

Relaxation Processes, MaxEnt Formalism and Einstein's Formula for the Probability of Fluctuations

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Relaxation process is the spontaneous transition of an isolated system from one to another macroscopic state. It is assumed that the entropy increase associated with this process is a functional of dynamical variables (fluxes). This fact makes entropy production a dynamical variable. It is shown within Jaynes' MaxEnt formalism that almost all possible microscopic fluxes are accompanied by maximal entropy production. Using Einstein's formula for probability of fluctuation, we obtain that the probability of the change in entropy is proportional to the exponential function of the entropy change divided by the Boltzmann constant. This result is applied to the system close to the equilibrium and the well-known relationships between thermodynamic forces and fluxes are reproduced.

Keywords
relaxation process
probability of fluctuation

INTRODUCTION

Macroscopic systems consist of an extremely large number of microscopic particles. This large number makes it, in most cases, practically impossible to detect the microscopic evolution of the system. Even if the microscopic evolution of the system is known, it bears, from the experimental point of view, a great deal of useless information. The best we can extract from the experimental measurement are the mean values of the physical quantities. It is an experimental fact that these values are, up to fluctuations that are usually several orders smaller than the measured mean values, practically independent of the microscopic state of the system.

Let $\{J_i\}$ be the set of independent macroscopic physical quantities. Then the thermodynamic state of the system is defined by macroscopically small intervals $\{J_i, J_i + dJ_i\}$ and thermodynamic entropy. In the case of an isolated system, thermodynamic entropy is equal to $k \ln W$, where W is the number of microscopic states that have values of physical quantities in these intervals. The number of microscopic states as a function of macroscopic physical quantities is an extremely sharp function close to the measured values, *i.e.*, almost all microscopic states have values of physical quantities extremely close to the measured values.

The equilibrium state of the isolated system is determined by maximum thermodynamic entropy. In this

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case, macroscopic quantities are practically time independent.

If macroscopic quantities are not equal to the equilibrium values, they change in the course of time in such a way as to bring the system into the state of maximum thermodynamic entropy. In this paper, we ask if there is some function that describes the evolution of the isolated system (relaxation) towards the equilibrium state. In the theory of non-equilibrium processes this function would be the counterpart to thermodynamic entropy of equilibrium processes.

RELAXATION PROCESSES

Relaxation Processes and MaxEnt Formalism

We consider an isolated system in the non-equilibrium state. In order to keep track of all possible microscopic events that are compatible with constraints imposed on the non-equilibrium processes, Dewar^{1,2} recently introduced an ensemble of »trajectories« within the interval of time $(0, t)$ in the phase space of the system. He called these »trajectories« paths. A path is defined by the initial microscopic state, *i.e.*, there is one to one correspondence between the initial state and paths in the case of an isolated system. Relaxation processes are characterized by fluxes and we define the set $\{f_{\Gamma i}(\vec{r}, t)\}$ where $f_{\Gamma i}(\vec{r}, t)$ is the i -th time dependent flux associated with path Γ . It is an experimental fact that almost all of these paths have practically the same values of the fluxes $\{f_i(\vec{r}, t)\}$ where $f_i(\vec{r}, t)$ is the mean value of the i -th time dependent flux. In other words, the relaxation practically depends on a set of a very small number of the initial mean values of the fluxes.

In order to apply Jaynes' information theory formalism,^{3,4} one has to define the objects of interest. Once the events of interest have been defined, Jaynes' information theory formalism can be applied. It consists of the maximization of Shannon's information entropy $S_I = -\sum_i p_i \ln p_i$ with respect to p_i , where p_i is the probability of the occurrence of the i -th event, provided the constraints are taken into account. This algorithm is known as MaxEnt.

At first sight, it seems that objects of interest could be paths. Equal probabilities of initial microscopic states and one to one correspondence between initial states and paths imply that all paths of the isolated system are equally probable. It comes out from the foregoing property between the ensemble of initial states and the ensemble of paths that the state information entropy is equal to the path information entropy in the case of relaxation processes. Similar conclusion has been derived for stationary processes in Ref. 5.

Evidently, no conclusion regarding the macroscopic time evolution of the system can be deduced from this choice of objects of interest.

