# METHOD OF DETERMINING A STRUCTURAL FORM OF THE FREE ENERGY SATISFYING THE REQUIREMENTS OF THE SCALING HYPOTHESIS

V. A. Rykov and G. B. Varfolomeeva

UDC 536.71

We discuss a method of finding a structural form of the free energy satisfying the scaling hypothesis based on the simultaneous analysis of the asymptotic forms of the derivatives of the free energy and power functionals.

The problem of describing the thermodynamic behavior in a wide region about the critical point was solved in [1-12] with the help of nonanalytic equations of state. This was done by choosing initial thermodynamic functions: the chemical potential $\mu(\rho, T)$ [1, 3], the specific heat at constant volume $C_V(\rho, T)$ [5-9], and the internal energy $u(\rho, T)$ [10-12], which consist structurally of two terms: a nonanalytic term satisfying the power laws of scaling theory, and a regular function reproducing the features of the pure material for small densities $\rho$ and pressures p [7-12]. Then with the help of appropriate thermodynamic equalities, relating the initial thermodynamic functions and thermal parameters, the equation of state is constructed.

In [1-5] a parametric representation of the scaling equation of state was used, which gives all of the scaling features of the critical point. In [13] a method of joining the scaling equation of state and the virial expansion with the help of local equations of state was proposed. In the calculation of the thermal properties, this approach leads to formidable mathematical difficulties because of the necessity of integrating and differentiating the scaling, virial, and local equations of state.

For practical purposes, it is more convenient to write the nonanalytic equation of state as a single-structural form, one term of which gives the scaling features near the critical point and the other correctly reproduces the temperature dependence of the lowest virial coefficients in the regular part of the thermodynamic surface. An attempt to use the physical variables $\rho$, T to solve the problem was made in [8], but the structure of the singular term $C_{Vn}(\rho, T)$ of the specific heat at constant volume $C_V(\rho, T)$ was chosen in [8] in a not completely successful way. In particular, the use of this function led to the failure to describe the scaling behavior of the material in the asymptotic vicinity of the critical point. According to [8], the derivatives $(\partial p/\partial v)_T$ and $d^2p/dt^2$ on the critical isochore turn out to be analytic functions, which does not give the required divergence of the isothermal compressibility $K_T \sim \tau^{-\gamma}$ on the critical isochore, and also contradicts accurate experimental data supporting the nonanalytic nature of the derivative $d^2p/dT^2$ [14]. Analogous problems also occur with the singular terms of the thermodynamic functions $C_V(\rho, T)$ and $u(\rho, T)$ used in [7, 9-12].

Thus the problem of working out a simple and effective method of constructing the nonanalytic terms in the thermodynamic functions which satisfy the requirements of the scaling hypothesis is still of current interest.

The present paper is also devoted to the solution of this problem. But as an initial thermodynamic function we use the free energy $F(\rho, T)$. The choice of $F(\rho, T)$ is natural, because in the $\rho$, T plane the free energy is a characteristic function [15] and one can determine in a simple way the thermodynamic functions used as a starting point in [1-12] in terms of the free energy.

According to the scaling hypothesis, in the region near the critical point, the equilibrium properties of pure materials are described by simple power laws [16]

$$\Delta p|_{\tau=0} \sim \Delta\rho\, |\Delta\rho|^{\delta-1}, \quad C_{v,\tau=0} \sim |\Delta\rho|^{-\alpha/\beta}, \quad K_{T,\tau=0} \sim |\Delta\rho|^{-\gamma/\beta}, \tag{1}$$

---

Leningrad Technical Institute of the Refrigeration Industry. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 48, No. 3, pp. 455-461, March, 1985. Original article submitted November 4, 1983.

0022-0841/85/4803-0341$09.50

$$C_{v,\underset{x=x_c}{\Delta\rho=0}} \sim |\tau|^{-\alpha}, \quad K_{T,\underset{x=x_c}{\Delta\rho=0}} \sim |\tau|^{-\gamma}. \tag{1}$$

Here $\alpha$, $\beta$, $\delta$, $\gamma$ are the critical exponents which satisfy the Griffiths relations $\beta(\delta-1)=\gamma$, $\alpha+\beta\delta+\beta=2$ [16].

