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ISOMORPHISM OF CRITICAL PHENOMENA

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A proof of the isomorphism hypothesis is presented, based on two assumptions: the similarity hypothesis and the assumption that an algebra of singular operators exists. The analysis is performed for the case of a dilute solution near the liquid-gas critical point.

FISHER[1] put forward the hypothesis of the isomorphism of a phase transition under the introduction of an additional thermodynamic degree of freedom. The meaning of this hypothesis is as follows: let X be an extensive quantity, corresponding to the new degree of freedom, and let x be the thermodynamic force conjugate to it. Suppose that for $X = 0$ the thermodynamic potential Ω contains a singular part $\Omega_S(T, \mu)$ (T is the temperature and μ denotes the other variables), which has a singularity at the point $T = T_c$, $\mu = \mu_c$. Then, for $X \neq 0$, the singular part of the potential remains the same function of its arguments, under the condition that x is fixed. Only the quantities T_c and μ_c change—these become functions of x. Fisher also assumed that T_c and μ_c, as functions of x, have no singularities. In applications, the case when the role of X is played by an impurity concentration, and the role of x by the corresponding chemical potential, is the most interesting. As examples, one can suggest a weak solution close to the critical point, or a magnet with impurity spins. To check his hypothesis, Fisher considered the exactly soluble model of a plane Ising lattice in which additional "particles" are positioned on the bonds, changing the magnitude of the exchange constant. The number of these impurities was assumed to be a conserved quantity (cf. also the paper by Lushnikov[2]). The thermodynamic consequences of the isomorphism hypothesis have been studied in detail by Anisimov, Voronel', and Gorodetskiĭ[3].

In this paper, we give a proof of the hypothesis of isomorphism based on two assumptions: the similarity hypothesis (cf., e.g.,[4,5]) and the assumption of the existence of an operator algebra[6].

For definiteness, we shall consider a weak solution close to the critical point. We write the Hamiltonian of the system in the form

$$H = H_0 + H_1 + H_{int}, \tag{1}$$

where H_0 is the Hamiltonian of the pure substance, H_1 is the impurity Hamiltonian, and H_{int} is the Hamiltonian of the interaction of the impurity with pure substance. We shall neglect the direct interaction of the impurity atoms, assuming their concentration to be small. In our approximation, H_1 coincides with the kinetic energy of the impurity atoms. Concerning H_0, we assume that it can be written as an integral of the energy density $\epsilon(r)$. The interaction H_{int} is assumed to be a contact interaction:

$$H_{int} = g\int \rho_0(\mathbf{r})\rho_1(\mathbf{r})\,dV. \tag{2}$$

Here, $\rho_0(\mathbf{r})$ and $\rho_1(\mathbf{r})$ are the particle-number densities of the pure substance and impurity respectively.

We shall seek the thermodynamic potential Ω in the variables T, V, μ_0 and μ_1 (μ_0 and μ_1 are the chemical potentials of the pure substance and impurity). It follows from the form of the Hamiltonian (1) and (2) that, for a fixed distribution $\rho_0(\mathbf{r})$, the impurity particles represent an ideal gas in an external scalar field $\varphi(\mathbf{r}) = g\rho_0(\mathbf{r})$. The partition function $Z_1(\beta, \mu, \varphi)$ of an ideal gas in an arbitrary external field $\varphi(\mathbf{r})$ can be obtained in explicit form:

$$Z_1(\beta, \mu, \varphi) = \exp\left\{n^0(\mu)\int e^{-\beta\varphi(\mathbf{r})}\,dV\right\}, \tag{3}$$

where

$$n^0(\mu) = \frac{(2\pi mT)^{3/2}}{(2\pi\hbar)^3}e^{\beta\mu}. \tag{4}$$

Knowing $Z_1(\beta, \mu, \varphi(\mathbf{r}))$, we can obtain the complete partition function Z:

$$Z = \operatorname{Sp}\{e^{\beta(\mu_0N_0 - H_0)}Z_1(\beta, \mu_1, g\rho_0(\mathbf{r}))\}. \tag{5}$$

Using (3), we rewrite (5):

$$Z = \operatorname{Sp}\exp\left\{\beta(\mu_0N_0 - H_0) + n^0(\mu_1)\int e^{-\beta g\rho_1(\mathbf{r})}\,dV\right\}. \tag{6}$$

Up to this point, our calculations have been exact, Starting from this point, we shall use the operator-algebra hypothesis. Strictly speaking, this hypothesis has been proved only for the two-dimensional Ising model[6]. However, it appears to be plausible also for the general case of a phase transition[7,8].