Since the probabilities of fluxes $\{f_i(\vec{r}, t)\}$ are well pronounced quantities, the probability of any function of fluxes is a well pronounced function, too. This means that any function or functional of fluxes is a good object of interest.

We generally consider relaxation processes in which the isolated system spontaneously changes its state. We note that the final state of the system need not be an equilibrium state. We therefore focus on the entropy production $d_i S / dt$.

Having in mind that entropy production is a function of fluxes, we define the functional:

$$\Delta S = \int_0^t \frac{d_i S}{dt} dt. \quad (1)$$

The physical meaning of ΔS is the entropy increase of the system in the course of time. If the thermodynamic entropies of initial and final states are $S(0)$ and $S(t)$,⁶ respectively, then we can establish the relationship between equilibrium and non-equilibrium statistical mechanics by the following hypothesis:

$$S(t) - S(0) = \overline{\Delta S}. \quad (2)$$

Here $\overline{\Delta S}$ is the mean value of the functional in Eq. (1).

We choose functional ΔS as the object of interest. Following Ref. 7, information entropy of continuous distributions is:

$$S_I = -\int w(\Delta S) \ln \left[\frac{w(\Delta S)}{m(\Delta S)} \right] d(\Delta S). \quad (3)$$

Here, $w(\Delta S)d(\Delta S)$ is the probability that the functional ΔS assumes the values between ΔS and $\Delta S + d(\Delta S)$ while $m(\Delta S)$ is a measure function. In this case, the latter function can be taken as a constant. The normalization constraint is:

$$\int w(\Delta S) d(\Delta S) = 1. \quad (4)$$

Another constraint is equation (2):

$$S(t) - S(0) = \int w(\Delta S) \Delta S d(\Delta S). \quad (5)$$

The constrained maximization of information entropy (3) with respect to $w(\Delta S)$ is performed according to the standard procedure⁸ by introducing Lagrange's multipliers λ and μ and seeking for the maximum of the Lagrangian function F :

$$F = -\int w(\Delta S) \ln \left[\frac{w(\Delta S)}{m(\Delta S)} \right] d(\Delta S) + \lambda \left(\int w(\Delta S) d(\Delta S) - 1 \right) + \mu \left(\int w(\Delta S) \Delta S d(\Delta S) - S(t) + S(0) \right). \quad (6)$$

The outcome of the maximization of F is:

$$w(\Delta S) = Z^{-1} \exp(\mu \Delta S), \quad (7)$$

where

$$Z = \int \exp(\mu \Delta S) d(\Delta S), \quad (8)$$

is the partition function.

In order to pass from a continuous description to a discrete one, we have to multiply the probability density $w(\Delta S)$ with $\prod_i dJ_i$, where dJ_i are macroscopically small intervals of fluxes, *i.e.*, they define the macroscopic non-equilibrium state of the system:

$$p(\Delta S) = w(\Delta S) \prod_i dJ_i = Z^{-1} \exp(\mu \Delta S) \prod_i dJ_i. \quad (9)$$

Assuming $\mu > 0$, it follows from Eq. (7) that the most probable value of the functional ΔS is its maximum value. In a short interval of time δt , the equation (1) can be written as:

$$\Delta S = \frac{d_i S}{dt} \delta t + O(\delta t^2). \quad (10)$$

It follows from the foregoing equation that the most probable time evolution of the isolated system is accompanied by the maximum entropy production.

In order to determine the Lagrangian multiplier μ , we invoke Onsager's argument concerning non-equilibrium processes.⁹ The main idea is the assumption that the entropy increase during the macroscopic irreversible process is equivalent to the entropy increase during regression of the fluctuation.

The probability of the fluctuation is given by Einstein's formula:¹⁰

$$p = C \cdot e^{\frac{\Delta S}{k}}, \quad (11)$$

where ΔS is negative. Here, we extend this expression to the regression of fluctuation applying it to both kinds of processes (fluctuation and its regression).

