

Nonclassical Behavior of the van der Waals Gas

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The partition function of the van der Waals gas is represented by a functional integral which is evaluated by summing the value of the integrand over its absolute and all of its secondary maxima. This leads to a one-to-one correspondence with the Ising model with nearest-neighbor interactions only. Whereas the classical behavior of the van der Waals gas is due to the absolute maximum in function space, the nonclassical behavior is shown to derive from the combined contribution of all the secondary maxima. The relation of this work to inverse range expansions and to the droplet model of condensation is discussed.

KEY WORDS: Critical behavior; van der Waals gas; droplet model of condensation; Ising model; functional integration.

1. INTRODUCTION

In the last decade much effort has been directed to the study of the van der Waals gas. This is a system of classical particles which interact with a pair interaction which is the sum of a hard-core repulsion and a long-range attraction:

$$V(\mathbf{r}) = V_{hc}(\mathbf{r}) + V_{lr}(\mathbf{r}) \quad (1a)$$

$$V_{hc}(\mathbf{r}) = \begin{cases} 0 & \text{if } |\mathbf{r}| > \sigma \\ +\infty & \text{if } |\mathbf{r}| < \sigma \end{cases} \quad (1b)$$

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Usually the attractive part of the interaction has the form (D is the dimension)

$$V_{\text{Ir}}(\mathbf{r}) = -\gamma^D W(\gamma\mathbf{r}) \quad (1c)$$

The range of this interaction is of the order of γ^{-1} , and one is interested in the case in which the range is large compared to the diameter of the hard core, but finite:

$$\sigma \ll \gamma^{-1} < \infty \quad (2)$$

Lebowitz and Penrose⁽¹⁾ proved rigorously that the equation of state of the van der Waals gas, in the limit $\gamma \downarrow 0$, is the van der Waals equation of state, including the Maxwell construction (this is the "classical limit" of the theory). This result, which had previously been obtained heuristically by van Kampen,⁽²⁾ motivated attempts by several authors to study the case of small γ by a type of perturbation theory in which the grand canonical pressure of the system is developed in a power series in γ (see Ref. 3 for a review of the literature). As a result of the perturbation-theoretic origin of these γ expansions, the critical behavior which results from them is of the same type as the critical behavior predicted from the van der Waals equation of state: The critical exponents still have their classical values. This conclusion is almost certainly incorrect. Consequently one expects that, whereas the γ expansion is probably an excellent approximation to the true pressure outside of the critical region, terms in the pressure which are nonanalytic in γ must become dominant when the temperature approaches the critical temperature, and that these nonanalytic terms lead to nonclassical critical exponents. It is the aim of the present paper to explore this possibility in a somewhat heuristic fashion.

2. FUNCTIONAL INTEGRAL REPRESENTATION

It can be shown^(4,5) that the grand canonical partition function of the van der Waals gas can be represented by a functional integral of the form

$$\begin{aligned} Z(z, \beta, \Omega) = \mathcal{N}^{-1} \int \exp \left\{ \frac{1}{2} \beta \int_{\Omega} d^D \mathbf{r} \int_{\Omega} d^D \mathbf{r}' \phi(\mathbf{r}) V_{\text{Ir}}^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right. \\ \left. + \beta \int_{\Omega} p_{\text{hc}}(z \exp \beta \phi) d^D \mathbf{r} \right\} d[\phi(\mathbf{r})] \end{aligned} \quad (3)$$

In this expression Z denotes the grand canonical partition function; z is the fugacity (with a shifted origin for the chemical potential); β^{-1} is the product of the absolute temperature and Boltzmann's constant; Ω is the volume of the system. The kernel $V_{\text{Ir}}(\mathbf{r} - \mathbf{r}')$ is supposed to be negative-definite; its inverse

is denoted by $V_{\text{ir}}^{-1}(\mathbf{r} - \mathbf{r}')$. The pressure of the hard-core system is denoted by $p_{\text{hc}}(z)$. Finally, the normalization is

$$\mathcal{N} = \int \exp \left\{ \frac{1}{2} \beta \int_{\Omega} d^D \mathbf{r}' \int_{\Omega} d^D \mathbf{r} \phi(\mathbf{r}) V_{\text{ir}}^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}') \right\} d[\phi(\mathbf{r})] \quad (4)$$