The operator-algebra hypothesis consists in the statement that, near the critical point, all the singular quantities can be described by means of a certain complete set of singular operators $\hat{O}_n$, so that any singular operator $\hat{A}$ not appearing in the complete set can be represented in the form of a superposition:

$$\hat{A} = \sum_n \lambda_n\hat{O}_n. \tag{7}$$

The operator algebra (7) is valid in the sense that it gives correct results in the calculation of mean values.

In the specific case of the liquid-gas critical point, the most singular operators are the operators of the particle-number density $\hat{\rho}_0$, the energy density $\hat{\epsilon}$, the stress tensor $\hat{\Pi}_{ik}$, etc.

We expand the operator $\exp(-\beta g\rho_0(\mathbf{r}))$ in the basis of the operator algebra:

$$e^{-\beta g\hat{\rho_0}(\mathbf{r})} = a\hat{\rho_0}(\mathbf{r}) + b\hat{\varepsilon}(\mathbf{r}) + \ldots, \tag{8}$$

where a and b are constant quantities. In the expansion (8), we have neglected all but the most singular terms. Substituting (8) into (6), we obtain a sum coinciding in form with the partition function $Z_0(\beta, \mu_0)$ of the pure substance, but with shifted values of the arguments, $\beta \rightarrow \beta + \delta\beta$, $\mu \rightarrow \mu + \delta\mu$, where $\delta\beta$ and $\delta\mu$ are connected with the parameters of the theory by the relations

$$\delta\beta = -n^0(\mu_1)b, \quad \delta\mu = \beta^{-1}n^0(\mu_1)(a + b\mu_0). \tag{9}$$

Thus, we have found a connection between the potential $\Omega(\beta, \mu_0, \mu_1)$ of the solution and the potential $\Omega_0(\beta, \mu)$ of the pure solvent:

$$\Omega(\beta, \mu_0, \mu_1) = \Omega_0(\beta + \delta\beta, \mu_0 + \delta\mu). \tag{10}$$

The formula (10) confirms the hypothesis of isomorphism.

By similar methods, we can calculate the correlation functions

$$G_{ik}(\mathbf{r}, \mathbf{r}') = \langle \rho_i(\mathbf{r}) \rho_k(\mathbf{r}') \rangle \quad (i, k = 0, 1). \tag{11}$$

For example, we consider $G_{11}(\mathbf{r}, \mathbf{r}')$. We introduce an external field $\chi(\mathbf{r})$ acting on the particles of type 1. Knowing the partition function $Z_1(\beta, \mu, \varphi)$ for the ideal gas, we can easily obtain G_{11} by differentiation:

$$G_{11}(\mathbf{r}, \mathbf{r}') = T^2 \frac{\delta^2}{\delta\chi(\mathbf{r})\delta\chi(\mathbf{r}')} \ln Z |_{\chi=0},$$

$$Z = \operatorname{Sp} \exp \left\{ \beta(\mu_0 N_0 - H_0) + n^0(\mu_1) \int e^{-\beta(g\rho_0(\mathbf{r}) + \chi(\mathbf{r}))} dV \right\}. \tag{12}$$

Hence, we find

$$G_{11}(\mathbf{r}, \mathbf{r}') = [an^0(\mu_1)]^2 G_{00}(\mathbf{r}, \mathbf{r}'). \tag{13}$$

Analogously,

$$G_{10}(\mathbf{r}, \mathbf{r}') = an^0(\mu_1) G_{00}(\mathbf{r}, \mathbf{r}'). \tag{14}$$

As regards $G_{00}(\mathbf{r}, \mathbf{r}')$, functionally it coincides with the correlator of the densities in the pure substance with values of β and μ changed in accordance with (9). An analogous renormalization of the critical temperature occurs in an antiferromagnet placed in an external magnetic field. For the proof, we can make use of the expansion of the partition function in a series in powers of the magnetic field. In the non-zero even terms of the series, the coefficients are lattice sums of spin correlators of the corresponding order. In these coefficients, the spin sums S_+ over neighboring sublattices are weakly singular quantities (the role of the order parameter is played by the difference of the sublattice moments). Therefore, the correlators S_+ fall off rapidly with increasing distance. It can be assumed that the correlators are non-zero when the points in them coincide pairwise. We expand the quantity S_+^2 in the basis of the algebra and confine ourselves to the term proportional to $\hat{\varepsilon}$. The series obtained is easily identified with the initial partition function, with the shifted temperature $\tau^* = \tau - \text{const} \cdot H^2$.

We emphasize that we do not know how to elucidate in advance which quantity plays the role analogous to that of the chemical potential in the case of the mixture. This must be ascertained specially for each specific case.

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