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Method of Symmetry-Breaking Potential in Statistical Mechanics of the Long-Range Order

Huzio NAKANO and Masumi HATTORI*

Department of Applied Physics
Nagoya University, Nagoya
**Department of Physics*
Nagoya Institute of Technology, Nagoya

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In investigating a long-range ordering in a certain system, it is required to obtain the free energy of the system as a function of the long-range order parameter σ, which is given by

$$F(\sigma)=-kT\ln Z'(\sigma), \tag{1}$$

where $Z'(\sigma)$ is the partition function in a sub-Γ space designated by the value σ. The thermal-equilibrium value of σ is determined by minimizing $F(\sigma)$ with respect to it.

It is easier to calculate the canonical partition function $Z(\eta)$ than $Z'(\sigma)$, where $Z(\eta)$ is given by

$$Z(\eta)=\sum e^{\eta\sigma}Z'(\sigma). \tag{2}$$

The summation (integration) over σ in (2) is taken over the whole Γ-space. The canonical average of σ can be obtained from (2) as

$$\sigma=\partial\ln Z(\eta)/\partial\eta. \tag{3}$$

Evaluating (2) by means of the saddle-point method, we get

$$Z(\eta)\cong e^{\eta\sigma^\dagger}Z'(\sigma^\dagger)\,[2\pi/d^2\ln Z'(\sigma^\dagger)/d\sigma^{\dagger 2}]^{1/2}, \tag{4}$$

where the saddle-point $\sigma^\dagger$ is determined by the equation

$$\eta=-\partial\ln Z'(\sigma^\dagger)/\partial\sigma^\dagger. \tag{5}$$

By substituting (4) into (3) and by making use of the relation (5), we can see that $\sigma=\sigma^\dagger$ except for a negligible fluctuation term and therefore $\sigma^\dagger$ in (5) can be substituted for σ. By making use of (1) and (5) we thus obtain

$$F(\sigma)=F(0)+kT\int_0^\sigma\eta d\sigma, \tag{6}$$

where η as a function of σ is obtained by solving (3). The minimum condition for the free energy (6) is expressed as $\eta=0$.

In quantum-mechanical case, $Z'(\sigma)$ is expressed as

$$Z'(\sigma)=\mathrm{Tr}_\sigma\exp(-\beta H)=\sum_i\langle\sigma,i|e^{-\beta H}|\sigma,i\rangle \tag{7}$$

where Tr_σ denotes the diagonal sum in the subspace designated by the eigenvalue σ, H represents the Hamiltonian of the system and i denotes the quantum number composing a complete set of orthogonal states $|\sigma,i\rangle$ together with the quantum number σ. Thus $Z(\eta)$ defined by (2) can be rewritten as

$$\begin{aligned}Z(\eta)&=\sum_\sigma\sum_i e^{\eta\sigma}\langle\sigma,i|e^{-\beta H}|\sigma,i\rangle\\&=\mathrm{Tr}(e^{\eta\sigma}e^{-\beta H}).\end{aligned} \tag{8}$$

Kramers and Opechowski[1] have discussed an expression such as (8) for the ferromagnetic system, in which η and σ represent the external magnetic field and the orthogonal component of the total magnetization parallel to that field, respectively. In this case in which σ commutes with H, the diagonal sum in (8) can be rewritten as $\mathrm{Tr}(e^{\eta\sigma-\beta H})$. In general, it is necessary to use two or more parameters, $\sigma_1,\cdots,\sigma_n$. The antiferromagnetic system is one of such cases, where σ_1 and σ_2 are the sublattice magnetizations parallel to the easy axis. We get in this case

$$Z(\eta_1,\eta_2)=\mathrm{Tr}(e^{\eta_1\sigma_1+\eta_2\sigma_2}e^{-\beta H}), \tag{9}$$

