13. Yu. I. Balkarei, M. G. Evtikhov, and M. I. Elinson, Mikroelektronika, 11, No. 1, 25-29 (1982).
14. S. P. Kurdyumov, Sov. Probl. Mat. Fiz. Prikl. Mat., 217-243 (1982).
15. T. S. Akhromeeva, S. P. Kurdyumov, and G. G. Malinetskii, Nov. Zhizni, Nauke, Tekhnike, Ser. Mat. Kiber., No. 5, Moscow (1985).
16. V. A. Nikolaeva, V. I. Ryzhii, and B. N. Chetverushkin, "Numerical simulation of stratification of a hot electron-hole plasma in binary heterostructures," Moscow (1985) (Preprint Inst. Prikl. Mat. Akad. Nauk SSSR, No. 107).
17. A. A. Samarskii, Theory of Difference Schemes [in Russian], Moscow (1983).
18. A. A. Samarskii and E. S. Nikolaev, Methods of Solving Grid Equations [in Russian], Moscow (1978).
19. O. S. Mazhorova and Yu. P. Popov, Zh. Vychisl. Mat. Mat. Fiz., 20, No. 4, 1005-1020 (1980).
20. O. S. Mazhorova, "An iterative method of solving two-dimensional matrix equations," Moscow (1979) (Preprint Inst. Prikl. Mat. Akad. Nauk SSSR, No. 48).
21. B. N. Chetverushkin, Mathematical Simulation of dynamics Problems of an Emitting Gas [in Russian], Moscow (1985).
22. M. I. Volchinskaya and B. N. Chetverushkin, Zh. Vychisl. Mat. Mat. Fiz., 17, No. 2, 428-436 (1977).

DESCRIPTION OF THE NEIGHBORHOOD OF THE PHASE EQUILIBRIUM LINE AND METASTABLE REGION WITH THE PARAMETERIC EQUATION OF SCALING THEORY

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The deficiencies of the parameteric equation of scaling theory in the neighborhood of the phase equilibrium line and in the metastable region are analyzed.

The equation of state obtained in the well-known parametric representation of the scaling theory [1, 2] is widely used in calculations in the critical region. The first approximation of this representation, the so-called linear model, is the most widely studied. In this model the pressure and heat capacity at constant volume are calculated as follows [1, 2]:

$$\Delta p = (1+\Delta\rho)\,\Delta\mu(\rho,\ T) - |\Delta\rho|^{\delta+1}\,a(x) - A(T), \tag{1}$$

$$\frac{\rho C_v}{T} = \frac{Mp_K}{T_K^2}\,[|\Delta\rho|^{-\alpha/\beta} f(x) - \mu''(\rho_K,\ T)\,\Delta\rho + B(T)], \tag{2}$$

$$\tau = r(1-b^2\theta^2),\ \Delta\rho = kr^\beta\theta,\ \Delta\mu = |\Delta\rho|^\delta h(x). \tag{3}$$

Here we use the conventional notation in scaling theory. The scaling functions in (1) through (3) are determined in terms of the parameter θ:

$$h(x) = a\theta(1-\theta^2)(k|\theta|)^{-\delta},\ f(x) = \frac{ak\gamma(\gamma-1)}{2\alpha b^2}\,(k|\theta|)^{\alpha/\beta}. \tag{4}$$

In order to proceed further one must relate the scaling variable $x = \tau/|\Delta\rho|^{1/\beta}$ with θ and also with expression for the scaling function of the isothermal compressibility $f_z = [\delta h(x) - \beta^{-1}xh'(x)]^{-1}$. From (3) one easily obtains

$$x = (1-b^2\theta^2)\,(k|\theta|)^{-1/\beta}, \tag{5}$$

$$f_z(x) = \frac{k}{a}\,(k|\theta|)^{\delta-1}\left[1 + \frac{2(\beta+\gamma)-3}{1-2\beta}\,\theta^2\right]^{-1}. \tag{6}$$

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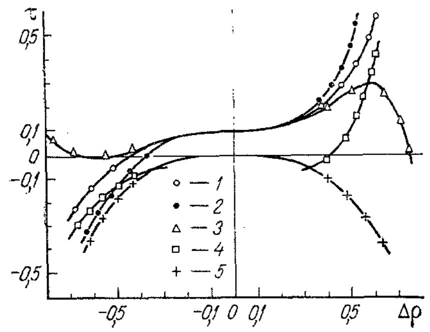

Fig. 1

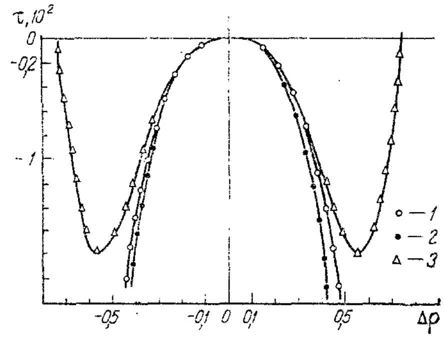

Fig. 2

Fig. 1. The critical region: 1) experiment; 2) linear scaling theory model; 3) equation of [3]; 4) calculated subcritical isotherm according to the linear scaling theory model; 5) phase equilibirum line.

Fig. 2. Phase equilibrium lines: 1) experiment; 2) linear scaling theory model; 3) equation of [3].

In this parametric representation the saturation line is given by $\theta^2 = 1$ such that for $\theta^2 < 1$ equations (1) through (6) describe the single-phase region and for $\theta^2 > 1$ they describe the metastable region.

