NEGATIVE AND LIMITING TEMPERATURES

Yu. B. RUMER

Institute of Radio Physics and Electronics, Siberian Section, Academy of Sciences, U.S.S.R.

Submitted to JETP editor February 16, 1960

J. Exptl. Theoret. Phys. (U.S.S.R.) **38**, 1899-1902 (June, 1960)

It is shown that in the mathematical apparatus of statistical physics the possibility of the existence of negative and limiting positive temperatures in a thermodynamic system is connected with the analyticity of the sum of states as a function of the reciprocal of the temperature.

A number of papers in recent years have explained the usefulness of considering the "partition function" $Z(\lambda)$ for a thermodynamic system not only for real positive values of the temperature variable $\beta = 1/kT$ Re λ, but also in the entire complex plane. In fact, if we write $Z(\lambda)$ as a Laplace integral

$$Z(\lambda) = \int_0^\infty \rho(E) e^{-\lambda E} dE, \qquad (1)$$

where $\rho(E)$ is the spectral density for the energy of the system, then on inverting the transformation (1) we get

$$\rho(E) = \frac{1}{2\pi i} \int_{\sigma - i\infty}^{\sigma + i\infty} Z(\lambda) e^{\lambda E} d\lambda, \qquad (2)$$

where the integral is taken along a straight line Re $\lambda = \sigma$ which lies entirely in the region of analyticity of the function $Z(\lambda)$.

If the energy spectrum is bounded below, then, without loss of generality, we can take the lower limit of the spectrum to be zero. If the energy spectrum of the system is bounded above, i. e., if $\rho(E) = 0$ for $E > E_{max}$, then the function $Z(\lambda)$ is analytic in the entire plane of the variable λ.

If the energy spectrum is not bounded above, then the region of analyticity of the function $Z(\lambda)$ depends on the degree of increase of the function $\rho(E)$. If

$$\log \rho(E)/E \to a \quad \text{as } E \to \infty, \qquad (3)$$

then the function $Z(\lambda)$ is analytic in the entire region Re $\lambda > a$.

From Eq. (1) we obtain in the usual way

$$-\frac{d}{d\lambda} \ln Z(\lambda) = \frac{1}{Z(\lambda)} \int_0^\infty E\rho(E) e^{-\lambda E} dE = \bar{E}(\lambda),$$

$$\frac{d^2}{d\lambda^2} \ln Z(\lambda) = \overline{(E - \bar{E}(\lambda))^2} = \overline{(\Delta E)^2} = -\frac{d\bar{E}(\lambda)}{d\lambda}, \qquad (4)$$

where $\bar{E}(\lambda)$ and $\overline{(\Delta E)^2}$ are the mean energy and the dispersion of the energy according to the complex distribution $\rho(E) e^{-E\lambda}$. On the real axis of the plane of $\lambda = \sigma + i\tau$ these quantities take the real and positive values

$$\bar{E}(\sigma) > 0, \qquad -d\bar{E}(\sigma)/d\sigma > 0. \qquad (5)$$

For large values of the energy E the integral (1) can be calculated approximately by the method of steepest descent. With logarithmic accuracy we have

$$\ln \rho(E) = \ln Z(\beta) + \beta E, \qquad (6)$$

where the saddle point β is a root of the equation

$$Z'(\beta) + Z(\beta) E = 0, \qquad (7)$$

or, when we take the definition (4) into account, a root of the equation

$$\bar{E}(\beta) = E. \qquad (7')$$

We shall prove that the saddle point lies on the real axis. Differentiating Eq. (6) with respect to E and regarding β as a function of E defined by the equation (7), we get

$$\frac{d \ln \rho(E)}{dE} = \left(\frac{Z'(\beta)}{Z(\beta)} + E\right) \frac{d\beta}{dE} + \beta = \beta. \qquad (8)$$

Since the left member of Eq. (8) is real, we must have Im $\beta = 0$.

We shall prove that the saddle point is unique. If the energy spectrum is not bounded above, then from the definition (4) it follows that

$$\bar{E}(a) = \infty, \qquad \bar{E}(\infty) = 0.$$

Since in virtue of Eq. (5) the function $\bar{E}(\sigma)$ decreases monotonically in the range $a < \sigma < \infty$, taking all values from ∞ to 0, the equation (7) has one and only one root.

If the energy spectrum is bounded above, the function $\bar{E}(\sigma)$ falls off monotonically in the interval

$$\bar{E}(-\infty) = E_{max} < E(\sigma) < E(\infty) = 0$$

and (7) has one solution in the interval $-\infty < \beta < \infty$.

We see from (4), (6), and (8) that

$$F(\beta) = -\beta^{-1} \ln Z(\beta), \qquad S(E) = \ln \rho(E), \qquad kT = 1/\beta \quad (9)$$

are the free energy, entropy, and temperature of the system. One usually considers thermodynamic systems in which $\rho(E)$ does not increase with the energy faster than algebraically, i. e., $\ln \rho(E)/E \to 0$ as $E \to \infty$, and consequently $Z(\lambda)$ is an analytic function of the complex variable λ in the entire right-hand half-plane.

