ANALYSIS OF THE SCALING EQUATION IN PHYSICAL VARIABLES FOR THE ASYMPTOTIC NEIGHBORHOOD OF THE CRITICAL POINT

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A comparison of the linear scaling theory model and the equation of state of [1] is carried out.

Recently there has been significant interest in the problem of constructing an equation of state in the critical region in terms of the physical variables [1-9]. The "pseudospinodal" hypothesis advanced in [5] has been extremely fruitful in solving this problem. In particular, in [1] this hypothesis was used to construct the scaling function for the heat capacity at constant volume:

$$f_1(x)=A_1(x+x_1)^{-\alpha}+A_2(x+x_2)^{-\alpha}+B_1(x+x_1)^{\gamma-2}+B_2(x+x_2)^{\gamma-2}. \tag{1}$$

Here A_i and B_i are coefficients and x_1 and x_2 are certain fixed values of the scaling variable.

The first two terms of (1) are responsible for correctly reproducing the features of the heat capacity at constant volume C_V in the critical region. The last terms give the singular behavior of the isothermal compressibility.

Two special cases of (1) also deserve attention:

$$f_2(x)=A_1(x+x_1)^{-\alpha}+A_2(x+x_2)^{-\alpha}+B_1(x+x_1)^{\gamma-2}, \tag{2}$$

$$f_3(x)=A_1(x+x_1)^{-\alpha}+B_2(x+x_2)^{\gamma-2}. \tag{3}$$

A form structurally analogous to (3) was used in [10].

The coefficients A_2 and B_2 in (1) and (2) are related to A_1 and B_1 [1]:

$$A_2=-A_1x_1/x_2,\quad B_2=-B_1x_1/x_2. \tag{4}$$

The analysis of [1] shows that each of these choices for f(x) gives a qualitatively correct description of the singular behavior of the thermodynamic functions in the asymptotic neighborhood of the critical point. In other words, the principal terms of the series expansions of the functions (1)-(3) agree with the corresponding terms of the scaling functions in the linear model in the limits $x \to 0$ (critical isotherm), $x \to \infty$ (critical isochore), and $x \to -x_0$ (the liquid–vapor equilibrium line). The differences between the functions (1)-(3) show up in the higher-order terms of the expansions. Strictly speaking, these remarks pertain completely only to the neighborhood of the critical isochore ($x \to \infty$). In the vicinity of the critical isotherm or phase equilibrium line the functions (1)-(3) are practically the same and completely correspond to the well-known Griffiths conditions [6]. However, in the neighborhood of the critical isochore the situation is different. In the three cases (1)-(3) for f(x), the expansion $f(x \to \infty)$ will have the form $f_{1-3}(x)\overset{x\to\infty}{=}C_1x^{-\alpha}+C_2x^{\gamma-2}+\ldots,$ where C_1 and C_2 are coefficients uniquely related to the A_i and B_i. Thus the differences in the structure of f(x) in (1)-(3) do not affect the asymptotic behavior of f(x) in the limit $x \to \infty$. From this preliminary analysis we can conclude that the singular part of the heat capacity at constant volume predicted with the help of the functions (1)-(3) is practically identical and only certain quantitative differences can appear.

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If we consider the scaling function for the chemical potential h(x), we obtain (1)-(3) in the limit $x \to \infty$ [1]:

$$h_1(x \to \infty) = d_{11}x^{\gamma} + d_{12}x^{-\alpha} + \dots , \tag{5}$$

$$h_2(x \to \infty) = d_{21}x^{\gamma} + d_{22}x^{\gamma-1} + \dots , \tag{6}$$

$$h_3(x \to \infty) = d_{31}x^{\gamma} + d_{32}x^{1-\alpha} + \dots \tag{7}$$

We see that the expansions (5)-(7) have different terms following the principal asymptotic term. This can significantly affect the characteristics of the equation in reference to the thermal properties of the material and, in particular, the isothermal compressibility. The present paper considers this question as well.

Expressions (1)-(3) involve a set of undetermined parameters: A_i, B_i, x_1, x_2. They can be determined by using experimental data, for example on c_V. There is also the possibility of relating the parameters of (1)-(3) to the critical indices and critical amplitudes obtained in the framework of the scaling theory. We show how this is done using the function (2) as an example.