In Fig. 1 we show the typical shape of the isotherms obtained from the linear scaling theory model. Note the unusual form of the subcritical isotherms, which is due to the fact that the function (5) is double-valued and has an extremum when $\theta^2 = ((1 - 2\beta)b^2)^{-1}$. In order to avoid ambiguities in calculations with the linear model, one imposes the restriction $\theta^2 \leq ((1 - 2\beta)b^2)^{-1}$. As seen from Fig. 1, the subcritical isotherms do not have an extremum in the metastable region. That is, in this approach there is no spinodal on the calculated thermodynamic surface. One can verify this directly by solving the equation $f_z^{-1}(x) = 0$, where $f_z(x)$ is given in the form (6). This equation does not have real roots. It then follows that the linear scaling theory model incorrectly describes the features of the thermodynamic surface in the metastable region. This deficiency of the linear model is probably also present in a certain neighborhood of the phase equilibrium line in the direction of the single-phase region. Hence this deficiency of the linear model should affect the accuracy of the calculation of the caloric functions, for example C_V. Indeed, the working region of the linear model in density is $|\Delta\rho| \lesssim 0.2$ for the calculation of only thermal data [2]. This is illustrated in Fig. 1. For $T > T_K$ the isotherms are qualitatively correct. The heat capacity at constant volume C_V is correctly described inside a significantly narrower region: $|\Delta\rho| \lesssim 0.06$ [1].

Evidently this assumption confirms analysis based on an equation of state expanded into the critical region which takes into account the next approximation of the scaling theory. In this case we have [1, 3]:

$$\Delta\mu = ar^{\beta\delta}\theta(1 - \theta^2) + cr^{\beta\delta+\Delta}\theta, \tag{7}$$

$$\frac{\rho C_v}{T} = \frac{Mp_K}{T_K^2}\left[\frac{ak\gamma(\gamma - 1)}{2\alpha b^2}r^{-\alpha} - \frac{kc(\gamma + \Delta)r^{-\alpha+\Delta}}{2b^2(1 - (1 - 2\beta)b^2\theta^2)} - \right.$$
$$\left. - \mu''(\rho_K, T)\Delta\rho + B(T)\right]. \tag{8}$$

It follows from (8) that when $\theta^2 \to ((1 - 2\beta)b^2)^{-1}$ the heat capacity at constant volume diverges in the metastable region. That is, this equation for C_V satisfies the "pseudo-spinodal" hypothesis [4]. This in turn indirectly demonstrates the presence of a spinodal. One can see this directly by solving the equation $f_z^{-1}(x) = 0$ for the new scaling functions from (7) and (8). It is interesting to study how widely the boundaries of the working region of this equation can be extended using this device. It turns out that in the calculation of Δp the expanded equation of the scaling theory is correct for $|\Delta\rho| \lesssim 0.3$, and so in this sense little is changed from the linear model. Moreover, as seen from Fig. 1, the isotherms still behave qualitatively incorrectly when $|\Delta\rho|$ increases.

The picture is different for the calculation of C_V. Here while the equation qualitatively correctly gives the "pseudospinodal" and spinodal, its working region for the determination of C_V is extended almost up to $|\Delta\rho| \leq 0.3$. But as before, as one approaches the saturation line the calculated value of C_V becomes systematically too small compared to the experimental results [3]. In the connection with this, it is of interest to consider the positions of the spinodal and pseudospinodal. Indeed, the "pseudospinodal" equation $\theta^2 = ((1 - 2\beta)b^2)^{-1}$ corresponds to $x_{ps} = 1.75x_0$. This means that $x_S/x_0 < 1.75$ for the spinodal. The experimental data indicates that in terms of these coordinates the spinodal corresponds to $x_S/x_0 = 3.3$ [5]. The difference is significant.

But this, unfortunately, is not the only deficiency of the expanded scaling theory model. In the linear scaling theory model the equation of the phase equilibrium line is $\theta^2 = 1$. In this case, as seen from (1), (3), and (4), $\Delta\mu = 0$ and $\Delta\rho^V = \Delta\rho^\ell$. In the expanded model the phase equilibrium line is no longer given by the equation $\theta^2 = 1$. It follows from (7) that $\Delta\mu = 0$ when $(1 - \theta^2 + c/a(r^\Delta)) = 0$. The presence of the last term significantly deforms the phase equilibrium line. It is constructed in Fig. 2 for argon (the coefficients a and c and the index Δ were taken from [1, 3]). Hence the phase equilibrium line obtained from the expanded equation of state is incorrect in principle. This may not affect the quantitative characteristics of the equation. Therefore attempts to eliminate the deficiencies of the linear model by introducing the next approximation in scaling theory [3] are in large measure unsuccessful. The working region of the equation of state can be widened somewhat, but the isotherms and phase equilibrium line then becomes qualitatively incorrect when we move away from the critical point. Therefore the structure of the equation of state in the parameteric form (in the linear model, as well as in the next approximation) is in need of correction which would take into account more rigorously the physical behavior of matter in the critical region.

LITERATURE CITED

1. V. A. Rabinovich, A. A. Vasserman, B. A. Koval'chuk, and A. T. Berestov, Thermophysical Properties of Matter and Materials [in Russian], Issue 13, Moscow (1979), pp. 24-39.
2. W. L. Greer, J. M. H. Levelt Sengers, and J. V. Sengers, J. Phys. Chem. Ref. Data, 5, No. 1, 1-53 (1976).
3. M. A. Anisimov, A. T. Berestov, S. B. Kiselev, and V. A. Rabinovich, Thermophysical Properties of Matter and Materials [in Russian], Issue 13, Moscow (1979), pp. 140-149.
4. C. M. Sorensen and Mark D. Semon, Phys. Rev., A21, 340-346 (1980).
5. V. P. Skripov, Metastable Liquids [in Russian], Moscow (1975).