FORM OF THE ASYMPTOTIC EQUATION OF STATE FOR A LIQUID–GAS SYSTEM IN THE FRAMEWORK OF THE VAN DER WAALS THEORY

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UDC 536.71

Based on analyzing the van der Waals equation it has been demonstrated that, with a correct choice of the ordering field and of the liquid-gas order parameter, the asymptotic equation of state physical systems in the critical region may be extended over the entire existence domain of the liquid and the gas.

Introduction. Near the critical point, the behavior of various physical systems, such as magnetics, binary liquid mixtures, and individual substances, may be described by a common asymptotic equation of state [1]

$$h = h(\eta, t) = \eta|\eta|^{\delta-1} h\left(\frac{t}{|\eta|^{1/\beta}}\right), \tag{1}$$

where $t = (T - T_{cr})/T_{cr}$ is the reduced temperature. Even though the forms of the asymptotic equations of state (1) are diverse, after appropriate rearrangements they transform into one another [2]. This is due to the fact that the basis for all asymptotic equations is one and the same fact, viz., a spontaneous emergence, at a temperature below critical, of a nonzero order parameter η in the zero ordering field h. To be specific, we will write one of the widely applied asymptotic equations, namely, a linear model of the parametric equation of state [3]

$$h = a_1 r^{\beta\delta}\theta(1-\theta^2); \quad \eta = K_1 r^{\beta}\theta; \quad t = r(1 - b_1^2\theta^2), \tag{2}$$

where a_1 and K_1 are the individual constants of the specific physical system; b_1 is the equation constant to which a universal meaning is often ascribed; and r and θ are the parametric variables defining, correspondingly, the distance to the critical point and the way of approaching it. On the critical isotherm $t = 0$, $\theta = 1/b_1$ for $\eta > 0$ and $\theta = -1/b_1$ for $\eta < 0$. On the line of the zero ordering field $h = 0$, $\theta = 0$ when $t > 0$ and $\theta = \pm 1$ when $t < 0$. At a temperature below critical there spontaneously appears an order parameter with the temperature dependence

$$\eta = \pm B(-t)^{\beta}, \tag{3}$$

where B is the critical amplitude of the order parameter.

Initially the asymptotic equations of state (1) were formulated for magnetic systems and afterwards extended to other physical systems. The distinctive feature of the magnetic systems is a complete symmetry of the ordering field, i.e., of the magnetic field strength H and of order parameter, i.e., of the magnetization M.

For a liquid–gas system, the deviation of the density from the critical value $\eta = (\rho - \rho_{cr})/\rho_{cr} = \Delta\rho$ is generally taken as the order parameter, and the deviation of the chemical potential μ from its temperature dependences on the boundary curve $\mu_\sigma(T_\sigma)$ for $t \leq 0$ and on the critical isochore μ (T, $\Delta\rho = 0$) for $t \geq 0$, as the ordering field. In this case, the chemical potential must have a common temperature dependence on the boundary curve and on the critical isochore. The pressure ρ might also be selected as the ordering field of the liquid–gas system; however, experimental studies [4] give grounds to believe that the derivative d^2p_σ/dT^2_σ at the critical point goes to infinity, and the relation $p_\sigma(T_\sigma)$ is nonanalytic. This circumstance and the greater symmetry of the thermodynamic surface in the $\mu-\rho-T$ variables served

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All-Russian Scientific-Research Center on Materials and Substances of the State Standard of the Russian Federation, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 64, No. 3, pp. 341-349, March, 1993. Original article submitted April 10, 1992.

as a basis for choosing the chemical potential as the ordering field of the liquid–gas system. However, a rigorous proof of analyticity of the chemical potential is lacking, and the quantities $\Delta\rho$ and $\Delta\mu$, though more symmetric as compared to other thermodynamic functions with identical critical indexes, do possess a noticeable asymmetry. Therefore, there are no serious reasons to assume that the question as to the form of the asymptotic equation of state and as to the correct choice of the order parameter and the ordering field for the liquid–gas system has been solved conclusively.