The integrations in (3) and (4) are to be extended over real random functions, defined on Ω . For a definition of the process of functional integration and its extension to nondefinite kernels and complex random functions, see Ref. 5. It is shown there that the representation (3) of the partition function is not an exact result, but a good approximation provided the range of the attraction is very large compared to the diameter of the hard core.

For calculational convenience we shall assume a specific form for the function W which occurs in (1c):

$$W(\boldsymbol{\rho}) = (2\pi)^{-D} \int \{ [\exp(-i\mathbf{k} \cdot \boldsymbol{\rho})] / (q_1 \mathbf{k}^2 + q_2) \} d^D \mathbf{k} \quad (5)$$

Here q_1 and q_2 are arbitrary positive constants. The function W has now the form of a Kac potential for $D = 1$ and the form of a Yukawa potential for $D = 3$. The analysis of this paper can be extended to more general forms of the potential; this would not lead to qualitatively different results. Substituting (5) into (1c) gives for the inverse of V_{ir} the explicit form

$$V_{\text{ir}}^{-1}(\mathbf{r}) = [(q_1/\gamma^2)\Delta - q_2] \delta(\mathbf{r}) \quad (6)$$

where Δ denotes the D -dimensional Laplacian and $\delta(\mathbf{r})$ the D -dimensional Dirac function. The reason for the specific form of W now becomes obvious: Upon substitution of (6) into (3) and (4) one finds the Landau-Ginzburg form

$$Z(z, \beta, \Omega) = \mathcal{N}^{-1} \int \exp \left\{ - \int_{\Omega} [(\beta q_1/2\gamma^2)(\nabla\phi)^2 + A(\phi)] d^D \mathbf{r} \right\} d[\phi(\mathbf{r})] \quad (7)$$

$$\mathcal{N} = \int \exp \left\{ - \int_{\Omega} [(\beta q_1/2\gamma^2)(\nabla\phi)^2 + \frac{1}{2}\beta q_2 \phi^2] d^D \mathbf{r} \right\} d[\phi(\mathbf{r})] \quad (8)$$

$$A(\phi) = \frac{1}{2}\beta q_2 \phi^2 - \beta p_{\text{hc}}(z \exp \beta \phi) \quad (9)$$

A functional integral of this type has been studied by Langer,⁽⁶⁾ who obtained the analytic continuation of the grand canonical pressure $p(z)$ from the gas branch ($z < z_0$), around the condensation point z_0 , into the metastable branch ($z > z_0$). A similar functional integral forms the starting point of Wilson's theory of critical behavior.⁽⁷⁾

Before we close this section we want to show how the van der Waals equation of state appears. The absolute maximum of the integrand of (7)

occurs for a field $\bar{\phi}$ which is constant in space and equal to the absolute minimum of the function $A(\phi)$; it must be a solution of

$$q_2 \bar{\phi} = \rho_{\text{hc}}(z \exp \beta \bar{\phi}) \quad (10)$$

From the general shape of the density $\rho_{\text{hc}}(z)$ of the hard-core system one infers that there exists a temperature T_w such that (10) has only one solution for $T > T_w$ but three solutions $\bar{\phi}_g < \bar{\phi}_0 < \bar{\phi}_l$ for $T < T_w$. Here $\bar{\phi}_g$ and $\bar{\phi}_l$ are minima of $A(\phi)$; they are separated by a barrier with maximum at $\bar{\phi}_0$. Identification of the functional integral (7) with the absolute maximum of the integrand gives