Following the above mentioned Onsager's argument we equate expressions (9) and (11):

$$C \cdot e^{\frac{\Delta S}{k}} = Z^{-1} \exp(\mu \Delta S) \prod_i dJ_i, \quad (12)$$

which gives

$$\mu = 1/k. \quad (13)$$

Relaxation Processes Close to Equilibrium

Assuming that the initial state of the isolated system is close to its equilibrium state, the entropy increase is the positive definite bilinear function of fluxes:

$$\frac{d_i S}{dt} = \sum_{ij} \int_V R_{ij} f_i f_j dV > 0. \quad (14)$$

According to the conclusion in the previous section, the entropy production must achieve its maximum value. In the case of the isolated system, the only constraint is the conservation of energy. If the system is close to equilibrium, the intensive thermodynamic quantities are locally well defined and the first law of thermodynamics ensures the conservation of energy. The standard procedure is to introduce thermodynamic forces as gradients of the intensive variables.^{11,12} The entropy production is then given by:

$$\frac{d_i S}{dt} = \sum_i \int_V X_i f_i dV, \quad (15)$$

where X_i is the thermodynamic force conjugated to flux f_i .

Since $\{f_i\}$ is the set of independent variables, the following relation comes out of (14) and (15):

$$\sum_i X_i f_i = \sum_{ij} R_{ij} f_i f_j. \quad (16)$$

One can easily verify that entropy production has its maximum value if the fluxes are the solution of the system of equations:

$$X_i = \sum_j R_{ij} f_j. \quad (17)$$

This is a well-known relationship between fluxes and thermodynamic forces in linear non-equilibrium thermodynamics.^{9,11,12}

We note that time is a parameter in relaxation processes. In order to be more explicit, we refer to non-equilibrium processes close to equilibrium. Thermodynamic forces are, due to the first law of thermodynamics, functions only of space gradients of intensive variables. At the same time, fluxes are functions of forces only. In order to solve the time dependence of the problem, one has to know the mechanism of changing the intensive variables due to the sinking or springing of fluxes. A simple example is the schoolwork problem¹³ of the relaxation of two finite capacities of heat reservoirs at different initial temperatures, connected with a narrow wire of known thermal resistance.

CONCLUSIONS

In this paper, we assume that entropy increase in the relaxation process is a functional of the fluxes. We find within MaxEnt formalism that the largest possible entropy increase is the most probable entropy increase (Eq. 7). Using Einstein's formula for the probability of fluctuation, we obtain that the probability of the change of entropy is proportional to the exponential function of the entropy change divided by the Boltzmann constant.

We note here that there is a discrepancy between our result and the fluctuation theorem. In the case of stationary processes, Dewar^{1,2} and Evans¹⁴ found that the ratio of probability of entropy increase and entropy decrease for the same amount ΔS_s is:

$$\frac{p_{\Delta S}}{p_{-\Delta S}} = \exp\left(\frac{\Delta S_s}{k}\right). \quad (18)$$

This result is known as the fluctuation theorem. However, it follows from equations (7) and (13) that in the case of isolated systems the above ratio is:

$$\frac{p_{\Delta S}}{p_{-\Delta S}} = \exp\left(\frac{2\Delta S}{k}\right). \quad (19)$$

Discrepancy between the results in equations (18) and (19) demands additional analysis. This will be the subject of our further work.

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SAŽETAK

Relaksacijski procesi, MaxEnt formalizam i Einsteinova formula za vjerojatnost fluktuacija

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Relaksacijski proces je spontani prijelaz izoliranog sistema iz jednog makroskopskog stanja u drugo. Pretpostavlja se da je porast entropije u tom procesu funkcional dinamičkih varijabla (tokova). Stoga je produkcija entropije dinamička varijabla. Primjenjujući Jaynesov formalizam maksimalne entropije pokazano je da se praktički svi mikroskopski tokovi ostvaruju uz maksimalnu produkciju entropije. Pomoću Einsteinove formule za vjerojatnost fluktuacije dobiva se da je vjerojatnost promjene entropije u relaksacijskom procesu razmjerna eksponencijalnoj funkciji kvocijenta promjene entropije i Boltzmannove konstante. Ovaj je rezultat primijenjen na sistem koji se nalazi u termodinamičkom stanju blizu ravnotežnog stanja, te su reproducirane poznate relacije između termodinamičkih sila i tokova.