In order to solve this problem we first expand the expression for h(x). The scaling theory gives the following relations between the scaling functions of the heat capacity f(x), free energy $a(x)$, and chemical potential h(x) [7]:

$$a''(x) = -f(x),\ h(x) = (\delta + 1)\,a(x) - xa'(x)/\beta. \tag{8}$$

The above relations can be used to find h(x), if we also use (2) and (4):

$$h(x) = \frac{A_1x_1}{\beta(1-\alpha)}\left[(x+x_1)^{1-\alpha} - (x+x_2)^{1-\alpha}\right] + \frac{B_1}{\gamma(\gamma-1)}(x+x_1)^{\gamma-1}\left(2x + (\delta+1)x_1\right) + (\delta+1)\,C_0, \tag{9}$$

where

$$C_0 = \frac{A_1x_1}{(1-\alpha)(2-\alpha)}\left[(x_2 - x_0)^{1-\alpha} - (x_1 - x_0)^{1-\alpha}\right] - \frac{B_1(x_1 - x_0)^{\gamma-1}}{\gamma(\gamma-1)(\delta+1)}\left((\delta+1)x_1 - 2x_0\right). \tag{10}$$

This choice for the constant C_0 ensures the equality of the chemical potentials on the phase equilibrium curve $[h(-x_0) = 0]$.

As indicated above, one of the purposes of the present paper is to study the possibility of determining the values of the coefficients A_1 and B_1 in (2) and (9) in terms of the scaling amplitude a, which is introduced in the linear scaling theory model. The linear model gives the following results for the asymptotic neighborhood of the critical point

$$f_{\mathrm{lm}}(x) = \frac{ak}{2\alpha b^2}\gamma(1-\gamma)(k|\theta|)^{\alpha/\beta},\ h_{\mathrm{lm}}(x) = a\theta(1-\theta^2)(k|\theta|)^{-\delta}. \tag{11}$$

The notation is conventional for the scaling theory.

In order to relate A_1 and B_1 with the critical amplitude, we compare the behavior of the functions f(x) and h(x) as given here with the functions $f_{\ell m}(x)$ and $h_{\ell m}(x)$ in the neighborhood of the critical isochore ($x \to \infty$). In this case we obtain

$$f_{(2)}(x) \overset{x\to\infty}{=} A_1(1 - x_1/x_2)\,x^{-\alpha},\ h_{(9)}(x \to \infty) = \frac{2B_1}{\gamma(\gamma-1)}\,x^{\gamma}, \tag{12}$$

$$f_{\mathrm{lm}}(x \to \infty) = \frac{ak}{2\alpha b^2}\gamma(1-\gamma)\,x^{-\alpha},\ h_{\mathrm{lm}}(x \to \infty) = \frac{a}{k}\,x^{\gamma}. \tag{13}$$

Comparing the corresponding expressions, we find

$$A_1 = \frac{ak}{2\alpha b^2}\gamma(1-\gamma)\frac{1}{1 - x_1/x_2}, \tag{14}$$

$$B_1 = \frac{a}{2k}\gamma(\gamma-1). \tag{15}$$

An important intermediate result is that the number of adjustable parameters of the scaling functions (2) and (9) is reduced by one and is now equal to three: a, x_1, x_2. With the above relations for the coefficients A_1 and B_1 in terms of a we can write for f(x)

$$f(x)=\frac{ak\gamma(1-\gamma)}{2\alpha b^2(1-\omega_1/\omega_2)}\left[(x+\omega_1x_0)^{-\alpha}-\frac{\omega_1}{\omega_2}(x+\omega_2x_0)^{-\alpha}\right]+\frac{a}{k}\gamma(\gamma-1)(x+\omega_1x_0)^{\gamma-2}, \tag{16}$$

where x_0 is the value of x on the phase equilibrium line; $\omega_1 = x_1/x_0$, $\omega_2 = x_2/x_0$.

The undetermined parameters ω_1 and ω_2 appear in the above expression for f(x). Their values can be found from an analysis of the experimental data (a discussion of this possibility is a separate subject). Of equal interest is a method similar to that used above to find A_1 and B_1: a comparibility analysis between the linear scaling theory model and the equations given here. We consider the functions $f_{\ell m}(x)$ and $f_{(16)}(x)$ on the critical isotherm (x = 0) and on the phase equilibrium line ($x = -x_0$) and require that $f_{\ell m}(x = 0) = f_{(16)}(x = 0)$ and $f_{\ell m}(-x_0) = f_{(16)}(-x_0)$. We then obtain

$$\begin{gathered}\left[(\omega_1-1)^{-\alpha}-\frac{\omega_1}{\omega_2}(\omega_2-1)^{-\alpha}\right]=\left(1-\frac{\omega_1}{\omega_2}\right)\left[\frac{\alpha b^2}{(b^2-1)^{2\beta}}(\omega_1-1)^{\gamma-2}+(b^2-1)^{\alpha}\right],\\ \left[\omega_1^{-\alpha}-\frac{\omega_1}{\omega_2}\omega_2^{-\alpha}\right]=\left(1-\frac{\omega_1}{\omega_2}\right)\left[\frac{\alpha b^2}{(b^2-1)^{2\beta}}\omega_1^{\gamma-2}+(b^2-1)^{\alpha}b^{-\alpha/\beta}\right].\end{gathered} \tag{17}$$