$$\beta p(z, \beta) = \max[-A(\bar{\phi}_g), -A(\bar{\phi}_l)] \quad (11)$$

The two minima $\bar{\phi}_g(z, \beta)$ and $\bar{\phi}_l(z, \beta)$ are functions of z and β . The minimum $\bar{\phi}_g$ will be the absolute minimum of $A(\phi)$ provided $z < z_0(\beta)$; $\bar{\phi}_l$ will be the absolute minimum for $z > z_0(\beta)$. Clearly T_w plays the role of the critical temperature and z_0 is the point where the phase transition occurs if $T < T_w$. That (11) is really the grand canonical form of the van der Waals equation of state can be seen by first calculating the density $\rho(z, \beta)$ from (11) and then eliminating z and $\bar{\phi}$. One finds in this way

$$p(\beta, \rho) = p_{\text{hc}}(\rho) - (1/2q_2) \rho^2 \quad (12)$$

3. CORRESPONDENCE WITH NEAREST-NEIGHBOR ISING MODEL

Whereas in the previous section only the absolute maximum of the integrand of (7) was considered, we shall now also take the secondary maxima into account. They are all the solutions of the Euler-Lagrange equation

$$(\beta q_1 / \gamma^2) \Delta \bar{\phi} = (\partial / \partial \bar{\phi}) A(\bar{\phi}) \quad (13)$$

which obey the appropriate boundary conditions on the surface of Ω . The solutions $\bar{\phi}(\mathbf{r})$ of (13) will in general be space-dependent. Consider a given $\bar{\phi}(\mathbf{r})$ and draw the surfaces $\bar{\phi}(\mathbf{r}) = \text{const}$. For a given point $\mathbf{r}_0 \in \Omega$, Eq. (13) can be transformed to a local set of orthogonal coordinates, two of which are tangential to the surface $\bar{\phi}(\mathbf{r}) = \bar{\phi}(\mathbf{r}_0)$ whereas the third one is orthogonal to this surface. If the component of $\mathbf{r} - \mathbf{r}_0$ along the third local coordinate axis is denoted by α , then the solution of (13) can be replaced, in a vicinity of \mathbf{r}_0 , by the solution of the equation

$$\frac{\beta q_1}{\gamma^2} \frac{d^2}{d\alpha^2} \bar{\phi}(\alpha) = \frac{d}{d\bar{\phi}} A(\bar{\phi}) \quad (14)$$

This is the equation of motion of a classical particle with mass $\beta q_1 \gamma^{-2}$ moving along the $\bar{\phi}$ axis in time α and in a potential $-A(\bar{\phi})$. From (9) and the qualitative properties of the hard-core reference system it can be verified that the potential $-A(\bar{\phi})$ looks as follows. For temperatures below T_w and a value of z slightly below $z_0(\beta)$ the potential shows two maxima, at $\bar{\phi}_g$ and $\bar{\phi}_l$, separated by a minimum at $\bar{\phi}_0$. For large positive or negative values of $\bar{\phi}$ the potential $-A(\bar{\phi})$ will decrease to $-\infty$. In this potential the only bounded motions are motions in which the particle either lies on top of the "gas" or "liquid" hill, or oscillates between a value of $\bar{\phi}$ slightly larger than $\bar{\phi}_g$ and a value of $\bar{\phi}$ slightly smaller than $\bar{\phi}_l$. The particle remains for an extended period of time close to the top of either of the two hills. The "time" l to go from the "gas" to the "liquid" phase is of the order of

$$l = \frac{\bar{\phi}_l - \bar{\phi}_g}{(d\bar{\phi}/d\alpha)_0}$$

Using (14), we find explicitly

$$l = \frac{c}{\gamma}; \quad c = \frac{\bar{\phi}_l - \bar{\phi}_g}{\{(2/\beta q_1)[A(\bar{\phi}_0) - A(\bar{\phi}_{g,l})]\}^{1/2}} \quad (15)$$

