A9}$$

from which one finds

$$\vartheta_n^{(2)} = n^2 + n + \frac{1}{2} - [3l_1^2/(3l_1^2 - 4\nu_1)] \times \left( \frac{10}{3} n^2 - \frac{2}{3} n + \frac{2}{9} \right), \tag{A10}$$

and from (A4) one concludes that

$$\int_{-\infty}^{+\infty} dy y (K_0^{(1)2} + 2K_0^{(0)} K_0^{(2)}) = 0,$$

which leads to  $\alpha_2 = 0$ . One then can determine  $K_n^{(0)}(y)$  in the usual way; and so on!

**APPENDIX II. COMPLETION OF THE PROOF OF EQ. (41)**

The quantity  $R$  left undefined in Eq. (40) is given by

$$R = \frac{2}{3} \sum_{n=1}^{\infty} \frac{\sigma(\sigma - \Theta_n + \Theta_0)}{(\Theta_n - \Theta_0)^2} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 + 2 \int_{-\infty}^{+\infty} dz H_0^{(0)} \left\{ H_0^{(2)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(2)} \right\} + 2 \int_{-\infty}^{+\infty} dz H_0^{(1)} \left\{ H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)} \right\} - \frac{\Xi_0(\sigma) - \Xi_0(0)}{\sigma} - \frac{\nu_1}{2}, \tag{A11}$$

where the arguments of the eigenfunctions which

are not indicated are always meant to be  $z, s$ . This can be simplified by using the fact that

$$\sum_{n=0}^{\infty} b_n^2 = 1.$$

Substituting (35) and using (37) shows that the second and third terms in (A11) are equal to

$$-\frac{2}{3} \sum_{n=1}^{\infty} \frac{\sigma^2}{(\Theta_n - \Theta_0^2)} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2,$$

so that one gets

$$R = -\frac{2}{3}\sigma \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 - \frac{\Xi_0(\sigma) - \Xi_0(0)}{\sigma} - \frac{\nu_1}{2}. \tag{A12}$$

One now has to calculate  $\Xi_0(\sigma) - \Xi_0(0)$ , for which the equation for  $H_n^{(2)}(z)$  is needed, which requires the extension of the expansion in Eq. (9) to order  $(\gamma\delta)^2$ . We will not give the explicit expression, but only note that the general form of the equations for the successive order eigenfunctions  $H_0^{(2)}(z)$  is

$$L_1 H_0^{(0)} = 0, \tag{A13a}$$

$$L_1 H_0^{(1)} = L_2 H_0^{(0)}, \tag{A13b}$$

$$L_1 H_0^{(2)} = L_2 H_0^{(1)} + L_3 H_0^{(0)}, \tag{A13c}$$

where the operators  $L_1$  and  $L_2$  can be read of Eqs. (12) and (13). The replacement of  $s$  by  $s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$  does not affect  $L_1$  but changes  $L_2$  and  $L_3$ , and we indicate this by writing  $L_2(\sigma)$ ,  $L_3(\sigma)$  for the new operators. The eigenvalue  $\Xi_0$  occurs in  $L_3$ , and to evaluate  $\Xi_0(\sigma) - \Xi_0(0)$  one needs  $L_3(\sigma) - L_3$ . From the extension of the expansion (9) to order  $(\gamma\delta)^2$  one finds

$$[L_3(\sigma) - L_3] H_0^{(0)}(z) = \frac{2\sigma}{3} z^2 H_0^{(0)}(z) - [\Xi_0(\sigma) - \Xi_0(0)] H_0^{(0)}(z),$$

so that

$$\Xi_0(\sigma) - \Xi_0(0) = \frac{2\sigma}{3} \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)2} - \int_{-\infty}^{+\infty} dz H_0^{(0)} [L_3(\sigma) - L_3] H_0^{(0)}.$$

The last integral can be transformed with the help of (A13c), and then one gets

$$\Xi_0(\sigma) - \Xi_0(0) = \frac{2\sigma}{3} \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)2} + \int_{-\infty}^{+\infty} dz H_0^{(0)} [L_2(\sigma) H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - L_2 H_0^{(1)}]$$

$$\begin{aligned}
&= -\frac{\nu_1\sigma}{2} + \sigma\left(\frac{2}{3}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_0^{(1)} - \sigma\left(\frac{2}{3}\right)^{\frac{1}{2}} \\
&\times \int_{-\infty}^{+\infty} dz z H_0^{(0)} [H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)}] \\
&+ \int_{-\infty}^{+\infty} dz H_0^{(0)} L_2[H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)}], \tag{A14}
\end{aligned}$$

where we have used the equation of state (16), the relation

$$L_2(\sigma) = L_2 - \sigma\left(\frac{2}{3}\right)^{\frac{1}{2}}z + \Omega_0(0) - \Omega_0(\sigma), \tag{A15}$$

and the fact that

$$\int_{-\infty}^{+\infty} dz H_0^{(1)}(z, s') H_0^{(0)}(z, s) = 0$$

for  $s' = s$  and for  $s' = s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$ .