It seems reasonable to begin to study this question with reverting to a more profound analysis of the fundamental van der Waals equation, which provided a basis for the theory of critical phenomena, rather than with constructing an artificial mathematical model (2) that describes the experimental relations of the thermodynamic functions on the isolated curves.

The analysis of this equation in the critical region is, as a rule, performed by expanding the thermodynamic functions in power series of the temperature and volume deviations from critical values and is completed by stating the fact that the values of the critical indexes obtained differ from the experimental evaluations, and this is quite natural. An important fact is that a simple equation based on clear physical premises qualitatively correctly defines the entire existence domain of the liquid and the gas, including the critical point. Since the van der Waals equation is of closed form, it should yield expressions of the same closed form for all thermodynamic functions in the critical region as well. Therefore, to study the asymptotic behavior of the van der Waals gas it is sufficient to write the equation in variables convenient for analyzing the critical region. The current work presents such a rearrangement of the van der Waals equation and the results of its analysis.

Form of the van der Waals Equation in the Critical Region. The van der Waals equation accounts for the gas reality in the form of corrections for the proper volume of molecules b^* and for the attractive force between them a^*/v^2:

$$(p + a^*/v^2)(v - b^*) = RT \tag{4}$$

and it proved to be capable of qualitatively adequately describing not only the gas region but also the liquid region, the line of phase transition, and the critical state.

Using the critical conditions

$$\left(\frac{\partial p}{\partial v}\right)_T^{\mathrm{cr}} = \left(\frac{\partial^2 p}{\partial v^2}\right)_T^{\mathrm{cr}} = 0,$$

we may express the constants of Eq. (4) a^*, b^*, and R in terms of the critical parameters p_{cr}, T_{cr}, and v_{cr} and write it in nondimensional variables

$$\pi = p/p_{\mathrm{cr}};\quad \tau = T/T_{\mathrm{cr}};\quad \varphi = v/v_{\mathrm{cr}};\quad \omega = \rho/\rho_{\mathrm{cr}};$$

$$\pi = \frac{k\tau}{\varphi - b} - \frac{a}{\varphi^2} = \frac{k\tau\omega}{1 - b\omega} - a\omega^2, \tag{5}$$

where

$$a = 3,\quad b = \frac{1}{3},\quad k = \frac{RT_{\mathrm{cr}}}{p_{\mathrm{cr}}v_{\mathrm{cr}}} = \frac{8}{3}. \tag{6}$$

Employing the thermodynamic relations

$$\left(\frac{\partial f}{\partial v}\right)_T = -p;\quad \mu = f + pv,$$

we derive from Eq. (5) the expressions for the free energy

$$f^* = \frac{f}{p_{\mathrm{cr}}v_{\mathrm{cr}}} = k\tau\ln(\varphi - b) - \frac{a}{\varphi} + f_0(\tau) \tag{7}$$

and for the chemical potential

$$\mu^* = \frac{\mu}{p_{\mathrm{cr}}v_{\mathrm{cr}}} = \frac{k\tau\varphi}{\varphi - b} - k\tau\ln(\varphi - b) - \frac{2a}{\varphi} + f_0(\tau) = k\tau\left(\frac{1}{1 - b\omega} - \ln\frac{1 - b\omega}{\omega}\right) - 2a\omega + f_0(\tau), \tag{8}$$

where $f_0(\tau)$ is the temperature dependence of the free energy of an ideal gas.