In this equation $\bar{\phi}_{g,l}$ means $\bar{\phi}_l$ if $z < z_0$ and $\bar{\phi}_g$ if $z > z_0$. The qualitative conclusion of this paragraph is that the fields $\bar{\phi}(\mathbf{r})$ which are secondary maxima of the integrand of (7) are constant nearly everywhere, equal to $\bar{\phi}_g$ in a "gas" region and equal to $\bar{\phi}_l$ in a "liquid" region. A "gas" region is separated from a "liquid" region by a transition layer of width l . The linear dimensions of the regions are very large compared to the width of the transition layer provided z is equal to or very near to the transition value $z_0(\beta)$. Obviously this picture makes sense only for temperatures below the mean-field critical temperature T_w .

Now, divide the volume Ω into cubical cells of volume l^D and attach a spin $\sigma_i = \pm 1$ to cell number i . For any secondary maximum $\bar{\phi}(\mathbf{r})$ one can determine the space average of $\bar{\phi}(\mathbf{r})$ over cell i ; according to the previous remarks, this average will be either $\bar{\phi}_l$ (in which case one defines $\sigma_i = +1$) or $\bar{\phi}_g$ (in which case $\sigma_i = -1$). It is clear that a cell with $\sigma_i = +1$ will contribute a term $-A(\bar{\phi}_l) l^D$ to the exponential in the integrand in (7); whereas a cell with $\sigma_i = -1$ will contribute a term $-A(\bar{\phi}_g) l^D$. If, however, a pair of neighboring cells carries spins with opposite signs, it is erroneous to attach weights according to these rules. This error is corrected for by adding a term

$$+ [A(\bar{\phi}_g) + A(\bar{\phi}_l)] l^D - \int_{-l}^{+l} \left[\frac{\beta q_1}{2\gamma^2} \left(\frac{d\bar{\phi}}{d\alpha} \right)^2 + A(\bar{\phi}) \right] l^{D-1} d\alpha$$

each time such a pair occurs. Substituting the solution of (14) here, we find explicitly a term

$$-(c'/c) l^D; \quad c' = (2\beta q_1)^{1/2} \int_{\bar{\phi}_g}^{\bar{\phi}_l} [A(\bar{\phi}) - A(\bar{\phi}_{g,l})]^{1/2} d\bar{\phi} \quad (16)$$

for each pair of neighboring cells which carry opposite spins.

Summing the values of the integrand of (7) over all secondary maxima thus results in the approximation

$$Z(z, \beta, \Omega) = \sum_{\{\sigma_i\}} \exp \left\{ -l^D \sum_i \left(\frac{1 + \sigma_i}{2} A_l + \frac{1 - \sigma_i}{2} A_g \right) - l^D \frac{c'}{c} \sum_{i,j} \frac{1 - \sigma_i \sigma_j}{2} \right\} \quad (17)$$

where $A_l \equiv A(\bar{\phi}_l)$ and $A_g \equiv A(\bar{\phi}_g)$. The prime on the third summation sign denotes a sum over pairs of nearest neighbors only. Clearly, two approximations were made in writing down this expression. The interfaces between the "gas" and "liquid" regions are approximated by the faces of the elementary cells in which the system is divided. Second, by summing all the σ_i independently over ± 1 one actually sums the value of the integrand of (7) over a class of points in function space which is larger than the class of the secondary maxima. The correspondence with the Ising model is now obvious. If α_D denotes the coordination number of the lattice ($\alpha_1 = 2, \alpha_2 = 4, \alpha_3 = 6$), and $f(\beta\mathcal{J}, \beta mH)$ denotes the Helmholtz free energy per lattice point of the nearest-neighbor Ising model,