Substituting (A14) in (A12) one obtains

$$\begin{aligned}
R &= -\frac{2\sigma}{3} \sum_{n=1}^{\infty} \frac{1}{\Theta_n - \Theta_0} \left[ \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_n^{(0)} \right]^2 \\
&- \left(\frac{2}{3}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z H_0^{(0)} H_0^{(1)} \\
&+ \left(\frac{2}{3}\right)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z H_0^{(0)} [H_0^{(1)}(z, s \\
&+ \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)}] \\
&- \frac{1}{\sigma} \int_{-\infty}^{+\infty} dz H_0^{(0)} L_2[H_0^{(1)}(z, s \\
&+ \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) - H_0^{(1)}]. \tag{A16}
\end{aligned}$$

Now express  $H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$  in terms of the complete set of functions  $H_n^{(0)}$ . From (A13b) written with  $s$  replaced by  $s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}$ , one obtains

$$\begin{aligned}
&H_0^{(1)}(z, s + \sigma\gamma(\gamma\delta)^{\frac{1}{2}}) \\
&= -\sum_{n=1}^{\infty} \frac{H_n^{(0)}}{\Theta_n - \Theta_0} \int_{-\infty}^{+\infty} dz H_n^{(0)} L_2(\sigma) H_0^{(0)}.
\end{aligned}$$

Eliminate in this way all the functions  $H^{(1)}$  from

the expression (A16) for  $R$ . Using again (A15) and the fact that the operator  $L_2$  is Hermitian, one finds the desired result

$$R = 0.$$

### APPENDIX III. PROOF OF EQ. (43)

We start from the equation

$$\begin{aligned}
\bar{n}_2(\delta^+; l) &= \frac{e^{-s\delta}}{l\lambda_0(s)} \iint_{-\infty}^{+\infty} dx dy \psi_0(x)\psi_0(y) \left[ \frac{W(x)}{W(y)} \right]^{\frac{1}{2}} \\
&\times P_\gamma(x | y, \delta) \exp \left\{ \frac{1}{2}(\nu_0\gamma)^{\frac{1}{2}}(x + y) \right\}, \tag{A17}
\end{aligned}$$

which is an exact consequence of the general formula [see II, Eq. (28a)] for the Laplace transform of  $\bar{n}_2(x; l)$ . To show this, multiply Eq. (28a) of II by  $\sigma \exp(\sigma\delta)$  and go the limit  $\sigma \rightarrow \infty$ . The left-hand side becomes  $l\bar{n}_2(\delta^+; l)$ . Using in the right-hand side the series [see II, Eq. (29)] for the resolvent  $R_{s+\sigma}$ , and the expression [See I, Eq. (9)] for the kernel  $K_{s+\sigma}(x, y)$ , it is easy to see that the first term of the series leads to (A17) since

$$\lim_{\sigma \rightarrow \infty} \sigma e^{\sigma\delta} p_s(x, y) = e^{-s\delta} P_\gamma(x | y, \delta),$$

and that all the further terms in the series vanish in the limit  $\sigma \rightarrow \infty$ .

One now "tames" the integral in (A17) by the same substitutions as used in Sec. II, replacing the variables  $x, y$  by  $z$  and  $\zeta$ . Expanding the integrand in powers of  $(\gamma\delta)^{\frac{1}{2}}$ , using the expansions (5), (6), (7) and (11) for  $\nu_0, l, s$ , and the eigenfunction  $H_0(z)$ , one finds up to order  $(\gamma\delta)^{\frac{1}{2}}$

$$\begin{aligned}
\bar{n}_2(\delta^+; l) &= \frac{1}{2\delta l} \left[ 1 - \frac{3}{2}l_1(\gamma\delta)^{\frac{1}{2}} \right. \\
&\left. + \frac{3}{2}(\gamma\delta)^{\frac{1}{2}} \int_{-\infty}^{+\infty} dz z^2 H_0^{(0)}(z)^2 \right], \tag{A18}
\end{aligned}$$

where also Eqs. (15) and (16) have been used. It is easy to verify that, to order  $(\gamma\delta)^{\frac{1}{2}}$ , (A18) is equivalent to Eq. (43).