The values of the parameters ω_1 and ω_2 in (16) can be found from the above system of equations. It is extremely important to note that in (17) only the critical indices appear (besides ω_1 and ω_2). Hence, ω_1 and ω_2 determined in this way will be universal to the same extent that the critical indices are universal. This leads to another important conclusion: with ω_1 and ω_2 determined in this way, the number of adjustable parameters of the equation of state reduces to one: it is necessary to know only the critical amplitude a. Here the potential of the equations of the present paper coincide with that of the linear scaling theory.

Above we considered the method of determining the constants of the equation of state in terms of the parameters of the linear model. In doing this, we analyzed the function f(x) in the form (2) in detail. This approach can also be applied in the cases (1) or (3) without any serious difficulties. For example, in the case (3) we obtain for f(x)

$$f(x)=\frac{ak}{2\alpha b^2}\gamma(1-\gamma)\left[(x+\omega_{11}x_0)^{-\alpha}-\frac{\alpha b^2}{k^2}(x+\omega_{22}x_0)^{\gamma-2}\right], \tag{18}$$

where ω_{11} and ω_{22} are determined from the following system of equations:

$$\begin{gathered}(\omega_{11}-1)^{-\alpha}-\frac{\alpha b^2}{(b^2-1)^{2\beta}}(\omega_{22}-1)^{\gamma-2}=(b^2-1)^{\alpha},\\ \omega_{11}^{-\alpha}-\frac{\alpha b^2}{(b^2-1)^{2\beta}}\omega_{22}^{\gamma-2}=(b^2-1)^{\alpha}b^{-\alpha/\beta}.\end{gathered} \tag{19}$$

The fundamental conclusion remains in force: the scaling function $f_{(18)}(x)$ gives the principal asymptotic terms of the thermodynamic functions in the critical region and has only a single adjustable parameter, the critical amplitude.

Earlier, from general considerations, it was noted that the choice of f(x) in the forms (1)-(3) should affect the results for c_V only weakly but can significantly affect the accuracy of the reproduction of K_T. Since we have found the final form of the function f(x) in (16) and (18) for the cases (2) and (3), respectively, we can examine quantitatively the above assertion. It is expedient to compare with the linear scaling theory. The parameters of the linear model are chosen to be the following [8, 9]: $\alpha = 0.114$, $\beta = 0.339$, $\gamma = 1.208$, $a = 17.61$, $x_0 = 0.2422$. The numerical values are for argon, one of the most widely studied materials. This information is sufficient to determine ω_1 and ω_1 [for $f_{(16)}(x)$], and also ω_{11} and ω_{22} [for $f_{(18)}(x)$]. Using (17) and (19), respectively, we compute the following values of these parameters: $\omega_1 = 2.33961$, $\omega_2 = 2.69192$, $\omega_{11} = 2.64$, $\omega_{22} = 10.00$. Hence all of the coefficients of Eqs. (16) and (18) are determined and we can compare how accurately the scaling function for the heat capacity is reproduced by the functions $f_{(16)}(x)$ and $f_{(18)}(x)$. In Fig. 1 the deviation of f(x) calculated by (16) and (18) from $f_{\ell m}(x)$ obtained in the linear scaling theory is shown. We see that the deviation $\delta f = (f(x) - f_{\ell m}(x))/f_{\ell m}(x)\cdot 100\%$ in both cases does not exceed the error in determining f(x) from the experimental data, which is about 1-3% [8]. However, for $f_{(18)}(x)$ the deviation from $f_{\ell m}(x)$ is close to this limit, whereas

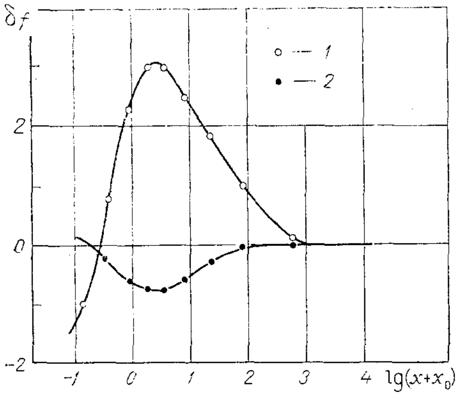

Fig. 1

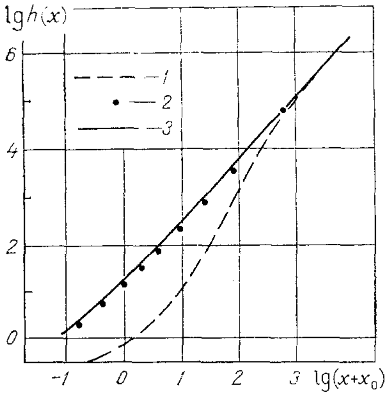

Fig. 2

Fig. 1. Deviation of the scaling function for the heat capacity at constant volume obtained in the present paper from $f_{\ell m}(x)$: curve 1) calculated from (18); 2) calculated from (16).