We write the free energy F($\rho$, T) as a sum of two functions

$$F(\rho, T)=\rho^n F_n(\rho, T)+F_r(\rho, T), \tag{2}$$

where $\rho^n F_n(\rho, T)$ and $F_r(\rho, T)$ are the nonregular and regular parts of the free energy, respectively.

Because $p=\rho^2(\partial F/\partial\rho)_T$, $\rho C_v=-T(\partial^2\rho F/\partial T^2)_\rho$, $K_T^{-1}=\rho(\partial p/\partial\rho)_T$, it follows directly from (1) that very close to the critical point the partial derivatives of the nonregular function $F_n(\rho, T)$ have the following asymptotic forms:

$$\left(\frac{\partial F_n}{\partial\rho}\right)_{T,\tau=0} \sim \Delta\rho\,|\Delta\rho|^{\delta-1}, \quad \left(\frac{\partial^2 F_n}{\partial T^2}\right)_{\rho,\tau=0} \sim |\Delta\rho|^{-\alpha/\beta}, \tag{3}$$

$$\left(\frac{\partial^2 F_n}{\partial\rho^2}\right)_{T,\tau=0} \sim |\Delta\rho|^{\gamma/\beta}, \quad \left(\frac{\partial^2 F_n}{\partial T^2}\right)_{\rho,\underset{x=x_c}{\Delta\rho=0}} \sim |\tau|^{-\alpha}, \quad \left(\frac{\partial^2 F_n}{\partial\rho^2}\right)_{T,\underset{x=x_c}{\Delta\rho=0}} \sim |\tau|^{\gamma}.$$

Close to the critical point, the behavior of the function $F_n(\rho, T)$ is described, according to (3), by power laws with noninteger exponents. Therefore, we look for the solution of the problem in the class of power functionals. We studied the following power-type dependenses:

$$F_n(\rho, T)=Z_1(\rho, T)^{\xi_1}, \tag{4}$$

$$F_n(\rho, T)=(Z_1(\rho, T)+Z_2(\rho, T)^{\xi_2})^{\xi_1}, \tag{5}$$

$$F_n(\rho, T)=Z_1(\rho, T)^{\xi_1}+Z_2(\rho, T)^{\xi_2}, \tag{6}$$

where

$$Z_1(\rho, T)=\sum_{i,j=0} A_{ij}\tau^{\varphi_i}\Delta\rho^{\varepsilon_j}; \quad Z_2(\rho, T)=\sum_{i,j=0} B_{ij}\tau^{\psi_i}\Delta\rho^{\eta_i};$$

$$\varphi_0=\varepsilon_0=\psi_0=\eta_0=0; \quad A_{00}=0; \quad \varphi_0<\varphi_1<\ldots;$$

$$\psi_0<\psi_1<\ldots; \quad \varepsilon_0<\varepsilon_1<\ldots; \quad \eta_0<\eta_1<\ldots$$

Obviously when $\tau \to 0$ and $\Delta\rho \to 0$, the singular $\rho^n F_n(\rho, T)$ of the free energy and its derivatives determine the terms (4) through (6) with the smallest values of the exponents $\varphi_i$, $\varepsilon_j$, $\psi_i$, and $\eta_j$. Thus the first stage of the problem reduces to determining the quantities $\varphi_1$, $\varepsilon_1$, $\psi_1$, $\eta_1$, $\xi_1$, and $\xi_2$ in terms of the critical exponents $\alpha$, $\beta$, $\delta$, and $\gamma$.

We show that a solution is possible by looking for the singular terms of the thermodynamic functions. We first analyze (5) from which it follows directly that

$$\left(\frac{\partial F_n}{\partial\rho}\right)_T=\xi_1(Z_1(\rho, T)+Z_2(\rho, T)^{\xi_2})^{\xi_1-1}Z_3(\rho, T), \tag{7}$$

