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FLUCTUATION IN THE SYSTEM WITH NEGATIVE ABSOLUTE TEMPERATURES

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In a recent paper one of us [1] described the conditions for stable equilibrium in the systems with negative absolute temperatures (NAT). These conditions are at NAT

$$\delta E(S, x_i) = 0 \qquad \delta^2 E(S, x_i) < 0 \tag{1}$$

that is the second variation of internal energy $E(S, x_i)$, as function of entropy and generalized coordinates must be negative.

We get the condition (1) directly from the theory of fluctuations. We assume a closed system which is separated in the sub-systems but each of these sub-systems may be taken for a thermodynamic systems and the other sub-systems form surrounding. In the thermodynamical equilibrium the total interna energy is $E = \sum_i E_i$ and the total entropy $S = \sum_i S_i$, where E_i and S_i are the mean energy of i—th system and S_i its maximal value of entropy. For the description of the state of the whole termodynamical system let us choose this characteristic parameters

$$S, x_1, x_2, \ldots, x_n \tag{2}$$

where x_i are generalized coordinates of the equilibrium state. Further let us choose the deviation of the characteristic parameters from their equilibrium state

$$\delta S = S' - S \qquad \delta x_1 = x_1' - x_1, \ldots, \delta x_n = x_n' - x_n \tag{3}$$

where S' and x_i' are entropy and generalized coordinates of nonequilibrium state. It may be easily shown that δS and δx_i are zero in the thermodynamical equilibrium.

The probability of fluctuation of entropy in an adiabatically isolated system is given by Einstein's relation

$$P = \exp\left(\frac{S' - S}{k}\right) \tag{4}$$

where k is Boltzmann's constant. This deviation may be caused by fluctuation of entropy in one sub-system. As $S' - S < 0$ the probability of small fluctuation is much grester than it is in the case of a large fluctuation.

But the non-equilibrium state with entropy S' may be attained by performing work on i-th sub-system at constant entropy S'. In this case S' is the initial equilibrium state. This processes occurs at $S' = \text{const.}$ and therefore the performed work has the minimal value. Also we have for this work A_{min}

$$A_{min} = \Delta E - T\Delta S - \sum_i X_i \Delta x_i \tag{5}$$

where ΔE, ΔS and Δx_i is the deviation of mean energy, entropy and mean generalized coordinates of the assumed sub-system. As we have pointed out that smaller fluctuations are more probable we may use the expansion theorem for $\Delta E(S, x_i)$

$$\Delta E(S, x_i) = \frac{\partial E}{\partial S}\delta S + \sum_i \frac{\partial E}{\partial x_i}\delta x_i + \frac{1}{2}\left\{\frac{\partial^2 E}{\partial S^2}\delta S^2 + \right.$$

$$\left. + \frac{\partial^2 E}{\partial S \partial x_1}\delta S \delta x_1 + \ldots + \frac{\partial^2 E}{\partial x_i \partial x_j}\delta x_i \delta x_j + \ldots + \frac{\partial^2 E}{\partial x_n^2}\delta x_n \delta x_n\right\} \tag{6}$$

It should be noted that expression in brackets is the second variation of internal energy. Substituting (6) in (5) we get

$$A_{min} = \frac{1}{2}\delta^2 E(S, x_i). \tag{7}$$

It may be easily shown that [2]

$$S' - S = \frac{-A_{min}}{T} \tag{8}$$

and thus

$$P = \text{const.} \exp(-\beta A_{min}) = \text{const.} \exp\left(-\frac{1}{2}\beta\delta^2 E\right). \tag{9}$$

From the relation $0 \leqq P \leqq 1$ it may be concluded that

$$\beta\delta^2 E \geqq 0 \tag{10}$$

also β and $\delta^2 E$ must have the same sign. At NAT ($\beta < 0$) the second variation $\delta^2 E(S, x_i)$ is negative.

We consider now the special case for which $\beta = 0$, that is $T = \pm\infty$. In this case the probability is zero because for $\beta = 0$ the denominator in (13) goes to infinity. Also for $\beta = 0$ it is only one state of the considered system, that is the state with maximal entropy. This is in good agreement with the results of Coleman and Noll [3].

Thus, form the theory of fluctuations it follows that the equilibrium state at NAT may be attained at the maximum of internal energy. This relation has validity also in the system with negative energy in which the equilibrium may be attained at NAT and at maximum of negative internal energy [4], [5].

