Nature of the singularity of the "diameter" of the coexistence curve near the critical point

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It is shown that allowance for the ternary interaction between particles in the lattice-gas model leads to a singularity of the "diameter" of the coexistence curve. An estimate is presented of the required accuracy, and a new method is proposed for the experimental observation of this singularity.

In recent experiments[1] on the liquid-vapor equilibrium of single-component systems near critical points, it was observed that the quantity $(\rho_L + \rho_g)/2$ (the so-called "diameter" of the coexistence curve) depends in singular manner on the temperature:

$$[(\rho_L + \rho_g)/2] - \rho_c \sim |t|^{1-\alpha} \tag{1}$$

in contrast to the known empirical linear rule for the diameter. Here ρ_L and ρ_g are the densities of the coexisting liquid and gas phases, ρ_c is the critical density, $t = (T - T_c)/T_c$ is the dimensionless deviation of the temperature from the critical value, and $\alpha > 0$.

In this article we explain these experimental results within the framework of a lattice gas, with allowance for the ternary interaction between the particles.

Following Wilson,[2] we write down the Hamiltonian of the considered model in the Landau-Ginzburg form:

$$H = \int dx \left\{ \frac{1}{2}(\nabla\phi)^2 + \frac{1}{2}t\phi^2 + \frac{1}{4!}u\,\phi^4 - \frac{1}{3!}\lambda t\phi^3 - h\phi \right\}. \tag{2}$$

Here $\phi = 2\rho - 1$ and h is the deviation of the chemical potential μ from its critical value μ_c. We separate in (2) the zeroth Fourier compontne $\phi_0 \equiv \phi(k=0) = (1/V) \times \int \phi(r)\,dr$ (V is the volume of the system and **k** is the wave vector). Denoting the corresponding Hamiltonian by $H(\phi_0, \phi_c)$, we obtain an equation of state in the form[3]

$$h = \left\langle \frac{\partial H(\phi_0, \phi_c)}{\partial \phi_0} \right\rangle \tag{3}$$

The averaging in (3) is over the distribution function $\exp\{-H(\varphi_0, \varphi_c)/T\}$.

The densities of the coexisting phases are obtained from Eq. (3) with the additional condition $\langle\rho\rangle = N/V = \rho_c$ (N is the number of particles in the system):

$$\phi_{0(L,g)} = \pm B|t|^{\beta} + \lambda|t|^{1-\alpha}, \tag{4}$$

where $\beta = 1/2 - \epsilon/6$, and $\alpha = \epsilon/6$ ($\epsilon = 4 - d$, d is the dimensionality of space). This leads directly to Eq. (1).

A similar result was obtained earlier phenomenologically in[4] on the basis of Pokrovskiĭ's hypothesis[5] that the density operator in a real liquid does not have a definite dimensionality, and is a linear combination of the order-parameter and energy-density operators.

It is easy to estimate the density-measurement accuracy necessary to observe a curvature of the coexistence-curve diameter:

$$(\delta\rho/\rho) \lesssim \alpha\lambda(1-\alpha)^{1/\alpha}|t_0|^{1-\alpha}, \tag{5}$$

where $t_0 = (T_0 - T_c)/T_c$ is the measurement interval. For most substances $\lambda \sim 1$ (for example, $\lambda \approx 0.68$, ≈ 0.75, ≈ 0.85, ≈ 0.92, and ≈ 1.06 for O_2, Ar, CO_2, SF_6, and C_2H_4, respectively) and $(\delta\rho/\rho) \lesssim 0.03\%$ at $t_0 \sim 10^{-2}$.

We note in conclusion that in the presence of asymmetry the interface between the liquid and the gas should move, even in the case of critical filling, in accordance with the expression $l \sim \lambda|t|^{1-\alpha-\beta}$ (where l is the deviation of the meniscus from the point where it vanishes), and this can also serve as a method for experimentally observing the indicated singularity.

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