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THERMODYNAMICS, FLUCTUATION AND STATISTICS

C. G. CHAKRABARTI[1], Calcutta

The paper deals with a statistical theory of thermodynamic equilibrium on the basis of the macroscopic theory of fluctuation.

ТЕРМОДИНАМИКА, ФЛУКТУАЦИИ И СТАТИСТИКА

В работе рассматривается статистическая теория термодинамического равновесия на основе макроскопической теории флуктуаций.

I. INTRODUCTION

The importance of the macroscopic theory of fluctuation in the fundation of a macroscopic theory of statistical thermodynamics was first pointed out by Szilard [1]. The unification of the macroscopic theory of fluctuation with classical thermodynamics was stressed by Lewis [2] and Callen [3]. In some earlier papers [4] we have tried in the spirit of Szilard's work, to develop a macroscopic theory of statistical thermodynamics by incorporating fluctuation in the thermodynamic theory of measurement [5]. In this paper we wish to extend the theory to study the statistical properties of thermodynamic equilibrium of a generalized system.

II. PROBABILITY AND FLUCTUATION

We consider a generalized thermodynamic system immersed in a reservoir $R(\Theta)$ where the parameters $\Theta=(\Theta_1, \Theta_2, \ldots, \Theta_n)$ represent the state of the reservoir $R(\Theta)$. The system is in random interaction with the environment (reservoir) $R(\Theta)$ and this random behaviour of the system is described by the probability distribution $P(\varkappa|\Theta)$ of the set of extensive variables $\varkappa=(\varkappa_1, \varkappa_2, \ldots, \varkappa_n)$ conditioned by the parameters $\Theta=(\Theta_1, \Theta_2, \ldots, \Theta_n)$. The distribution $P(\varkappa|\Theta)$ describes the state of the system in a thermodynamic equilibrium with the environment $R(\Theta)$. Let $P(\varkappa|\Theta+\Delta\Theta)$ be the probability distribution of $\varkappa$ conditioned by the parametric value $\Theta+\Delta\Theta$, where the deviation $\Delta\Theta$ may be due to the spontaneous fluctuation

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[1] Department of Applied Mathematics University of Calcutta, CALCUTTA-700009, India.

in equilibrium or due to the relaxation of the system to equilibrium. $P(\varkappa|\Theta+\Delta\Theta)$ corresponds to a neighbouring non-equilibrium (partial equilibrium) state near the complete equilibrium and has the same functional form as that of $P(\varkappa|\Theta)$ [6]. From the concept of conditional distribution, the information associated with the deviation $\Delta\Theta$ is given according to Rényi [7] by the information-gain

$$K(\Theta+\Delta\Theta|\Theta)=\int \log \frac{P(\varkappa|\Theta+\Delta\Theta)}{P(\varkappa|\Theta)} P(\varkappa|\Theta+\Delta\Theta)\, d\varkappa \,. \tag{1}$$

Again, if $\bar{\omega}(\Delta\Theta)$ be the probability of fluctuation or deviation $\Delta\Theta$, the information associated with the occurrence of the deviation $\Delta\Theta$ is also given by the self-information $-K \log \bar{\omega}(\Delta\Theta)$ (in thermodynamic unit). Accordingly, the probability of fluctuation $\bar{\omega}(\Delta\Theta)$ is given by

$$\bar{\omega}(\Delta\Theta)\sim e^{-K(\Theta+\Delta\Theta|\Theta)}. \tag{2}$$

Expanding $K(\Theta+\Delta\Theta|\Theta)$ in powers of $\Delta\Theta$, we have under some regularity conditions [8]

$$K(\Theta+\Delta\Theta|\Theta)=\frac{1}{2}\sum_{\alpha,\beta} H_{\alpha\beta}(\Theta)\,\Delta\Theta_\alpha\Delta\Theta_\beta\,, \tag{3}$$

where

$$H_{\alpha\beta}(\Theta)=\left\langle\frac{\partial^2 \log P(\varkappa|\Theta)}{\partial\Theta_\alpha\,\partial\Theta_\beta}\right\rangle=\int \frac{\partial^2 \log P(\varkappa|\Theta)}{\partial\Theta_\alpha\,\partial\Theta_\beta} P(\varkappa|\Theta)\, d\varkappa \tag{4}$$

are the elements of Fisher's information matrix $(H_{\alpha\beta})$. With the expression (3), the probability of fluctuation becomes

$$\bar{\omega}(\Delta\Theta)\sim \exp\left(-\frac{1}{2}\sum_{\alpha\beta} H_{\alpha\beta}(\Theta)\,\Delta\Theta_\alpha\Delta\Theta_\beta\right), \tag{5}$$

which is the Gaussian approximation to the probability of fluctuation.

