

The choice of the proper order parameter and the asymmetry effects in the critical behavior

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The effects of the critical behavior in real systems caused by the asymmetry of the Hamiltonian are discussed within the framework of the canonical formalism. It is shown that the spurious $\tau^{2\beta}$ -term in the critical asymptotic behavior of the rectilinear diameter of the density:

$$\phi_d = D_{1-\alpha} |\tau|^{1-\alpha} + D_{2\beta} |\tau|^{2\beta} + \dots, \quad \tau = (T_c - T)/T_c$$

is caused by the asymmetrical terms of the Hamiltonian. Within the perturbation theory these are the quasilocal $\phi (\nabla\phi)^2$ and the local ϕ^5 terms. It is shown that the ratio of the amplitudes $D_{1-\alpha}/D_{2\beta}$ takes the universal character modulo non-universal factor which depends on the thermodynamic class of the corresponding states. This implies also the universality of the ratio of the amplitudes of these singular terms in isomorphic variables. They are conjugated (in thermodynamical sense) to the canonical order parameter field which restores the symmetry of the Hamiltonian. As a sequence, the equation of state in such variables is fully symmetrical with respect to coexisting phases. The procedure of calculation of these variables performed for the number of model equations of states for molecular liquids. This conclusion is checked via analysis of the experimental data for a number of liquids. The dependence of the critical amplitudes on the intermolecular interactions is discussed. The structure of the next to leading asymptotic terms in compressibility and the singularity of the Tolman length are determined. The connection between the proposed approach and the “complete” scaling hypothesis proposed by M. Fisher and coll. is discussed.