The behavior of thermodynamic functions in the critical region is specified by remoteness from the critical point. Therefore, to analyze the asymptotic behavior of the van der Waals gas requires that Eq. (5) be written in the variables

$$\Delta p = \pi - 1; \quad t = \tau - 1; \quad \Delta p = \omega - 1. \tag{9}$$

On substituting the variables (9) into Eq. (5) and grouping terms with the same powers of $\Delta\rho$, we arrive at

$$\begin{gathered}[\Delta p(1-b) - kt] - \Delta\rho\,(b\Delta p + kt) = (k - 1 + ab - a + b) + \\ + \Delta\rho\,(k + 3ab - 2a + b) + \Delta\rho^2(3ab - a) + \Delta\rho^3 ab.\end{gathered} \tag{10}$$

If we resort to numerical values of the coefficients a, b, and k (6), we may see that the expressions for the coefficients at the zeroth, first, and second powers of $\Delta\rho$ on the right side of Eq. (10) are equal to zero, and the van der Waals equation reduces to the form

$$\Delta p - \frac{k}{1-b}\,t = \frac{ab}{1-b}\,\Delta\rho^3 + \frac{\Delta\rho\,(b\Delta p + kt)}{1-b}, \tag{11}$$

$$\left(\Delta p - \frac{k}{1-b}\,t\right)\left(1 - \frac{b}{1-b}\,\Delta\rho\right) = \frac{ab}{1-b}\,\Delta\rho^3 + \frac{k}{(1-b)^2}\,t\Delta\rho, \tag{12}$$

$$(\Delta p - 4t)\left(1 - \frac{1}{2}\,\Delta\rho\right) = \frac{3}{2}\,\Delta\rho^3 + 6t\Delta\rho. \tag{13}$$

This same result can also be obtained by the traditional method of expansion in a power series of the density and temperature deviations from critical values.

On expanding the chemical potential in a power series of the density and temperature with a view to the expressions for higher derivatives at the critical point,

$$\left(\frac{\partial^n\mu^*}{\partial\omega^n}\right)_\tau^{\text{cr}} = \frac{8}{3}\,(n-1)!\left[\frac{3n+2}{2^{n+1}} + (-1)^{n+1}\right], \tag{14}$$

$$\left(\frac{\partial^n\mu^*}{\partial\tau\partial\omega^{n-1}}\right)^{\text{cr}} = \frac{8}{3}\,(n-2)!\left[\frac{3n-1}{2^n} + (-1)^n\right], \tag{15}$$

we write the equation for the chemical potential (8) in the variables (9)

$$\Delta\mu = \mu^* - \mu_0 - \mu_1 t - f_0(t) = \frac{3}{2}\,\Delta\rho^3[1 + f(\Delta\rho)](1 + t) + 6t\Delta\rho, \tag{16}$$

where

$$\mu_0 = \frac{8}{3}\ln\frac{3}{2} - 2; \quad \mu_1 = 4 + \frac{8}{3}\ln\frac{3}{2};$$

$$\begin{gathered}f(\Delta\rho) = -\frac{1}{4}\,\Delta\rho + \frac{9}{20}\,\Delta\rho^2 - \frac{1}{4}\,\Delta\rho^3 + \frac{31}{112}\,\Delta\rho^4 - \frac{27}{128}\,\Delta\rho^5 + \\ + \frac{13}{64}\,\Delta\rho^6 - \frac{7}{40}\,\Delta\rho^7 + \frac{459}{2816}\,\Delta\rho^8 - \frac{151}{1024}\,\Delta\rho^9 + \ldots\end{gathered} \tag{17}$$

After the designation has been introduced

$$t^* = \frac{t}{1+t}, \quad \Delta\rho^* = \Delta\rho\,[1 + f(\Delta\rho)]^{1/2} \tag{18}$$

Eq. (16) is brought to a form coinciding with Eq. (13)

$$\Delta\mu\,\frac{[1 + f(\Delta\rho)]^{1/2}}{1+t} = \frac{3}{2}\,(\Delta\rho^*)^3 + 6t^*\Delta\rho^*. \tag{19}$$

The asymptotic behavior of thermodynamic functions of the van der Waals gas on different ways to the critical point has been analyzed thoroughly in [5]. Here we will consider corollaries of Eqs. (13) and (19) for the critical isotherm, the critical isochore, and the boundary curve.