$$-\beta f(\beta\mathcal{J}, \beta mH) = \lim_{N \rightarrow \infty} (1/N) \ln \sum_{\{\sigma_i\}} \exp \left\{ \beta mH \sum_i \sigma_i + \frac{1}{2} \beta \mathcal{J} \sum_{i,j} \sigma_i \sigma_j \right\} \quad (18)$$

then the grand canonical pressure of the van der Waals gas is found to be

$$\beta p(z, \beta) = -\frac{1}{4} \alpha_D (c'/c) - \frac{1}{2} (A_g + A_l) - l^{-D} \beta f((c'/c) l^D, \frac{1}{2} (A_g - A_l) l^D) \quad (19)$$

Let us close this section with the calculation of a few properties of the inclusions. The average total volume occupied by "liquid", $\langle \Omega_l \rangle$, is found from (17) as

$$\langle \Omega_l \rangle = \left\langle l^D \sum_i \frac{1 + \sigma_i}{2} \right\rangle = - \frac{\partial \ln Z}{\partial A_l} = -\Omega \frac{\partial \beta p}{\partial A_l}$$

The total volume fractions filled with "liquid" and "gas" are thus given by

$$x_l \equiv \langle \Omega_l \rangle / \Omega = -\partial \beta p / \partial A_l \quad (20a)$$

$$x_g \equiv \langle \Omega_g \rangle / \Omega = -\partial \beta p / \partial A_g \quad (20b)$$

The average total surface of the interface (S) is found in the same way:

$$S = \left\langle l^{D-1} \sum'_{i,j} \frac{1 - \sigma_i \sigma_j}{2} \right\rangle = -\Omega l^{D-1} \frac{\partial \beta p}{\partial (l^D c'/c)} \tag{21}$$

This quantity will later be used for an order-of-magnitude estimation of the linear dimensions of the inclusions on the diameter of the coexistence curve.

4. TESTS

The approximation method which was discussed in the previous section can be applied to the two cases for which the van der Waals gas can be solved rigorously: the one-dimensional system for arbitrary γ and the multidimensional system for $\gamma \downarrow 0$.

Substitution of the solution of the one-dimensional Ising model in an external magnetic field into (19) gives for $T < T_w$

$$\beta p(z, \beta) = -\frac{1}{2}(A_g + A_l) + \frac{1}{l} \ln \left\{ \cosh \frac{l}{2}(A_l - A_g) + \left[\sinh^2 \frac{l}{2}(A_l - A_g) + \exp\left(-2\frac{c'}{c}l\right) \right]^{1/2} \right\} \tag{22}$$

In the region near the transition point one has $|A_l - A_g| l \ll 1$ and one finds

$$\beta p(z, \beta) = -\frac{1}{2}(A_g + A_l) + \frac{1}{2}[(A_l - A_g)^2 + (4/l^2) \exp(-2c'/\gamma)]^{1/2} \tag{23}$$

Comparing this with the exact solution of the model of Kac *et al.*,⁽⁸⁾ one finds that (23) is in qualitative agreement with the rigorous result (the solution of this model in the grand canonical ensemble is discussed in Refs. 4, 5; also compare related work by Helfand⁽⁹⁾ and van Kampen⁽¹⁰⁾). As a matter of fact, the correspondence between the one-dimensional Ising model and the one-dimensional van der Waals gas holds even in a part of the complex z plane which is much larger than a small vicinity of the point $z_0(\beta)$, as can be seen by comparing the Yang-Lee distributions of zeros for the two systems.⁽¹¹⁾

The result of Lebowitz and Penrose can be derived from (19) as follows: The limit $\gamma \downarrow 0$ in the van der Waals gas is, according to (18) and (19), the limit $T \downarrow 0$ in the corresponding Ising model. At the absolute zero of temperature all the spins in the Ising model will point in the direction of the magnetic field:

$$\lim_{T \downarrow 0} f(\beta \mathcal{J}, \beta m H) = -m |H| - \frac{1}{4} \alpha_D \mathcal{J}$$

Substitution into (19) gives

$$\lim_{\gamma \downarrow 0} \beta p(z, \beta) = -\frac{1}{2}(A_g + A_l) + \frac{1}{2} |A_g - A_l| = \max[-A_g, -A_l] \tag{24}$$

which, according to Section 2, leads to the van der Waals equation of state (12).