$$\begin{aligned}\left(\frac{\partial^2 F_n}{\partial\rho^2}\right)_T &= \xi_1(\xi_1-1)(Z_1(\rho, T)+Z_2(\rho, T)^{\xi_2})^{\xi_1-2}Z_3(\rho, T)^2+\\ &+\xi_1(Z_1(\rho, T)+Z_2(\rho, T)^{\xi_2})^{\xi_1-1}\left[\sum_{i,j=0} A_{ij}\tau^{\varphi_i}\Delta\rho^{\varepsilon_j-2}\frac{\varepsilon_j(\varepsilon_j-1)}{\rho_c^2}+\right.\\ &+\xi_2\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i}\Delta\rho^{\eta_j-2}\frac{\eta_j(\eta_j-1)}{\rho_c^2}\right)Z_2(\rho, T)^{\xi_2-1}+\\ &\left.+\xi_2(\xi_2-1)\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i}\Delta\rho^{\eta_j-1}\frac{\eta_j}{\rho_c}\right)^2 Z_2(\rho, T)^{\xi_2-2}\right],\end{aligned} \tag{8}$$

$$\left(\frac{\partial^2 F_n}{\partial T^2}\right)_\rho = \xi_1(\xi_1 - 1)(Z_1(\rho, T) + Z_2(\rho, T)^{\xi_2})^{\xi_1} \times$$

$$\times\left[\sum_{i,j=0} A_{ij}\tau^{\varphi_i - 1}\Delta\rho^{\varepsilon_j}\frac{\varphi_i}{T_c} + \xi_2\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i - 1}\Delta\rho^{\eta_j}\frac{\psi_i}{T_c}\right)Z_2(\rho, T)^{\xi_2 - 1}\right]^2 +$$

$$+\xi_1(Z_1(\rho, T) + Z_2(\rho, T)^{\xi_2})^{\xi_1 - 1}\left[\sum_{i,j=0} A_{ij}\tau^{\varphi_i - 2}\Delta\rho^{\varepsilon_j}\frac{\varphi_i(\varphi_i - 1)}{T_c^2} +\right.$$

$$\left.+\xi_2\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i - 2}\Delta\rho^{\eta_j}\frac{\psi_i(\psi_i - 1)}{T_c^2}\right)Z_2(\rho, T)^{\xi_2 - 1} + \xi_2(\xi_2 - 1)\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i - 1}\Delta\rho^{\eta_j}\frac{\psi_j}{T_c}\right)^2 Z_2(\rho, T)^{\xi_2 - 1}\right],$$

where

$$Z_3(\rho, T) = \operatorname{sign}(\Delta\rho)\left[\sum_{i,j=0} A_{ij}\tau^{\varphi_i}\Delta\rho^{\varepsilon_j - 1}\frac{\varepsilon_j}{\rho_c} + \xi_2\left(\sum_{i,j=0} B_{ij}\tau^{\psi_i}\Delta\rho^{\eta_i - 1}\frac{\eta_j}{\rho_c}\right)Z_2(\rho, T)^{\xi_2 - 1}\right].$$

We carry out a simultaneous analysis of the partial derivatives of the function $F_n(\rho, T)$ as given by (7) through (9), and the scaling relations (3).

We put $\tau = 0$ in (7), (8), and find that relations (3) are satisfied if we have the equality $\varepsilon_1\xi_1 = 1+\delta = 2+\gamma/\beta$ . It also follows from (8) that $\xi_1 = 1$ or $\xi_1 = 2$, because in the opposite case the derivative $(\partial^2 F_n/\partial\rho^2)_T$ either vanishes ($\varepsilon_1 > 2$) or diverges ($\varepsilon_1 < 2$, $\varepsilon_1 = 1$) on the critical isochore ($\Delta\rho = 0$) and this contradicts (3).

On the other hand, if $A_{10} \neq 0$, then it follows from (9) that $\varphi_1 = 1$ or $\varphi_1 = 2$ because in the opposite case the derivative $(\partial^2 F_n/\partial T^2)_\rho$ either diverges ($\varphi_1 < 2$, $\varphi_1 \neq 1$) or vanishes ($\varphi_1 > 2$) at $\tau = 0$, and this also contradicts (3). But according to (3), when $\Delta\rho = 0$ (see (8)) we must have $\varphi_1\xi_1 = 2 - \alpha$, which is not consistent with the above condition relating $\varepsilon_1$, $\xi_1$, and $\delta$. The contradiction is resolved if in (5) and (7) through (9) we have $A_{10} = 0$, $A_{01} \neq 0$ or $A_{10} \neq 0$, $A_{01} = 0$. We considered both of these possibilities. It turns out that if $A_{10} \neq 0$, $A_{01} = 0$, then a solution of the problem of the power type (8) does not exist. Therefore we will take $A_{10} = 0$, $A_{01} \neq 0$.