On the critical isotherm, the equations for the pressure and the chemical potential have the form

$$\Delta\rho = \frac{3}{2}\,\frac{\Delta\rho^3}{1-\Delta\rho/2} = \frac{3}{2}\Delta\rho^3\left(1+\frac{1}{2}\Delta\rho+\frac{1}{4}\Delta\rho^2+\frac{1}{8}\Delta\rho^3+\ldots\right),$$

$$\Delta\mu = \frac{3}{2}\Delta\rho^3\,[1+f(\Delta\rho)] = \frac{3}{2}\Delta\rho^3\left(1-\frac{1}{4}\Delta\rho+\frac{9}{20}\Delta\rho^2-\frac{1}{4}\Delta\rho^3+\ldots\right).$$

The asymptotic behavior of Δp and $\Delta\mu$ on the critical isotherm is defined by the critical index $\delta = 3$ and the critical amplitude $D = 3/2$. Both relations have a correction factor in the form of infinite power series of the density. The relation for the chemical potential near the critical point appears more symmetric because of the smaller value of the coefficient for the first correction factor. However, away from the critical point, when other terms of the series should be taken into account, the relation for $\Delta\mu$ is more complex, since at large n the common term of the series of the correction factor for $\Delta\mu$, $a_n = 8/3n(-1)^{n+1} + 1/2^{n-2} + 1/3n2^{n-3}$, has larger values than does the common term of the series for Δp, $a_n = 1/2^n$.

The following relations are fulfilled on the critical isochore:

$$\Delta p - 4t = 0, \tag{20}$$

$$\mu^* - \mu_0 - \mu_1 t - f_0(t) = 0. \tag{21}$$

At a temperature below critical, relations (20) and (21) are fulfilled at nonzero values of the density

$$-t = \frac{1}{4}\Delta\rho^2;\quad \Delta\rho = \pm 2(-t)^{1/2}, \tag{22}$$

$$-t^* = \frac{1}{4}(\Delta\rho^*)^2;\quad \Delta\rho^* = \pm 2(-t^*)^{1/2}. \tag{23}$$

Relations (22) and (23) represent the temperature dependence of the order parameter in the zero ordering field (3) and are characterized by the critical index $\beta = 1/2$ and the critical amplitude $B = 2$.

The liquid $\Delta\rho'$ and gas $\Delta\rho''$ densities in Eq. (22) correspond to equal pressures $\pi' = \pi''$ and different chemical potentials $\mu' \neq \mu''$, whereas in Eq. (23), conversely, to equal chemical potentials $\mu' = \mu''$ and different pressures $\pi' \neq \pi''$. Relations (22) and (23) may be called the equations of a "pseudobinodal curve" because the equation of the binodal curve must be determined from the condition of simultaneous equality of the temperatures, pressures, and chemical potentials of coexisting phases.

The equation of the binodal curve for the van der Waals gas in the region $0 \leq (-t) \leq 0.25$ may be represented as

$$\Delta\rho_\sigma = \pm 2(-t)^{0.5} + 0.399038(-t)^{1.0} \mp 0.520139(-t)^{1.5} + 0.159985(-t)^{2.0} \mp 0.077032(-t)^{2.5} \tag{24}$$

or approximately

$$\Delta\rho_\sigma = \pm 2(-t)^{0.5} + 0.4(-t)[1+0.4(-t)] \mp 0.52(-t)^{1.5}[1+0.15(-t)],$$

and the elasticity curve as

$$\frac{\Delta p_\sigma + 4(-t)}{t^2} = 4.788948 - 0.787475(-t) - 1.141547(-t)^2. \tag{25}$$