5. THE TWO-DIMENSIONAL VAN DER WAALS GAS

In two dimensions an exact solution is available in the point where $A_g = A_l$; that is, in the transition point. Substituting the well-known expression² for the field-free two-dimensional Ising model into (19), one obtains

$$\beta p(z_0, \beta) = -A_{g,l} + \frac{\gamma^2}{c^2} \ln \left[1 + \exp \left(-2 \frac{cc'}{\gamma^2} \right) \right] \\ + \frac{\gamma^2}{c^2} \frac{1}{8\pi^2} \int_0^{2\pi} d\omega_1 \int_0^{2\pi} d\omega_2 \ln \left[1 - \frac{\sinh(cc'/\gamma^2)}{\cosh^2(cc'/\gamma^2)} (\cos \omega_1 + \cos \omega_2) \right] \quad (25)$$

The first term on the right-hand side derives from the absolute maximum in function space; the two remaining terms represent the total contribution of all the secondary maxima. Expanding the logarithms in these terms, one verifies that they contribute nonanalytic terms of the order

$$(\gamma^2/c^2) \exp(-cc'/\gamma^2) \quad (26)$$

to the pressure. The nonanalytic terms will in general be extremely small, indicating the validity of the γ expansion, unless the temperature is in the region where

$$c(T) c'(T) = O(\gamma^2) \quad (27)$$

In this temperature region the second and third terms in (25) become equally important as the first and actually cause a shift in the critical temperature from the mean-field value T_w down to a new critical temperature T_c , which is the temperature where the integral in (25) has its only singularity:

$$\sinh[c(T_c) c'(T_c)/\gamma^2] = 1 \rightarrow c(T_c) c'(T_c) = \gamma^2 \ln(1 + \sqrt{2}) \quad (28)$$

The critical behavior is thus entirely due to nonanalytic terms, which are not contained in the γ expansion.

The total length of the "gas-liquid" interface per unit volume is found by substituting (25) into (21):

$$\frac{S}{\Omega} = 2 \frac{\gamma}{c} \frac{\exp(-2cc'/\gamma^2)}{1 + \exp(-2cc'/\gamma^2)} + \frac{\gamma}{c} \left[\frac{1}{\cosh(cc'/\gamma^2)} - 2 \frac{\sinh^2(cc'/\gamma^2)}{\cosh^3(cc'/\gamma^2)} \right] \frac{1}{8\pi^2} \\ \times \int_0^{2\pi} d\omega_1 \int_0^{2\pi} d\omega_2 \frac{\cos \omega_1 + \cos \omega_2}{1 - [\sinh(cc'/\gamma^2)/\cosh^2(cc'/\gamma^2)](\cos \omega_1 + \cos \omega_2)} \quad (29)$$

² The simplest method of solution is given in Ref. 12.

This quantity vanishes in the limit $\gamma \downarrow 0$, indicating that in this limit only infinitely large inclusions occur. For finite values of γ , S/Ω is of order $(\gamma/c) \exp(-cc'/\gamma^2)$.