It then follows from (9) that $\psi_1 = 1$ or $\psi_2 = 2$ because if $\psi_1 < 2$ and $\psi \neq 1$, the derivative $(\partial^2 F_n/\partial T^2)_\rho$ diverges on the critical isotherm $\tau = 0$ and $\psi_1 > 2$, it is equal to zero, which contradicts (3). Now substituting $\Delta\rho = 0$ in (9) and comparing with (3) we obtain another relation $\psi_1\xi_1\xi_2 = 2 - \alpha$. On the other hand, when $\Delta\rho \to 0$ it follows from (3) and (8) that if $\varepsilon_1 = 1$ we must have the relation $\psi_1\xi_2(\xi_1 - 1) = \gamma$, and if $\varepsilon_1 = 1$ we must have $\psi_1\xi_2$-$(\xi_1 - 2) = \gamma$.

In order to correctly describe the behavior of $C_v$ on the critical isotherm (see (3), (9)) it is sufficient to require that if $\psi_1 = 1$ the relation $\eta_1(\xi_1\xi_2 - 1) - \alpha/\beta$ be satisfied and if $\psi_1 = 2$, the relation $\eta_1(\xi_1\xi_1 - 2) = -\alpha/\beta$.

Now we substitute $\tau = x_c|\Delta\rho|^{1/\beta}$ in (8) and (9) and find that in order to satisfy (3) on the coexistence curve it is sufficient to put $\varepsilon_1\xi_1 = 2 + \gamma/\beta$ and $\psi_1\xi_1\xi_2 = 2 - \alpha$.

We write the relations obtained above for the exponents $\varepsilon_1$, $\psi_1$, $\eta_1$, $\xi_1$, $\xi_2$ and the critical exponents:

$$\eta_1\xi_2 = \varepsilon_1, \quad \varepsilon_1\xi_1 = 1 + \delta, \quad \psi_1\xi_1\xi_2 = 2 - \alpha, \tag{10}$$

where $\varepsilon_1$, $\psi_1$ = 1 or 2.

Therefore the simultaneous analysis of the derivatives of the function $F_n(\rho, T)$ and the scaling relations (3) yield a structure of $F_n(\rho, T)$ within the class of power functionals which satisfies all of the requirements (3):

$$F_n(\rho, T) = (A_{01}\Delta\rho^{\varepsilon_1} + (B_{01}\tau^{\psi_1} + B_{10}\Delta\rho^{\eta_1})^{\xi_2})^{\xi_1}, \tag{11}$$

where $A_{01}, B_{01}, B_{10} > 0$; $\varepsilon_1, \eta_1, \psi_1, \xi_1, \xi_2$ are real exponents satisfying (10).

The above method of looking for the singular terms of the thermodynamic functions was used to analyze the power laws (4) and (6). It was shown that the problem does not have a solution of the form (4). In the class of functionals (6) the following structural form of $F_n(\rho, T)$ was found, satisfying all of the requirements of (3):

$$F_{\mathrm{n}}(\rho, T) = -(A_{01}\tau^{\varphi_1} + A_{10}\Delta\rho^{\varepsilon_1})^{\xi_1} + \Delta\rho^2(B_{01}\tau^{\psi_1} + B_{10}\Delta\rho^{\eta_1})^{\xi_2}, \tag{12}$$

where $A_{10}, A_{01}, B_{01}, B_{10} > 0$; $\varphi_1, \varepsilon_1, \xi_1, \psi_1, \eta_1, \xi_2$ are real exponents satisfying the following relations

$$\begin{gathered} \varphi_1\xi_1 = 2 - \alpha, \quad \varepsilon_1\xi_1 = 1 + \delta, \quad \varphi_1 = 1 \text{ or } 2, \\ \eta_1 = \psi_1/\beta, \quad \psi_1\xi_2 = \beta(\delta - 1), \quad \psi_1 = 1 \text{ or } 2. \end{gathered} \tag{13}$$

We now use the structural forms of $F_n(\rho, T)$ obtained above to construct both scaling and wide-range equations of state satisfying the power laws (1) of the scaling theory.