III. FLUCTUATION AND STATISTICS

Fundamental to statistics is the probability distribution $P(\varkappa|\Theta)$, which determines the state of the system in a thermodynamic equilibrium with the environment. However, to find the state for the unknown values of the parameters Θ is to act under uncertainty. This uncertainty is removed from the information about Θ or the deviation $\Delta\Theta$. The measure of information about $\Delta\Theta$ obtained from the distribution (5) is given by the quadratic form $\frac{1}{2}\sum_{\alpha\beta} H_{\alpha\beta}\Delta\Theta_\alpha\Delta\Theta_\beta$. The determination of the probability distribution $P(\varkappa|\Theta)$ then consists in minimizing the

information $\sum_{\alpha\beta} H_{\alpha\beta}\Delta\Theta_\alpha\Delta\Theta_\beta$ subject to the constraints characterizing the thermodynamic equilibrium of the system with the environment. The constraints are the averages of the extensive variables $\langle\varkappa_\alpha\rangle=a_\alpha(\alpha=1, 2, \ldots, n)$. The minimization is equivalent to the discarding of all information about Θ, retaining only the information given in the form $\langle\varkappa_\alpha\rangle=a_\alpha$. The minimization is given by the lower-bound of the information-inequality [8]

$$(\Delta\Theta_\alpha)'(H_{\alpha\beta})(\Delta\Theta_\beta)\geqq(\Delta\Theta_\alpha)'\left(\frac{\partial<\langle\varkappa_\beta\rangle}{\partial\Theta_\alpha}\right)(L_{\alpha\beta})^{-1}\left(\frac{\partial\langle\varkappa_\alpha\rangle}{\partial\Theta_\beta}\right)(\Delta\Theta_\beta) \tag{6}$$

where $L_{\alpha\beta}=\langle\Delta\varkappa_\alpha, \Delta\varkappa_\beta\rangle$ is the co-variance of $\varkappa_\alpha$ and $\varkappa_\beta$ and $(L_{\alpha\beta})^{-1}$ is the reciprocal of the co-variance matrix $(L_{\alpha\beta})$. $(\Delta\Theta_\alpha)'$ is the transpose of the deviation matrix $(\Delta\Theta_\alpha)$. The equality in (6) holds for the expoential distribution

$$P(\varkappa|\Theta)=\exp\left(\sum_\alpha \varkappa_\alpha\Theta_\alpha\right) h(\varkappa)/Z(\Theta), \tag{7}$$

where the parameters Θ_α are determined by

$$\langle\varkappa_\alpha\rangle=\frac{\partial}{\partial\Theta_\alpha}\log Z(\Theta) \qquad (\alpha=1, 2, \ldots, n). \tag{8}$$

The distribution (7) is the generalized canonical distribution, the real form of Θ_α (the relations with temperature, chemical potential etc.) are determined by the connection with thermodynamics. For the equality of (6) we have

$$(H_{\alpha\beta})=\left(\frac{\partial\langle\varkappa_\beta\rangle}{\partial\Theta_\alpha}\right)(L_{\alpha\beta})^{-1}\left(\frac{\partial\langle\varkappa_\alpha\rangle}{\partial\Theta_\beta}\right), \tag{9}$$

from (7) and (8)

$$H_{\alpha\beta}=\left\langle\frac{\partial^2 \log P(\varkappa|\Theta)}{\partial\Theta_\alpha\,\partial\Theta_\beta}\right\rangle=\frac{\partial\langle\varkappa_\beta\rangle}{\partial\Theta_\alpha}=\frac{\partial\langle\varkappa_\alpha\rangle}{\partial\Theta_\beta}, \tag{10}$$

whence from (9) it follows that

$$L_{\alpha\beta}=\langle\Delta\varkappa_\alpha\Delta\varkappa_\beta\rangle=\frac{\partial\langle\varkappa_\alpha\rangle}{\partial\Theta_\beta}=\frac{\partial\langle\varkappa_\beta\rangle}{\partial\Theta_\alpha}, \tag{11}$$

which is the counterpart of the "*Fluctuation-dissipation*" theorem in equilibrium thermodynamics. Also for the positive definiteness of the Fisher information matrix $(H_{\alpha\beta})$ we have

$$H_{\alpha\alpha}=\frac{\partial\langle\varkappa_\alpha\rangle}{\partial\Theta_\alpha}>0 \qquad (\alpha=1, 2, \ldots, n), \tag{12}$$

which are the criteria of stability of the thermodynamic equilibrium. If we put $\alpha = \beta$ in (10), we get the fluctuation of the extensive variables

$$\langle (\Delta \varkappa_\alpha)^2 \rangle = \frac{\partial \langle \varkappa_\alpha \rangle}{\partial \Theta_\alpha} = \frac{\partial^2}{\partial \Theta_\alpha^2} \log Z(\Theta). \tag{13}$$

Finally, for the extensive variable $\varkappa_\alpha$, others kept fixed, then from (5) we have

$$\langle (\Delta \varkappa_\alpha)^2 \rangle \cdot \langle (\Delta \Theta_\alpha)^2 \rangle = 1 \tag{14}$$

or

$$\Delta(\varkappa_\alpha) \cdot \Delta(\Theta_\alpha) = 1, \tag{15}$$

where $\Delta(\varkappa_\alpha)$ and $\Delta(\Theta_\alpha)$ are the root-mean-square deviations of $\varkappa_\alpha$ and Θ_α, respectively. The relations (15) are the phenomenological uncertainty relations between the conjugate variables of the thermodynamic system.

IV. CONCLUSIONS

The theory is based on the incorporation of fluctuation in thermodynamics, but unlike the usual process of considering the deviations in the extensive variables, it is based on the consideration of deviations in the intensive parameters.

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