The expression (29) holds at the transition point z_0 , where $A_g = A_l$. A glance at (17) shows that at this point there is strict invariance for the interchange of "gas" and "liquid". Therefore, on the average, half of the total volume Ω must be "gas"; the other half must be "liquid". If we assume that for an estimate of the order of magnitude of the linear dimension of the inclusions "gas" and "liquid" regions are divided in a chessboard-like pattern of squares with a surface l_1^2 , then we find $S/\Omega = 2/l_1$. The linear dimension of the inclusions can thus be estimated to be of order

$$l_1 \sim (2c/\gamma) \exp(+cc'/\gamma^2) \tag{30}$$

This is a very large quantity, with the exception of the region (27). If the temperature is raised, l_1 decreases; at T_c the second term on the right-hand side of (29) vanishes and one finds

$$l_1/l = 4 + 2\sqrt{2} = 6.8 \quad (\text{at } T_c) \tag{31}$$

Thus, even at T_c the size of the inclusions is still fairly large compared to the width of the interface.

The considerations of the preceding two paragraphs concerned the transition point z_0 . This point is the grand canonical image of the line in the (ρ, T) plane where the "gas" and "liquid" volume fractions both equal one-half. In order to study the boundaries of the coexistence region, one has to assume $z \neq z_0$ and one has to take the limit in which z tends to z_0 from a given side. This amounts to calculating the spontaneous magnetization of the two-dimensional Ising model. Substituting (19) into (20) and using the well-known formula for the spontaneous magnetization of the Ising model,³ one finds for the liquid boundary of the coexistence region the volume fractions

$$x_g = \frac{1}{2} - \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^{4\frac{1}{8}}\} \tag{32a}$$

$$x_l = \frac{1}{2} + \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^{4\frac{1}{8}}\} \tag{32b}$$

and for the gas boundary of the coexistence region

$$x_g = \frac{1}{2} + \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^{4\frac{1}{8}}\} \tag{33a}$$

$$x_l = \frac{1}{2} - \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^{4\frac{1}{8}}\} \tag{33b}$$

where

$$\chi = \tanh(cc'/2\gamma^2) \tag{34}$$

³ The simplest method of solution is given in Ref. 13.

This means that the pure liquid phase, that is, the phase which corresponds to the liquid boundary of the coexistence region, contains a small fraction of "gas" and a large fraction of "liquid". An analogous statement holds true for the pure gas phase. The volume fractions are easily found to be

$$x_g \sim \exp(-4cc'/\gamma^2), \quad x_l \sim 1 - \exp(-4cc'/\gamma^2), \quad \text{for the liquid} \quad (35a)$$

$$x_g \sim 1 - \exp(-4cc'/\gamma^2), \quad x_l \sim \exp(-4cc'/\gamma^2), \quad \text{for the gas} \quad (35b)$$

The picture which arises here for the thermodynamic liquid phase is a background of "liquid" in which "gas" bubbles float around, inside which one finds some "liquid" droplets, inside which, etc. A similar picture exists for the thermodynamic gas phase.

From the correspondence with the Ising model one expects that the critical exponents of the van der Waals gas will in general be identical to those of the nearest-neighbor Ising model. As an illustration we shall consider the exponent β . The number N of particles in the system follows from (7) by differentiation:

$$N(z) = \partial(\ln Z)/\partial(\ln z) = \left\langle \int_{\Omega} \rho_{\text{hc}}(z \exp \beta\phi) d^D\mathbf{r} \right\rangle \quad (36)$$

where $\rho_{\text{hc}}(z)$ denotes the density of the hard-core system, and where the average is taken over the weight functional

$$Z^{-1} \exp \left\{ - \int_{\Omega} [(\beta q_1/2\gamma^2)(\nabla\phi)^2 + A(\phi)] d^D\mathbf{r} \right\} \quad (37)$$