The free energy in the scaling hypothesis is given by [17]

$$\rho F(\rho, T) = |\Delta\rho|^{\delta+1} a(x) + \rho F_0(T) + A(T), \tag{14}$$

where $F_0(T)$, $A(T)$ are regular functions of temperature, $a(x)$ is the free energy scaling function which is coupled to the chemical potential $h(x)$ and specific heat $f(x)$ scaling functions by the differential equations

$$-xa'(x) + (2 - \alpha)a(x) = \beta h(x), \quad f(x) = a''(x). \tag{15}$$

We transform (2), (11), (12) to the form (15) and using the requirement that the chemical potentials be equal at $x = x_c$, where $x_c$ is a constant, we obtain the following representation for the scaling function $a(x)$:

$$a(x) = (A_{01} + (B_{01}x^{\psi_1} + B_{10})^{\xi_2})^{\xi_1} + C, \tag{16}$$

where the $\psi_1$, $\xi_1$, $\xi_2$ are determined from (10),

$$a(x) = -(A_{01}x^{\varphi_1} + A_{10})^{\xi_1} + (B_{01}x^{\psi_1} + B_{10})^{\xi_2} + C, \tag{17}$$

where the exponents $\varphi_1, \xi_1, \psi_1, \xi_2$ are determined from (13) and the constant C in (16) and (17) is found from $-x_c a'(x = x_c) + (2 - \alpha)a(x = x_c) = 0$.

Substituting successively (16) and (17) into (14), we find that near the critical point the scaling functions $h(x)$ and $f(x)$ behave according to simple power laws:

$$\lim h(x) = \begin{cases} \text{const} & (x \to 0), \\ x^{\nu} & (x \to \infty), \end{cases} \qquad \lim f(x) = \begin{cases} \text{const} & (x \to 0), \\ x^{-\alpha} & (x \to \infty). \end{cases} \tag{18}$$

The asymptotic forms for $f(x)$ and $h(x)$ in (18) are in complete agreement with the scaling hypothesis [16].

The scaling equation of state (14) qualitatively and quantitatively describes correctly only a small region about the critical point.

We show that from the singular terms (11) and (12) of the free energy (2) worked out here, an equation of state describing a wide region about the critical point and also the region of small densities and pressures can be constructed.

A physically correct free energy for small $\rho$ and $p$ has the form

$$F(\rho, T) = RT\ln\rho + RT\sum_{i=1} H^{(i)}(T)\rho^i, \tag{19}$$

where $H^{(i)}(T)$ are the virial coefficients.

On the other hand, it follows directly from (11) and (12) that $\rho^n F_n(\rho \to 0, T) \sim \rho^n$.

Hence the free energy (2), written in the form

$$F(\rho, T) = \rho^n F_{\mathrm{n}}(\rho, T) + RT\ln\rho + RT\sum_{i=1}^{n_1}\left(\sum_{j=0}^{n_2(i)} C_{ij}\left(1 - \frac{T_c}{T}\right)^j\right)\Delta\rho^i, \tag{20}$$

where $n \geqslant 2$ and $F_n(\rho, T)$ is the nonregular function (11) or (12), gives not only the scaling behavior (1) in the critical region, but also gives the ideal gas limit, and also correctly reproduces the temperature dependence of the second virial coefficient. In this way the structural form (20) compares favorably to the starting-point thermodynamic functions used in [10-12].

## NOTATION

$\mu$, chemical potential; $C_v$, specific heat at constant volume; $K_T$, isothermal compressibility; u, internal energy; p, pressure; $\rho$, density; T, absolute temperature; $\rho_c$, $p_c$, $T_c$, critical parameters; R, universal gas constant; $\alpha(x)$, h(x), f(x), scaling functions; $x = x_c$, equation of the coexistence curve; $x = \tau/|\Delta\rho|^{1/\beta}$ scaling variable; $\Delta\rho = (\rho - \rho_c)/\rho_c$; $\Delta p = (p - p_c)/p_c$; $\tau = (T - T_c)/T_c$; $C_{vn}$, singular term in the specific heat at constant volume; $\alpha$, $\beta$, $\delta$, $\gamma$, critical exponents; F, free energy; $H^{(1)}(T)$, second virial coefficient.