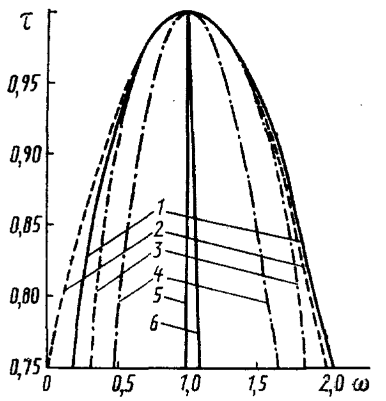

Fig. 1

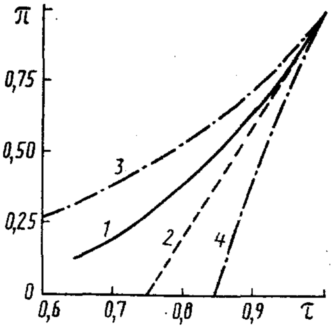

Fig. 2

Fig. 1. The relations $\tau(\omega)$ for the characteristic curves of the van der Waals equation at temperatures below critical: 1) binodal curve, $p' = p''$, $\mu' = \mu''$; 2) "pseudobinodal curve" for the pressure $p' = p''$, $\mu' \neq \mu''$; 3) "pseudobinodal curve" for the chemical potential $\mu' = \mu''$, $p' \neq p''$; 4) spinodal curve; 5) critical isochor; 6) "linear" diameter $(\omega' + \omega'')/2$.

Fig. 2. The relations $\pi(\tau)$ for the characteristic curves of the van der Waals equation at temperatures below critical: 1) elasticity curve; 2) "pseudobinodal curve" – critical isochore; 3) gas branch of the spinodal curve; 4) liquid branch of the spinodal curve.

There is one more characteristic curve below the critical temperature, viz., a spinodal curve which is determined from the condition

$$\left(\frac{\partial p}{\partial \rho}\right)_T = 0.$$

A density dependence of the temperature on the spinodal curve for the van der Waals gas is defined by the equation

$$\tau_s = \frac{9}{4}\omega_s\left(1 - \frac{\omega_s}{3}\right)^2$$

or

$$-t_s = \frac{3}{4}\Delta\rho_s^2\left(1 - \frac{1}{3}\Delta\rho_s\right). \tag{26}$$

Figures 1 and 2 depict the characteristic lines for the van der Waals gas at temperatures below critical in the diagrams $\tau-\omega$ and $\pi-\tau$. In the diagram $\tau-\omega$, the gas branch of the "pseudobinodal curve" (22) lies in a uniphase region, whereas the liquid branch is located in a two-phase region close to the binodal curve, i.e., it corresponds to a metastable state of the liquid. Both branches of the "pseudobinodal curve" (23) reside in the two-phase region and are intermediate between the binodal and spinodal curves. In the diagram $\pi-\tau$, the "pseudobinodal curve" (20) is intermediate between the elasticity curve and the liquid branch of the spinodal curve $\pi'_s(\tau_s)$.

Discussion of the Form of the van der Waals Equation in the Critical Region. The van der Waals equation, written for the pressure in the form (13) or for the chemical potential in the form (19), coincides with the asymptotic equation of state for physical systems in the critical region (1) ensuing from scaling theory [1, 6]:

$$(\Delta p - 4t)\left(1 - \frac{1}{2}\Delta\rho\right) = \Delta\rho^3\left(\frac{3}{2} + \frac{4t}{\Delta\rho^2}\right) = \Delta\rho\,|\Delta\rho|^{\delta-1} h\left(\frac{t}{|\Delta\rho|^{1/\beta}}\right), \tag{27}$$

$$\Delta\mu\,\frac{[1 + f(\Delta\rho)]^{1/2}}{1 + t} = (\Delta\rho^*)^3\left[\frac{3}{2} + \frac{4t^*}{(\Delta\rho^*)^2}\right] = \Delta\rho^*\,|\Delta\rho^*|^{\delta-1} h\left(\frac{t^*}{|\Delta\rho^*|^{1/\beta}}\right). \tag{28}$$