We shall study here two examples of "unusual" thermodynamic systems for which negative and limiting temperatures exist.

THE ISING MODEL

As is well known (cf., e. g., reference 1) for large n the sum of states $Z(\lambda)$ of a linear Ising chain consisting of n sites has the form

$$Z(\lambda) = (2\cosh J\lambda)^n, \quad (10)$$

where J is the interaction energy between similarly directed adjacent spins. In the derivation of Eq. (11) it is assumed that the interaction energies of similarly and oppositely directed spins have opposite signs. If we take the interaction energy of similarly directed spins to be zero, and that of oppositely directed spins to be 2J, Eq. (10) takes the form

$$Z(\lambda) = (2\cosh J\lambda e^{-J\lambda})^n. \quad (11)$$

Calculating $\rho(E)$ according to Eq. (2) by the method of steepest descents on the assumption $E/n = \epsilon$ (with the ratio ϵ finite for large n), we get

$$\ln \rho(E) = n[\ln(2\cosh J\beta) + \beta\varepsilon - J\beta], \quad (12)$$

where β is the root of the equation

$$\bar{\varepsilon}(\beta) = J(1 - \tanh J\beta) = \varepsilon. \quad (13)$$

Since the energy spectrum of the lattice is bounded above, arbitrary values of β are possible. It is not hard to show that the value $\beta = 0$ ($T = \infty$, $\bar{\epsilon} = J$) corresponds to complete absence of short-range order; $\beta = +\infty$ ($T = 0$, $\bar{\epsilon} = 0$) corresponds to the establishment of complete short-range order, with adjacent spins parallel; for $\beta = -\infty$ the spins are antiparallel. It is known, however, that in the linear Ising lattice there is no temperature whatever at which long-range order is established.

The situation is different for the plane Ising lattice. Here, as in the case of the one-dimensional chain, arbitrary values of β are possible. The formula found by Onsager[2] for the free energy $f(\beta)$ per site of the lattice

$$f(\beta) = \frac{1}{\beta}\left[\frac{1}{2}\ln 2 + \frac{1}{2\pi^2}\int_0^\pi\int_0^\pi \ln[\cosh^2 2J\beta - \sinh 2J\beta(\cos\omega + \cos\omega')]\, d\omega d\omega'\right] \quad (14)$$

(as before, J is the coupling constant between adjacent spins) is invariant with respect to the interchange $\beta \to -\beta$. It is well known that the plane Ising lattice has the property of ferromagnetism and makes a phase transition of the second kind with a logarithmic discontinuity of the specific heat at $\beta = \beta_c$, where β_c is given by the equation

$$\sinh 2J\beta_c = 1. \quad (15)$$

From what has been said it follows that the plane lattice also makes one other phase transition, at the negative temperature given by the equation

$$\sinh 2J\beta_c = -1. \quad (16)$$

If for $\beta_c > 0$ the contribution to the singular part of the integral (14) is given by $\omega, \omega' = 0$, which corresponds to ferromagnetic ordering, then for $\beta_c < 0$ the main contribution to the singularity comes from $\omega, \omega' = \pi$, i. e., the transition point is antiferromagnetic.

Obviously the presence of positive and negative Curie points, corresponding to transitions to ferromagnetic and antiferromagnetic states, is also characteristic of the Heisenberg model (provided, of course, that it leads to any phase transition at all).

GAS OF NONINTERACTING PARTICLES IN AN EXTERNAL FIELD WITH AN ASYMPTOTICALLY LOGARITHMIC POTENTIAL

In the space between the planes $z = 0$ and $z = H$ let there be an ideal gas consisting of N particles of mass m, which are in an axially symmetrical field (z, r, φ are cylindrical coordinates):

$$U(r) = \begin{cases} 0 & r < a \\ 2U_0 \ln(r/a) & r > a. \end{cases} \quad (17)$$

It is not hard to see that in this case the statistical weight $\rho(E)$ increases exponentially with increase of $E[\rho(E) \sim \exp(E/U_0)]$. Therefore it is to be expected that such a system possesses a limiting temperature. We shall confirm this supposition by an exact calculation.

We have for the sum of states per particle

$$Z(\lambda) = \left(\frac{2\pi m}{\lambda}\right)^{3/2} 2\pi H \int_0^\infty e^{-\lambda U(r)} r dr = \frac{\pi H (2\pi m)^{3/2} a^2}{\lambda^{5/2}(\lambda U_0 - 1)}. \quad (18)$$

This formula is true for $\lambda U_0 > 1$. For $\lambda U_0 < 1$ the integral diverges. Thus these exists a limiting temperature $T^* = U_0$, above which the system cannot be heated.

The physical cause of the phenomenon is that because of the slowness of the increase of the potential the particles spread very far apart as their energy increases, and their kinetic energy is small in comparison with their potential energy.

[1] T. L. Hill, Statistical Mechanics, Chapter 7 (McGraw-Hill Book Company, 1956).

[2] Yu. B. Rumer, Usp. Fiz. Nauk 53, 245 (1954).

Translated by W. H. Furry
363