## LITERATURE CITED

1. Sh. P. Adamov, M. A. Anisimov, A. T. Berestov, et al., "Equation of state and the calculation of thermophysical properties near the critical point," Inzh.-Fiz. Zh., 40, No. 1, 163-164 (1981).
2. M. A. Anisimov, A. T. Berestov, L. S. Veksler, et al., "The scaling hypothesis and the equation of state of argon in a wide region about the critical point," Zh. Eksp. Teor. Fiz., 66, No. 2, 742-757 (1974).
3. M. A. Anisimov, A. T. Berestov, V. P. Voronov, et al., "Critical exponents of fluids," Zh. Eksp. Teor. Fiz., No. 5, 1661-1669 (1979).
4. V. A. Rabinovich and Yu. E. Sheludyak, "Method of comparison of the equation of state in a wide region about the critical point. Thermophysical properties of materials," [in Russian], GSSSD, 16 (1982) (Physical Constants and Properties of Materials), pp. 108-124.
5. I. M. Abdulagatov, "Calculation of thermodynamic properties of pure materials in a wide region about the critical point using the method of 'pseudospinodal' curves," in: Thermophysical Properties of Materials in the Condensed State [in Russian], FAN SSSR, Makhachkala (1982), pp. 199-121.
6. I. M. Abdulagatov, B. T. Alibekov, D. I. Vikhrov, et al., "$C_v$—V—T equation of state of n-pentane," Zh. Fiz. Khim., 56, No. 1, 215-217 (1982).
7. I. M. Abdulagatov and B. T. Alibekov, "Equation of state of n-hexane satisfying the scaling behavior near the critical point," Zh. Fiz. Khim., 56, No. 10, 2628-2619 (1982).
8. I. M. Abdulagatov and B. T. Alibekov, "Method of 'pseudospinodal' curves in the description of the scaling behavior of materials near the critical point," Zh. Fiz. Khim., 57, No. 2, 468-470 (1983).
9. I. M. Abdulagatov and B. T. Alibekov, "Generalized equation of the $(C_v^*—\varphi—\tau)$ surface of n-alkane in a wide region about the critical point," Zh. Fiz. Khim., 56, No. 2, 438-439 (1983).
10. V. F. Lysenkov and E. S. Platunov, "Equation of state structurally taking into account the singularities in the internal energy," Teplofiz. Vys. Temp., 19, No. 3, 507-513 (1981).
11. E. S. Platunov, V. A. Rykov, and N. V. Vas'kova, "Construction of a unique equation of state using the saturation line as a reference," in: Cryogenic Techniques, Refrigeration and Air Conditioning Devices [in Russian], LTI (Lensoveta), Leningrad (1981).
12. E. S. Platunov, V. F. Lysenkov, and N. V. Vas'kova, "The use of two reference curves in the construction of an equation of state of liquids and gases," Teplofiz. Vys. Temp., 20, No. 2, 249-254 (1982).
13. A. T. Berestov and S. B. Kiselev, "On the matching of the scaling equation of state and the virial expansion," Teplofiz. Vys. Temp., 17, No. 1, 1202-1209 (1979).
14. M. Vicentini-Missoni, G. M. H. Levelt Sengers, and M. S. Green, "Scaling analysis of thermodynamic properties in the critical region of fluids," J. Res. NBS, 73A, No. 6, 563-583 (1969).
15. M. P. Vukalovich and I. I. Novikov, Engineering Thermodynamics [in Russian], Énergiya, Moscow (1968).
16. M. A. Anisimov, "Research on critical phenomena in fluids," Usp. Fiz. Nauk, 114, No. 2, 249-294 (1974).
17. R. B. Griffiths, "Thermodynamic functions for fluids and ferromagnets near the critical point," Phys. Rev., 158, No. 1, 176-187 (1967).