

Equation of state of matter near the liquid-vapor critical point

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(Submitted April 19, 1973)

Zh. Eksp. Teor. Fiz. 66, 983-985 (March 1974)

The asymmetry of the coexistence curve near the critical point arising as a result of the fact that the particle-number and energy densities do not possess definite scale dimensionalities is investigated.

Also investigated is the influence on the asymmetry of the term $\tau n^3(x)$, which is present in the free-energy expansion. The $P=P_c$ and $T=T_c$ curves are derived.

Pokrovskii (see [1]) has pointed out that the lattice-gas model contains no important features characteristic of real liquid-vapor systems. This is connected with the fact that in the lattice-gas model the fluctuations in the particle-number density n and the fluctuations in the energy density ϵ are statistically independent, whereas this is not so in a real system, i.e.,

$$\int d^3x \langle n(x)\epsilon(0) \rangle = -(\partial\mu/\partial T)_{V,N} (\partial N/\partial\mu)_{T,V} = A(\partial N/\partial\mu)_{T,V}, \quad (1)$$

where T is the temperature, μ the chemical potential, V the volume, N the number of particles in the volume V , $n(x)$ the particle-number density, and $\epsilon(x)$ the energy density. The quantities $n(x)$ and $\epsilon(x)$ are measured from their critical values.

Equation (1) is at variance with conformal invariance (see [2]) if it is assumed that the quantities $n(x)$ and $\epsilon(x)$ possess definite scale dimensionalities Δ_n and Δ_ϵ , since conformal invariance requires the orthogonality of quantities with different scale dimensionalities [2], i.e., $\langle n(x)\epsilon(0) \rangle = 0$. The conclusion offered by Pokrovskii is that definite scale dimensionalities can be ascribed not to the quantities $n(x)$ and $\epsilon(x)$ themselves, but to their linear combinations:

$$O_1 = (1-ab)^{-1}(n-be), \quad O_2 = (1-ab)^{-1}(e-an) \quad (2)$$

or

$$n = O_1 + bO_2, \quad e = aO_1 + O_2, \quad (3)$$

where a and b are constants.

For the dimensionalities of the quantities O_1 and O_2 , we shall use the notation adopted in the literature for n and ϵ :

$$\Delta_n \rightarrow \Delta_1 = \beta/\nu, \quad \Delta_\epsilon \rightarrow \Delta_2 = d-1/\nu,$$

where $d=3$ is the dimensionality of the space, ν is the correlation-length exponent ($R_c(\tau) \sim \tau^{-\nu}$), and β is the particle-number density exponent ($\langle n \rangle \sim (-\tau)^\beta$). The thermodynamic variables ξ and h conjugate to O_1 and O_2 can be expressed in terms of $\tau = (T-T_c)/T_c$ and $\tilde{\mu} = (\mu - \mu_c)/\mu_c$:

$$\xi = \tau + b\tilde{\mu}, \quad h = \tilde{\mu} + a\tau. \quad (4)$$

The purpose of the present paper is to investigate the asymmetry arising in the coexistence curve near the critical point as a result of the fact that the particle-number and energy densities do not possess definite scale dimensionalities. We also investigate the influence on the asymmetry of the term $\tau n^3(x)$, which is present in the power series expansion of the free energy $F(n)$ in the order parameter n .

According to scaling theory (see, for example, [3]), the average values of quantities possessing a definite scale dimensionality are determined by their transformation properties under uniform space dilatation:

$$\langle O_1 \rangle = \xi^\beta f(h/\xi^{\beta+\nu}), \quad \langle O_2 \rangle = \xi^{1-\alpha} g(h/\xi^{\beta+\nu}), \quad (5)$$

where $\alpha = 2 - \nu d$ is the exponent of C_{VN} , the specific heat at constant volume and constant particle number, $\gamma = \nu d - 2\beta$ is the exponent of the isothermal compressibility along the coexistence curve, and $f(k)$ and $g(k)$ are universal functions (see, for example, [3,4]). The equation of state is obtainable from (3) and (5):

$$\langle n \rangle = \langle O_1 \rangle + b \langle O_2 \rangle = \xi^\beta f(k) + b \xi^{1-\alpha} g(k). \quad (6)$$