Fig. 2. Dependence of the scaling function of the chemical potential on the scaling variable: curve 1) $h_{(18)}(x)$; curve 2) $h_{(16)}(x)$; curve 3) linear scaling theory.

for $f_{(16)}(x)$ it is significantly less. Hence both (18) and (16) can be used to calculate c_V for individual materials in the asymptotic neighborhood of the critical point. The function $f_{(18)}(x)$ has limited possibilities as far as the error in c_V is concerned, but for $f_{(16)}(x)$ there is a significant margin of safety. This fact will be significant in the calculation of the other thermodynamic functions. In order to study this question, we compute the function h(x) with (16) and (18) and then compare the result with $h_{\ell m}(x)$ [for the case (16) the function h(x) is given by (9); for $f_{(18)}(x)$ it can be obtained easily with the help of (8)]. In Fig. 2 we show the results for $h_{(16)}(x)$ and $h_{(18)}(x)$ for a wide range of x. As expected, the possibilities of $h_{(18)}(x)$ are much more limited than for $h_{(16)}(x)$. Although in the region of large x (neighborhood of the critical isochore) both approaches are practically equivalent and lead to the same accuracy as in the linear scaling theory, with decrease of x, $h_{(18)}(x)$ differs from the linear model and from $h_{(16)}(x)$. For $x < 3$, the deviation $\delta h = (h(x) - h_{\ell m}(x)/h_{\ell m}(x)\cdot 100\%$ for $h_{(18)}(x)$ becomes significant. In addition, for small x, $h_{(18)}(x)$ becomes negative, which is unphysical. On the other hand, the function $h_{(16)}(x)$ not only gives a qualitatively accurate description of the scaling function of the chemical potential, but also is comparable to the linear scaling theory in its quantitative accuracy.

Hence the approach suggested in [1] can be used to construct a scaling equation in terms of physical variables which is comparable in accuracy to the linear scaling theory in the calculation of the thermodynamic functions in the neighborhood of the critical point. The procedure used here for finding the constants of the equation reduces the number of adjustable parameters in the equation of state to one. The scaling equation constructed here has the advantage that its scaling functions are directly determined in terms of the physical variables such as density and temperature, and not in the parametric form characteristic of the linear scaling theory.

NOTATION

f(x), h(x), and $a(x)$, scaling functions for the heat capacity at constant volume, chemical potential, and free energy, respectively; $x = \tau/|\Delta\rho|^{1/\beta}$, scaling variable; $\tau = (T - T_c)/T_c$, $\Delta\rho = (\rho - \rho_c)/\rho_c$; T, absolute temperature; ρ, density; T_c, ρ_c, critical parameters; α, β, γ, and δ, critical indices; a, critical amplitude; c_V, specific heat at constant volume; K_T, isothermal compressibility; θ, parameter defined by the equation $x = (1 - b^2\theta^2)(k|\theta|)^{-1/\beta}$; $k = [(b^2 - 1)/x_0]^\beta$; $b^2 = (\gamma - 2\beta)/(1 - 2\beta)/\gamma$; x_0, value of the scaling variable on the phase equilibrium line.

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PREDICTION OF THE THERMOPHYSICAL PROPERTIES OF SOLIDS

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Proceeding from the established interrelations between thermophysical, elastic, and structural characteristics, the article analyzes the possibility of predicting the thermophysical properties of solids.

Prediction of the thermophysical properties of materials (heat capacity, thermal conductivity, coefficient of thermal expansion, etc.) is of considerable scientific and practical interest. It is known from solid-state physics [1] that

$$\alpha = \gamma C_v/(3\beta^2 r N_A z). \tag{1}$$

Here, according to [2], we have:

$$\gamma/(r\beta^2) = (m+4)\,\delta/(2V_{el}E). \tag{2}$$

Substituting (2) into (1), we have

$$C_v/\alpha = 6V_{el}N_A Ez/[(m+4)\,\delta]. \tag{3}$$

Furthermore, we take into account [3]:

$$E = AkT_{mp}N/V_{el}, \tag{4}$$

where A is a dimensionless coefficient, where for compounds with predominantly ionic type of chemical bonds A = 64, for metals A = 90. Then we have from (3) and (4):

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