# III. STATISTICAL THERMODYNAMICS[*]

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## A. CANONICAL AND MICROCANONICAL ENSEMBLES

Some time ago, we developed a formalism for the statistical thermodynamics of systems in thermodynamic equilibrium (1). Although it is closely related to traditional methods, the precise nature of this relation at first appeared obscure. The difficulty can be traced to an ambiguity in the use of ensembles in statistical mechanics, connected with the incomplete separation of two logical structures in the theory. It is, of course, well known that classical statistical mechanics can be developed from both the Boltzmann and the Gibbs points of view. However, the two lines of thought have never been completely disentangled, nor is it obvious what the distinctive features are that ought to be emphasized. The following analysis is felt to be useful in clarifying the concept of statistical ensembles.

In the Boltzmann scheme, a small subsystem of a large isolated system is described by a canonical distribution function. The large isolated system can be assumed to exist in many identical samples, and these may be said to form a microcanonical ensemble.

In the Gibbs scheme, one considers a finite system interacting with an infinite reservoir of definite temperature. The canonical, or temperature, ensemble is now defined as a set of systems interacting with the reservoir of given temperature and exhibiting a random distribution of the energy. The microcanonical, or energy, ensemble consists of systems within a narrow range of energy $u < U < u+du$, and is a subset of a canonical ensemble. The microcanonical ensemble has no definite temperature because we cannot ascertain the temperature of the reservoir with which it was last in contact.

Even though the Gibbsian ideas have been widely used, they have not been developed as a self-contained logical structure. In particular, Gibbs postulated the canonical ensemble merely on the basis of plausibility. This gap in the theory was filled by the use of considerations that belong to the Boltzmann context. In fact, the use of Liouville's theorem for establishing a priori probabilities seemed to require the use of an isolated microcanonical system as a point of departure.

The autonomous development of the Gibbsian concept of ensembles is possible if use is made of some of the techniques of mathematical statistics, such as the theory of parameter estimation. The importance of these methods for statistical thermodynamics

was first recognized by Mandelbrot (2). We shall outline the main aspects of the theory. For details we refer to our previous work (1) and to Mandelbrot (2). Further details will be given in a paper that is being prepared for publication in collaboration with P. M. Quay.

We consider an ensemble of systems, the energy, U, of which is a random variable. The randomness results from contact with a reservoir of temperature $1/\beta$ (Boltzmann's constant $k = 1$). Given $\beta$, the probability density of the energy u is given by the canonical distribution function

$$f(u/\beta) = g(u) \, e^{-\phi(\beta)-\beta u} \tag{1}$$

where $\phi$ is the logarithm of the partition sum; it is also called the Massieu function. The so-called structure function $g(u)$ depends only on the properties of the system and can be identified with the density of the quantum-mechanical energy spectrum. Equation 1 can be derived by using a phenomenological randomness assumption of Szilard (1, 2).

From Eq. 1, we obtain the average and the variance of the energy

$$\bar{u} = -\frac{d\phi}{d\beta} \tag{2}$$

$$\sigma_u^2 = \overline{(u-\bar{u})^2} = \frac{d^2\phi}{d\beta^2} \tag{3}$$

In order to establish contact with thermodynamics, we have to define the entropy in statistical terms. We consider Gibbs' index of probability, or random entropy function,

$$s(u, \beta) = \ln \frac{g(u)}{f(u/\beta)} = \phi + u\beta \tag{4}$$

that is a measure of the diffuseness of the distribution $f(u/\beta)$.

We define the canonical entropy as the average $\bar{s} = s(\bar{u}, \beta)$. Since Eq. 2 can be solved for $\beta = \beta(\bar{u})$, we obtain two fundamental equations connected by a Legendre transformation:

$$\bar{s} = s(\bar{u}) \tag{5}$$

$$\phi = \phi(\beta) = \bar{s} - \bar{u}\beta \tag{6}$$

We turn now to the discussion of the microcanonical method. We consider a system of given energy, $u_o$, and estimate the reservoir temperature that is most likely to impart such an energy to the system. Physically, this is the main problem of thermometry. It is, in fact, possible to calibrate a thermometer by means of controlled addition of energy.

We obtain the "maximum likelihood estimate" $\tilde{\beta}$ of the reciprocal temperature by solving the equation

$$\frac{\partial \ln f(u_o/\beta)}{\partial \beta} = -\frac{\partial s(u_o, \beta)}{\partial \beta} = -\frac{d\phi}{d\beta} - u_o = u(\tilde{\beta}) - u_o = 0 \qquad (7)$$

The microcanonical entropy is defined as

$$\tilde{s} = \min\{s(u_o, \beta)\} = \phi(\tilde{\beta}) + u_o\tilde{\beta} \qquad (8)$$

Eliminating $\tilde{\beta}$ from Eq. 7, we obtain

$$\tilde{s} = s(u_o) \qquad (9)$$

By comparing Eq. 9 with Eq. 5 and using Eq. 7, we find that the microcanonical entropy is the same function of the fixed energy as the canonical entropy is of the average energy. In particular, $\bar{s}(\bar{u}) = \tilde{s}(u_o)$, if $\bar{u} = u_o$. While the canonical entropy is associated with the uncertainty of the energy of individual members of the ensemble, the microcanonical entropy is connected with the uncertainty of the temperature. These conclusions remain valid for small systems in which fluctuations are of importance.

The microcanonical ensemble $u < U < u{+}du$ leads, also, to another kind of question. If we divide the system by an adiabatic partition, the probability density of a partition $u' + u'' = u$ is given by

$$p(u'/u_o) = \frac{g'(u') \, g''(u'')}{g(u)} \qquad (10)$$

This expression can be made the point of departure for the Boltzmann scheme. The entropy is now defined as

$$\overset{\wedge}{s}(u) = \ln g(u) \, du \qquad (11)$$

This quantity is somewhat smaller than $\tilde{s}$, but, for isolated systems, it is a formally correct alternative definition. Definition 11 is often used for subsystems with fluctuating energy, although, formally, this is not correct, since $\overset{\wedge}{s}$ is not rigorously additive for systems with fluctuating energy. The error can be estimated by comparing the correct $\bar{s}(\bar{u})$ with $\overset{\wedge}{s}(\bar{u})$.

We assume that the canonical distribution is approximated by a Gaussian distribution:

$$f(u) = g(u) \, e^{-\phi-\beta u} \approx \frac{du}{\left(2\pi\sigma_u^2\right)^{1/2}} \exp\left[-(u-\bar{u})^2 \Big/ \left(2\sigma_u^2\right)\right] \qquad (12)$$

Hence

$$\overset{\wedge}{s}(\tilde{u}) = \ln g(\bar{u}) \, d\bar{u} \approx \bar{s}(\bar{u}) + \ln \frac{d\bar{u}}{2\pi\sigma_u^2} \qquad (13)$$

The correction term is generally small, and vanishes for $d\bar{u} \approx \sigma_u$; that is, if a

"coarse-grained" distribution extending beyond the standard deviation is used.

It can be shown, from Eq. 10, that the energy of a small subsystem is distributed according to the canonical distribution. This follows easily, if definition 11 is used for the complementary large subsystem (3). The rigorous proof is quite involved (4).

Finally, we comment on the well-known statement that the Boltzmann method deals with molecules, whereas the Gibbs method deals with the entire macroscopic system. This distinction turns out to be of secondary importance. The Gibbs method can be applied fruitfully to single molecules coupled to a reservoir, and, the Boltzmann method, as described above, can be applied, at least in principle, to macroscopic subsystems.

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## References

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