From this equation, it is easy to obtain the $P=P_c$ and $T=T_c$ curves. In doing this, we should use the well-known asymptotic forms for $f(k)$ and $g(k)$ (see [3]) and the expansion of the chemical potential

$$\tilde{\mu} = A(P-P_c)/P_c + B\tau.$$

The critical isobar ($P=P_c$)

$$\langle n \rangle \sim \tau^{1/\delta} + \text{less singular terms}, \quad (7)$$

$$\delta = (\beta + \gamma)/\beta = \nu d/\beta - 1.$$

The critical isotherm ($T=T_c$)

$$\langle n \rangle \sim \left| \frac{P-P_c}{P_c} \right|^{1/\delta} + \text{less singular terms}. \quad (8)$$

Let us consider the coexistence curve in somewhat greater detail. The existence of this curve is manifested in the fact that the function $f(k)$ is two-valued on the line $h=0$, $\xi < 0$, i.e., the equation $F(z)=0$ ($F(z)$ is the inverse of the function $f(k)$) has two roots: z_1 and z_2 . We shall assume that at the critical point the Hamiltonian of the system is invariant under the transformation $O_1 \leftrightarrow -O_1$. Then $z_1 = -z_2$. In the variables $\tilde{\mu}$ and τ , the equation $h=0$ yields the relations $\tilde{\mu} = -a\tau$ and $\xi = (1-ab)\tau$ (notice that the condition of thermodynamic stability amounts to the requirement that $ab < 1$). The function $g(k)$ is connected with the specific heat and is therefore single-valued. Thus, we obtain for the liquid- and gas-density dependences along the coexistence curve the expressions:

$$n_1 - n_c = z_1 (1-ab)^\beta |\tau|^\beta + b g(0) (1-ab)^{1-\alpha} |\tau|^{1-\alpha},$$

$$n_g - n_c = -z_1 (1-ab)^\beta |\tau|^\beta + b g(0) (1-ab)^{1-\alpha} |\tau|^{1-\alpha} \quad (9)$$

or

$$n_1 - n_g = 2z_1 (1-ab)^\beta |\tau|^\beta,$$

$$n_1 + n_g - 2n_c = 2b g(0) (1-ab)^{1-\alpha} |\tau|^{1-\alpha} = C |\tau|^{1-\alpha}. \quad (10)$$

The quantity $n_1 + n_g - 2n_c$ characterizes the asymmetry of the coexistence curve.

In conclusion, let us investigate the influence exerted on the asymmetry of the coexistence curve by small corrections that are not invariant under the transformation $O_1 \leftrightarrow -O_1$. The most important correction, from this point of view, is the effective-Hamiltonian term

$$\mathcal{H}_{int} = g\tau O_1^3(x); \quad (11)$$

where $:O_1^3(\mathbf{x}):$ is the normal-ordered product in the Wick sense. The scale dimensionality of the operator \mathcal{H}_{int} , as computed with the aid of the ϵ -expansion up to first order in $\epsilon = 4-d$ (see, for example, [5]), is equal to

$$\Delta_3 = \Delta(\mathcal{H}_{\text{int}}) = 4 - d = 3.$$

Therefore, it does not change the dimensionalities Δ_1 and Δ_2 , and the asymmetry of the coexistence curve can be computed using perturbation theory:

$$\frac{n_g + n_l - 2n_c}{2n_c} \approx \frac{g\tau}{n_c} \int d^3x G_{31}(x) + C|\tau|^{1-\alpha},$$

$$G_{31}(x) = \langle :O_1^3(x): O_1(0) \rangle = |\tau|^{v(\Delta_1 + \Delta_3)} f(x^2 |\tau|^{2v}). \quad (12)$$

The integral in (12) diverges at large distances; therefore, we can estimate it from dimensional considerations:

$$\int d^3x G_{31}(x) \sim |\tau|^{v(\Delta_1 + \Delta_3 - d)},$$

while for the asymmetry of the coexistence curve we obtain

$$(n_g + n_l) / 2n_c - 1 \sim |\tau|^{v(\Delta_1 + \Delta_3 - d) + 1} + C|\tau|^{1-\alpha}.$$

Estimates of the dimensionalities Δ_1 and Δ_3 with the aid of the first-order ϵ -expansion yield

$$\Delta_1 + \Delta_3 - d = 0.$$

The experimental data (see the Table in [6] giving the densities of coexisting liquid and vapor near the critical point of heptane) indicate that such an asymmetry exists, but it is impossible to determine its exponent from the available data.

We are grateful to V. L. Pokrovskii for supervising the work and to M. A. Anisimov, A. T. Berestetskiĭ, and E. E. Gorodetskiĭ for a discussion.

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Translated by A. K. Agyei

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