Equations (13) and (19) can also be written in the parametric variables r and θ of the linear model. On substituting into Eq. (13) the expressions for the temperature

$$t = r(1 - b_1^2\theta^2)$$

and the density

$$\Delta\rho = K_1 r^{\beta}\theta = K_1 r^{1/2}\theta = 2(b_1^2 - 1)^{1/2} r^{1/2}\theta,$$

we obtain

$$\begin{aligned}(\Delta p - 4t)\left(1 - \frac{1}{2}\Delta\rho\right) &= \frac{3}{2}K_1^3 r^{3/2}\theta^3 + 6K_{1}\,{}^{/2}\theta(1 - b_1\theta^2) = \\ &= \frac{3}{2}(b_1^2 - 1)^{1/2} r^{3/2}\theta(1 - \theta^2) = a_1 r^{\beta\delta}\theta(1 - \theta^2).\end{aligned} \tag{29}$$

Similar transformation can also be made for Eq. (19) by expressing the parametric variables r and θ in terms of t^* and $\Delta\rho^*$ (18).

A comparison of Eq. (1) with Eqs. (27) and (28) makes clear that the thermodynamic surface of the liquid–gas system may be described by two equivalent methods. In the $p-\rho-T$ variables, the order parameter and the ordering field are

$$\eta = \Delta\rho, \quad h = (\Delta p - 4t)\left(1 - \frac{1}{2}\Delta\rho\right), \tag{30}$$

whereas, in the $\mu-\rho-T$ variables these are

$$\begin{aligned}\eta &= \Delta\rho^* = \Delta\rho\,[1 + f(\Delta\rho)]^{1/2}, \\ h &= [\mu^* - \mu_0 - \mu_1 t - f_0(t)]\,\frac{[1 + f(\Delta\rho)]^{1/2}}{1 + t}.\end{aligned} \tag{31}$$

With η and h chosen in the form (30) or (31), the asymptotic equation of state (1), as applied to the liquid–gas system, proves to be valid not only in a narrow vicinity of the critical point but also over the entire existence domain of the liquid and the gas.

Relations (30) and (31) demonstrate the distinctive property of the liquid–gas system which could not be detected with a formal generalization of regularities for the critical behavior of magnetic systems. Because these systems are completely symmetric, it does not matter whether the line of the zero ordering field H = 0 is extended from the side of low temperatures to the high-temperature region or vice versa. However, a characteristic thermodynamic function having zero values on any of the isolated curves is absent from the liquid–gas system. Such a quantity must be "constructed" artificially as the difference between the characteristic function and its temperature dependence on the isolated curve. It seemed natural to construct the line of zero values in the form of the difference between the pressure (or the chemical potential) and its temperature dependence on the boundary curve. With such an approach, the basic difficulties were presented by the proof of analyticity of the relation $p_\sigma(T_\sigma)$ or $\mu_\sigma(T_\sigma)$ and by the extension of the line h = 0 upwards of the critical temperature.

Since at a temperature below critical the liquid and the gas may be in metastable states, as is seen from Fig. 2, for the reference relation p(T) we may select not only the elasticity curve $p_\sigma(T_\sigma)$ but also the extension of the critical isochore to the low-temperature region and any other line lying between the gas $p_s''(T)$ and liquid $p_s'(T)$ branches of the spinodal curve and sharing a common tangent with the critical isochore at the critical point. The temperature dependence of the order parameter η (t, h = 0) is in this case defined by the temperature dependence of the orthobaric densities appropriate to the reference line p(T). Similar constructions can also be carried out in the $\mu-T$ diagram.