For a secondary maximum of this weight functional, characterized by a set of spins, the integral in (36) equals $\Omega_g \rho_g + \Omega_l \rho_l$, where $\rho_g \equiv \rho_{\text{hc}}(z \exp \beta\bar{\phi}_g)$ and $\rho_l \equiv \rho_{\text{hc}}(z \exp \beta\bar{\phi}_l)$. This gives for the density in the present approximation

$$\rho(z, \beta) = x_g \rho_g + x_l \rho_l \quad (38)$$

On the boundary of the coexistence region in (ρ, T) space the functions x_g and x_l have the values (32) and (33). This gives for the gas boundary of the coexistence region

$$\begin{aligned} \rho^{(\text{gas})}(T) &= \left(\frac{1}{2} + \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^4\}^{1/8}\right) \rho_g \\ &+ \left(\frac{1}{2} - \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^4\}^{1/8}\right) \rho_l \end{aligned} \quad (39a)$$

and for the liquid boundary

$$\begin{aligned} \rho^{(\text{liquid})}(T) &= \left(\frac{1}{2} - \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^4\}^{1/8}\right) \rho_g \\ &+ \left(\frac{1}{2} + \frac{1}{2}\{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^4\}^{1/8}\right) \rho_l \end{aligned} \quad (39b)$$

The width of the coexistence region in (ρ, T) space is, accordingly,

$$\rho^{(\text{liquid})}(T) - \rho^{(\text{gas})}(T) = \{1 - [\frac{1}{2}(\chi^{-1} - \chi)]^4\}^{1/8}(\rho_l - \rho_g) \quad (40)$$

In the vicinity of T_c [this is the temperature where $\chi(T_c) = \sqrt{2} - 1$] this quantity behaves as $(T_c - T)^{1/8}$, giving $\beta = \frac{1}{8}$.

The diameter of the coexistence region is the line

$$\frac{1}{2}[\rho^{(\text{gas})}(T) + \rho^{(\text{liquid})}(T)] = \frac{1}{2}(\rho_g + \rho_l) \quad (41)$$

versus T . In the vicinity of T_c both $\rho_g(T)$ and $\rho_l(T)$ are analytic functions of T . Accordingly, no singularity is found in the diameter of the coexistence region at the critical point, in the present approximation.

6. CONCLUDING REMARKS

In the present approximation the van der Waals gas can be brought into a one-to-one correspondence with the nearest-neighbor Ising model. The critical temperature was found to be situated slightly below the mean-field critical temperature T_w . The difference $T_w - T_c$ is $O(\gamma^2)$ in two dimensions and $O(\gamma^3)$ in three.

Whereas the one-dimensional system exhibits a phase transition only for $\gamma \downarrow 0$, the two- and three-dimensional systems condense for finite γ .

The main aim of this paper was to show that, if T approaches the mean-field critical temperature T_w within an amount of order γ^2 (for $D = 2$), the combined effect of the many secondary maxima takes over from the absolute maximum and causes a nonclassical type of critical behavior. Outside of the critical region the nonanalytic terms, which were found to be of order $(\gamma^2/c^2) \exp(-cc'/\gamma^2)$ in two dimensions, are extremely small, showing that here the γ expansion will be an excellent approximation.

Kac and Thompson⁽¹⁴⁾ (see also Thompson *et al.*⁽¹⁵⁾) have presented a method in which the most divergent terms in the γ expansion are summed. The resummed series exhibits a new critical temperature which is shifted (for $D = 2$) by an amount of order $\gamma \ln(1/\gamma)$ downward from T_w . They suggest that iteration of their procedure could produce the correct critical point. The present analysis suggests that the nonclassical behavior is entirely due to the combined effect of the secondary maxima and cannot be extracted from a study of the functional integral in a vicinity of the absolute maximum only.

We would finally like to remark that the method employed here can be looked upon as a derivation of a symmetrized droplet model of condensation (see Fisher⁽¹⁶⁾) from the principles of statistical mechanics. The linear dimensions of the droplets and bubbles was found to be of order

$(c/\gamma) \exp(+cc'/\gamma^2)$ on the diameter of the coexistence region. The present model for the van der Waals gas is symmetric in the roles of droplets and bubbles and leads to a description of a pure thermodynamic phase as always containing a finite volume fraction of the other thermodynamic phase, thereby leading to a hierarchy of droplets inside bubbles inside droplets, etc.

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