In the system under consideration, the probability of the system state, described by generalized coordinates the value of which lies between δS and $\delta S + d(\delta S)$, δx_1 and $d(\delta x_1)$, etc., may be taken with the aif of (8) and (9)

$$Pd(\delta x_1) \ldots d(\delta x_n) = \text{const.} \exp\left(-\frac{1}{2}\beta\delta^2 E\right) d(\delta x_1) \ldots d(\delta x_n). \tag{11}$$

The value of constant must be determined from the condition

$$\int \dots \int P d(\delta x_1) \dots d(\delta x_n) = 1$$

$$\dots = \text{const.} \int \dots \int \exp\left(-\frac{1}{2}\beta\delta^2 E\right) d(\delta x_1) \dots d(\delta x_n) \tag{12}$$

also

$$P d(\delta x_1) \dots d(\delta x_n) =$$

$$= \frac{\exp\left(-\frac{1}{2}\beta\delta^2 E\right) \mathrm{d}(\delta x_1) \dots d(\delta x_n)}{\int \dots \int \exp\left(-\frac{1}{2}\beta\delta^2 E\right) d(\delta x_1) \dots d(\delta x_n)} \tag{13}$$

Now we introduce the following relation

$$L_i = \frac{\partial(\delta^2 E)}{\partial(\delta x_i)} . \tag{14}$$

We shall show that L are the variations of generalized forces. The second variation of $E(S, x_i)$ may be written in the form

$$\delta^2 E = \delta\left(\frac{\partial E}{\delta S}\right)_{x_i} \delta S - \sum_i \delta\left(\frac{\partial E}{\partial x_i}\right)_{S, x_j \neq x_i} \delta x_i . \qquad [15]$$

From thus

$$\frac{\partial(\delta^2 E)}{\partial(\delta S)} = \delta\left(\frac{\partial E}{\partial S}\right)_{x_i} = \delta T \qquad \frac{\partial(\delta^2 E)}{\partial(\delta x_i)} = \delta X_i \tag{16}$$

where X_i are the generalized forces. It may be calculate the following average by the well known method [6]

$$\overline{\delta x_i L_i} = \int \dots \int \delta x_i L_j P d(\delta x_1) \dots d(\delta x_n). \tag{17}$$

With the aid of (13) and (14) we get

$$L_j = -\frac{2}{\beta} \frac{\partial \ln P}{\partial(\delta x_j)} \tag{18}$$

and after partial integration with respect to δx_j this integral is

$$\int \delta x_i \frac{\partial \ln P}{\partial(\delta x_j)} d(\delta x_i) = -\int P \delta_{ij} d(\delta x_j) . \tag{19}$$

From thus we get

$$\overline{\delta x_i L_j} = \frac{2}{\beta} \int \dots \int d(\delta x_1) \dots d(\delta x_n) \int P \delta_{ij} d(\delta x_j) = \frac{2}{3} \delta_{ij} . \tag{20}$$

Also

$$\overline{\delta x_i L_j} = \frac{2}{\beta} \delta_{ij} . \tag{21}$$

This relation has no means for $\beta = 0$.
With the aid of (16)

$$\overline{\delta x_i \delta X_j} = \frac{2}{\beta}\,\delta_{ij}\,. \tag{22}$$

This is in good agreement with the methods described in [2] and [6], but in this method the average of variations of generalized coordinates and forces in directly expressed by means of β, that is by means of temperatures. From the combined first and second laws of thermodynamics we may directly find the relations (22).

We made now a specific application of the relation (22) to spin system for which the combined law must be formulated in the form [1]

$$\mathrm{d}E = T\,\mathrm{d}S + H\,\mathrm{d}M. \tag{23}$$

With the aid of (22) and (23) we get immediatelly

$$\overline{\delta T \delta S} = \frac{2}{\beta} \qquad \overline{\delta H \delta M} = \frac{2}{\beta} \tag{24}$$

also

$$\overline{\delta x_i \delta X_j} \geqq 0 \qquad \text{for } \beta_{(+)} = \frac{1}{kT_{(+)}} > 0 \tag{25}$$

and

$$\overline{\delta x_i \delta X_j} \leqq 0 \qquad \text{for } \beta_{(-)} = \frac{1}{kT_{(-)}} < 0 \tag{26}$$

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SHRNUTÍ

FLUKTUACE V SYSTÉMU SE ZÁPORNÝMI ABSOLUTNÍMI TEPLOTAMI

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V předložené práci je ukázáno, že negativní definitnost druhé variace vnitřní energie systému se zápornými absolutními teplotami je zdůvodněna pomocí teorie fluktuací. Dále je ukázán výpočet korelací variací zobecněných sil a souřadnic spinového systému.