from which the thermal averages of the sublattice magnetizations are obtained as

$$\sigma_j=\partial\ln Z/\partial\eta_j. \quad (j=1,2) \tag{10}$$

Assuming that $\eta_1=-\eta_2\equiv\eta$, we get the re-

lation (4) for $\sigma \equiv \sigma_1 - \sigma_2$, where Z is given by (8). As σ does not commute with H, (8) is unequal to $\mathrm{Tr}(e^{\eta\sigma-\beta H})$ in this case. Similarly (9) does not equal to $\mathrm{Tr}(e^{\eta_1\sigma_1+\eta_2\sigma_2-\beta H})$. The canonical partition function of the form (9) has already been presented for antiferromagnetism by Kubo, Obata and Ohno.[2]

In the case of a classical system we define

$$Z(\eta(q)) = \int\cdots\int dp_1\cdots dp_f dq_1\cdots dq_f \times \exp[\sum_{i=1}^{f}\eta(q_i) - \beta H(p_1,\cdots,q_f)], \quad (11)$$

where $H(p_1,\cdots,q_f)$ denotes the Hamiltonian of the system with f degrees of freedom as a function of f pairs of generalized momenta and coordinates. By taking the functional derivative of (11) we get the average of the density

$$\rho(q) = \delta \ln Z(\eta(q))/\delta\eta(q). \quad (12)$$

By assuming $\eta(q) = \eta\sigma(q)$ with a given parameter η and a given function $\sigma(q)$ of q, (11) can be rewritten as

$$Z(\eta) = \int\cdots\int dp_1\cdots dp_f dq_1\cdots dq_f \times \exp[\eta\sum_{i=1}^{f}\sigma(q_i) - \beta H(p_1,\cdots,q_f)]. \quad (13)$$

Using (13), we get

$$\int \rho(q)\sigma(q)dq = \partial \ln Z(\eta)/\partial\eta. \quad (14)$$

We assume that $\sigma(q)$ (q denoting the space coordinate) is equal to $1/V'$ in a large number of spots with volume V' in total composing a lattice and is equal to $1/V''$ in the remaining volume V'', where $V'+V''$ equals the total volume of the system. On this assumption, (14) reduces to (3), where σ represents the difference between the densities in the volumes V' and V''. By substituting the solution of (3) into (6), we get the free energy. The finite σ as a solution of (7) corresponds to the solid phase and the vanishing σ to the liquid phase. In the case that q denotes the solid angle of the molecular orientation, the finite and vanishing σ's correspond to the ordered and disordered phases of the system of oriented molecules, respectively.

In this way, the method of symmetry-breaking potential is applicable to investigation of phase transitions in various systems. The present authors and Adachi[3] have studied the magnetism of the cobalt-dichalcogenide series $Co(S_xSe_{1-x})_2$, based on the free energy (6). Our research group is furthermore studying the melting phenomena[4] and orientational phase transitions of quantal as well as classical rotor systems (solid hydrogen and liquid crystal systems).

Classical thermodynamics does not necessarily supply a principle sufficient for the quantum-mechanical problem. In this respect the present method sometimes need be reconsidered. In particular, in the case of superfluidity, in which the quantized wave function ψ corresponds to an order parameter,[5] we cannot give the partition function (8) because we have no complete set of pairwisely orthogonal eigenfunctions of ψ. In this connection the overcomplete set of eigenfunctions of the annihilation operator for the Boson system[6] may be useful. We can only give in this case[7]

$$Z(\eta) = \mathrm{Tr}[\exp\{\eta\psi + \eta^*\psi^+ - \beta(H-\mu)\}], \quad (15)$$

where μ denotes the chemical potential. The notion of quantum-statistical ordering will be needed in order to get a unified insight into low temperature phenomena, including various cooperative alignments of spins.[8]

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Note added:

For the liquid system an equivalent method was proposed from a viewpoint of the grand-canonical ensemble by T. Morita and K. Hiroike [Prog. Theor. Phys. **25** (1961), 537]. The authors would like to thank Professor Hiroike who pointed it out.