In connection with the uncertainty of the choice of the reference line p(T) or μ(T) at a temperature below critical, there is a need to examine the possibilities of choosing it at a temperature above critical. In this case, a natural selection of the reference relation p(T) for constructing the line h = 0 is the critical isochore and its analytical extension in low-temperature regions. The isochores for the van der Waals gas are straight lines; therefore, the determination of the line below T_{cr} is evident. The isochores for real liquids and gases are curvilinear but the critical isochore, at least on the initial section, is close to a straight line, and this is revealed by experimental data. Then the ordering field expression for the real liquids and gases may also be "constructed" as

$$h \doteq (\Delta p - mt)[1 + \varphi(\Delta\rho)], \tag{32}$$

where $m = (\partial\pi/\partial\tau)^{cr}_{\omega}$ is the slope of the critical isochore at the critical point; and $\varphi(\Delta\rho) = 0$ at $\Delta\rho = 0$. The ordering field expression of the form (32) can be constructed based on the chemical potential as well. Both "constructions" of h are equivalent for the van der Waals gas. As the ordering field for the real liquids and gases, only one of the quantities p and μ can be used because the specific heat c_v goes to infinity on approaching the critical point along the critical isochore, and in accordance with the thermodynamics equation

$$c_V = Tv\left(\frac{\partial^2 p}{\partial T^2}\right)_v - T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_v$$

one of the derivatives must also go to infinity on this way to the critical point. In this case, however, nonanalyticity of the elasticity curve $p_\sigma(T_\sigma)$ can no longer form the basis of the choice of the chemical potential as the ordering field of the liquid–gas system. The deciding argument for such a choice is analyticity, and even more important is linearity of the critical isochore.

The range of applicability for the available scaling equations as to density does not generally exceed $|\Delta\rho| = 0.3$. With great difficulty it has been possible to extend it up to $|\Delta\rho| = 0.5$ by introducing correction terms or functional relations. But here the number of fitting parameters rises sharply and becomes comparable with the number of coefficients in the common virial equation of state describing the entire existence domain of the liquid and the gas except the neighborhood of the critical point.

The van der Waals equation suggests a radically new approach to solving the problem of the equation of state for real substances. The simple asymptotic equation of state, formulated in the framework of scaling theory, must be applicable over the entire existence domain of the liquid and the gas, whereas the noted difficulties of employing it at any distance well away from the critical point are caused by an incorrect choice of the ordering field and order parameter for the liquid–gas system.

Based on an analysis of the van der Waals equation we may propose the following recommendations for constructing such an equation of state.

1. The reference line for "constructing" the ordering field for the liquid–gas system is the critical isochore and its analytic extension to the two-phase region.
2. The temperature dependence for the order parameter is determined by the temperature dependence of the liquid and gas densities corresponding to the reference line p(T) or $\mu(T)$. If necessary, renormalization of the density and temperature of the form (18) should be performed to provide a purely power-law symmetric relation $\eta(t)$.
3. The ordering field expression should contain a density-dependent multiplier providing a purely power-law symmetric relation $h(\eta)$ on the critical isochore.

NOTATION

T, temperature; p, pressure; v, specific volume; ρ, density; f, free energy; μ, chemical potential; $\tau = t + 1 = T/T_{cr}$; $\pi = \Delta p + 1 = p/p_{cr}$; $\varphi = v/v_{cr}$; $\omega = \Delta\rho + 1 = \rho/\rho_{cr}$; h, ordering field; η, order parameter; β and δ, critical indexes; r and θ, parametric variables; a_1, K_1, b_1, constants of the linear model of the parametric equation of state; B and D, critical amplitudes; H, strength of the magnetic field; M, magnetization; a^*, b^*, a, b, constants of the van der Waals equation; R, universal gas constant; $f_0(t)$, temperature dependence of the free energy of the ideal gas; μ_0 and μ_1, coefficients of the temperature dependence of the chemical potential on the critical isochore; $\Delta\mu = \mu^* - \mu_0 - \mu_1 t - f_0(t)$; $f(\Delta\rho)$, function obtained from expanding the chemical potential of the van der Waals gas into a series; $m = (\partial\pi/\partial\tau)^{cr}_{\omega}$, $\varphi\Delta\rho)$, normalizing function in the ordering field expression; c_v, specific heat at constant volume. Subscripts: cr, critical state; σ, boundary curve; $'$, liquid; $''$, gas; s, spinodal curve.

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