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Thermodynamic Potentials for Systems at Negative Absolute Temperatures*

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It is shown on purely phenomenological grounds that for systems in equilibrium at negative absolute temperatures all the usual thermodynamic potentials, and in particular the energy, attain a maximum value instead of a minimum value.

RECENTLY Coleman and Noll¹ have shown in a rather indirect way (by use of a statistical model) that for a system at negative absolute temperature the state of equilibrium with fixed entropy and certain other fixed extensive parameters is that in which such a system has its maximum energy. For the corresponding situation at positive absolute temperature the equilibrium state is of course that in which the system has its minimum energy.

It is the purpose of this note to point out that well-known thermodynamic considerations can immediately prove that for negative absolute temperatures all the usual thermodynamic potentials, of which the energy is but one, tend to a maximum instead of to a minimum for systems in equilibrium.

We write the first law of thermodynamics for a given closed system as

$$dE = dQ - dW, \quad (1)$$

where dQ is the heat taken up and dW is the work done by the system for an increment dE in its energy. For our purposes, we need only explicitly consider pressure-volume work so that

$$dE = dQ - PdV. \quad (2)$$

The entropy change of the system may be split into two parts² since it may vary for two reasons only, either by exchange of entropy with the surroundings or by creation of entropy inside the system. If these two con-

tributions are written $d_e S$ and $d_i S$, respectively,

$$dS = d_e S + d_i S. \quad (3)$$

The classical definition of the second law leads to

$$\begin{aligned} d_e S &= dQ/T, \\ d_i S &= 0, \quad \text{reversible change,} \\ d_i S &> 0, \quad \text{irreversible change,} \end{aligned} \quad (4)$$

with T the absolute temperature. As pointed out by Ramsey³ this definition need not be changed for systems at negative absolute temperatures since deductions from it cover all the experimental facts in a consistent way.

Substitution of (3) and (4) into (2) gives

$$dE = TdS - Td_i S - PdV. \quad (5)$$

For a change at constant entropy and volume and positive temperature,

$$-dE \geq 0,$$

where the equality holds only for a reversible change, i.e., only for the strictly equilibrium situation. The energy may thus be termed a thermodynamic potential for the variables S and V and at equilibrium this potential attains its minimum value. The opposite is true for negative absolute temperatures where

$$+dE \geq 0.$$

If additional types of work terms had been included in Eq. (2), we should only have had to specify the corresponding extensive parameters to be held constant (in addition to V) for E to be an appropriate potential. For open systems we would have had to specify fixed mole numbers in addition, but the statement that the

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¹ B. D. Coleman and W. Noll, *Phys. Rev.* **115**, 262 (1959).

² E. A. Guggenheim, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1959), Vol. III, Part 2, p. 1.

³ N. F. Ramsey, *Phys. Rev.* **103**, 20 (1956).

energy has its maximum value for a system in equilibrium at a negative temperature would remain valid.

If $d_i S$ be written formally as

$$d_i S \equiv dQ'/T,$$

thereby introducing the "uncompensated heat," dQ' , of Clausius⁴ this heat must be *negative* or zero for systems at negative absolute temperatures.

We may consider all the other usual thermodynamic potentials in the same way. The heat content or enthalpy H is defined as

$$H = E + PV. \quad (6)$$

Substitution into (5) gives

$$dH = TdS - Td_i S + VdP. \quad (7)$$

For a change at constant S and P at positive temperatures

$$-dH \geq 0,$$

while for negative temperatures

$$+dH \geq 0.$$

⁴ See, for example, I. Prigogine and R. Defay, *Chemical Thermodynamics* (Longman's Green and Company, New York, 1954), Chap. III.

The Helmholtz free energy, F , is defined as

$$F = E - TS. \quad (8)$$

Substitution into (5) gives

$$dF = -SdT - Td_i S - PdV. \quad (9)$$

F is the appropriate potential for constant T and V and at positive temperatures

$$-dF \geq 0,$$

while for negative temperatures

$$+dF \geq 0.$$

The Gibbs free energy, G , is defined as

$$G = H - TS = E + PV - TS. \quad (10)$$

Substitution into (5) gives

$$dG = -SdT - Td_i S + VdP. \quad (11)$$

G is the appropriate potential for constant T and P and at positive temperatures

$$-dG \geq 0$$

while for negative temperatures

$$+dG \geq 0.$$

Effects of Collisions on the Cyclotron Radiation from Relativistic Particles*

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The effects of collisions on the cyclotron radiation from relativistic particles are investigated, supposing a uniform velocity for the particles. For the collision process it is assumed that the particles start to radiate at a certain time and are abruptly stopped by the collision, after which they start to radiate again with random phase. The probabilities for the occurrence of a certain time interval between two collisions are then assumed to be distributed according to a statistical law.

The field equations are derived from the familiar Liénard-Wiechert potentials and Fourier-analyzed. Simple integral representations are found for the combined spectral and angular

distribution of the radiation. Under the basic assumption that the particles make many revolutions between two collisions, it is shown that the radiation pattern is that of a series of spectral lines, each having a dispersion profile. The relative intensities of the lines are given by the formula well known from previous work neglecting collisions.

For the "slightly relativistic" energy range, $\beta_0 = 0.5-0.9$, of interest to thermonuclear experiments, graphs are given for the actual intensity distribution of the various harmonics as a function of the angle between the observer and the orbital plane.

1. INTRODUCTION

THERE are three major processes which are of interest for the spectral and angular distribution of radiation from any assembly of particles: Doppler effects due to collective or individual motions of the particles with respect to the observer, energy losses due to the emission of radiation, and disturbances of the wave trains due to collisions of the radiating particles.

There is, of course, no general rule to describe the various effects, since their consequences depend largely on the type of radiating particle and its quantum state. While usually the radiation characteristics can be said to be "continuous" or to form a spectral "line," according as the emission is from a free or a bound particle, the cyclotron or synchrotron¹ radiation

¹ The terms cyclotron radiation and synchrotron radiation are sometimes restricted in the literature to the radiation from either nonrelativistic or relativistic particles, respectively. We do not think that this semantic distinction is of great importance.

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