

XII. STATISTICAL THERMODYNAMICS*

Prof. L. Tisza
P. M. Quay†

In our previous report (Quarterly Progress Report, July 15, 1957, p. 118) we outlined the statistical phenomenological postulates that are sufficient for a rigorous derivation of the canonical distribution law of a thermodynamic system in which the energy is the only extensive variable that is subject to random fluctuations.

The canonical probability density function of the distribution of the energy u is

$$P(u/\beta) = g(u) e^{-\beta u} Z(\beta)^{-1} \quad (1)$$

where $\beta = 1/kT$, k is Boltzmann's constant, T is the absolute temperature, $g(u)$ is a structure function that depends only on the properties of the system, and $Z(\beta)$ is the partition sum determined from the normalization condition of the probability density function as

$$Z(\beta) = \int_0^{\infty} g(u) e^{-\beta u} du \quad (2)$$

It is assumed that the energy spectrum has no upper bound, and its lower bound is chosen as the zero of the energy.

By introducing the concept of entropy, it is, on the foregoing basis, possible to develop a theory which is phenomenological in the sense that the probabilistic elements are all implicit in the entropy definition. Otherwise, the theory is more general than traditional thermostatics, since fluctuations are taken into account. In the terminology of the Quarterly Progress Report, April 15, 1957, p. 166, we have an Ic theory instead of the classical II theory.

As a first step toward the definition of the entropy, we introduce the index of probability,

$$s(u, \beta) = k \ln \frac{g(u)}{P(u/\beta)} = k [\beta u + \phi(\beta)] \quad (3)$$

Here

$$\phi(\beta) = \ln Z(\beta) = -A(T)/kT \quad (4)$$

* This research was supported in part by the U. S. Air Force, Office of Scientific Research, Air Research and Development Command, under Contract AF49(638)-95. Reproduction in whole or in part is permitted for any purpose of the United States Government.

† National Science Foundation Predoctoral Fellow.

(XII. STATISTICAL THERMODYNAMICS)

is the Mathieu function, and $A(T)$ is the Helmholtz free energy. Since the energy u is a random variable, the same is true of $s(u, \beta)$.

In order to define the thermodynamic phenomenological entropy, we have to distinguish two cases:

- (i) the system is in contact with a reservoir of temperature T , hence β is constant.
- (ii) the system is isolated and has a fixed energy u .

These two cases correspond to the canonical and microcanonical ensembles of statistical mechanics. The discussion of the first case closely parallels the traditional method, and we shall confine ourselves to a short summary of the relevant formulas. The discussion of case ii has entirely novel features.

In case i the entropy is defined as the average of the random variable (see Eq. 3),

$$S(\beta) = \overline{s(u, \beta)} = k\beta\bar{u} + k \phi(\beta) \tag{5}$$

$$= \int_0^{\infty} P(u/\beta) \ln \frac{g(u)}{P(u/\beta)} du$$

The thermodynamic properties of the system are contained in the fundamental equation

$$\phi(\beta) = \frac{1}{k} S(\beta) - \beta U = -A(T)/kT \tag{6}$$

where

$$U = \bar{u} = -\frac{\partial \phi}{\partial \beta} \tag{7}$$

The energy fluctuation is

$$\overline{\Delta u^2} = \frac{\partial^2 \phi}{\partial \beta^2} > 0 \tag{8}$$

We turn now to case ii. The procedure most frequently applied is to define the entropy for an isolated system as

$$S = k \ln g(u) \tag{9}$$

The proper definition of the temperature is somewhat problematic in this case (1). Following a suggestion of Mandelbrot (2), we have assigned a temperature to isolated systems by using the maximum likelihood method of mathematical statistics (3). We found that in the present context the use of this method can be made plausible on the grounds of simple physical considerations.

Let us assume that before its isolation the system reached its state of energy u_0 through contact with a reservoir of temperature $T = 1/k\beta$. In classical thermostatics,

(XII. STATISTICAL THERMODYNAMICS)

an I1 theory, there is a unique functional relation between u_o and β . This is not true in the Ic theory, in which the energy is allowed to fluctuate within a canonical distribution. However, it is still possible to estimate the temperature.

Following the method of maximum likelihood estimation, we require that the probability density function (1), or more conveniently its logarithm, should be maximum in its dependence on β . Hence

$$\frac{\partial \ln P(u|\beta)}{\partial \beta} = -\frac{\partial \phi}{\partial \beta} - u_o = 0 \quad (10)$$

$$-\frac{\partial^2 \phi(\beta_o)}{\partial \beta^2} < 0 \quad (11)$$

if β_o is the solution of Eq. 10.

If we compare Eq. 7 with Eq. 10, we see that $1/k\beta_o$ is that temperature for which the canonical average is $\bar{u} = u_o$. This is consistent with the I1 theory, in which fluctuations are altogether neglected. However, in the present case the determination of the temperature from Eq. 10 is not sharp. Expanding $\ln P(u|\beta)$ as a function of β around β_o , and breaking off at the quadratic terms, we find that the estimated reciprocal temperatures have a standard deviation $\Delta\beta$ that obeys the relation

$$\Delta u \Delta\beta = k \quad (12)$$

where Δu is the standard deviation (rms fluctuation) of the energy in the canonical distribution of the temperature $1/k\beta_o$.

This relation has an interesting physical meaning. The transition from the present Ic theory to the I1 theory corresponds to a limiting process:

$$k \rightarrow 0, \Delta u \rightarrow 0, \Delta\beta \rightarrow 0 \quad (13)$$

In the I1 theory there is no difference between an isolated system of energy u_o and a system that is in contact with a reservoir, provided that $u_o = \bar{u}$. Moreover, both u and $\beta = 1/kT$ have sharp values, i.e., the energy of a system uniquely determines the temperature of the surroundings with which it might be in equilibrium, and, conversely, the temperature of a reservoir uniquely determines the energy of the system with which it is in contact.

The approximate validity of Eq. 13 assures us that the I1 theory is approximately correct. However, large values of Δu or $\Delta\beta$ are indications that in singular situations the phenomenological theory is close to the limits of its usefulness.

At a critical point, the energy fluctuations are very great ($\Delta u \rightarrow \infty$), hence the energy is not precisely determined by the reservoir temperature. The singularity at absolute zero exhibits the opposite features: $\Delta u \rightarrow 0$, $\Delta\beta \rightarrow \infty$. Physically, this means

(XII. STATISTICAL THERMODYNAMICS)

that with such low temperatures that the specific heat very nearly vanishes, the knowledge of the energy of the system does not enable us to draw any reliable inferences about the temperature of the surroundings. This means, in simple terms, that a substance with nearly vanishing specific heat is not an appropriate thermometric substance, which is well known to low-temperature physicists.

While the Ic theory is a great improvement over the I1 theory, as far as describing the aforementioned singular situations is concerned, the difficulties connected with these situations have not all been removed and call for further analysis.

L. Tisza, P. M. Quay

References

1. A. I. Khinchin, *Statistical Mechanics* (Dover Publications, Inc., New York, 1949), p. 142.
2. B. Mandelbrot, 1956 Symposium on Information Theory, held at M.I.T., Cambridge, Massachusetts, Sept. 10-12, 1956; *Trans. IRE*, vol. IT-2, no. 3, pp. 190-203 (Sept. 1956).
3. Cf. B. L. Van der Waerden, *Mathematische Statistik* (Springer Verlag, Berlin, 1957), p. 148.