EFFECT OF PERTURBATION TO THE THERMODYNAMIC SYSTEM

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According to the Le Chatelier's principle the spontaneous processes induced by a deviation from equilibrium are in a direction to restore the system to equilibrium. We give this principle in detailed and explicit form.

1. Introduction

It is important to know about a physical system whether it is stable or not. If it is in equilibrium state then it is known that the conditions of stability are $ds = 0$ and $d^2S < 0$ where S is the entropy function of the system [1]. Now we consider a system that is taken out of equilibrium by some imposed perturbation. According to the Le Chatelier–Braun principle the perturbation directly includes a process that reduces the perturbation.

The most generalized thermostatic form of this principle is due to Fényes and Tisza and is in close connection with the following inequality series [2, 3]

$$\frac{\partial y_1}{\partial x_1}\Big|_{x_2,\ldots,x_n} > \frac{\partial y_1}{\partial x_1}\Big|_{y_2,x_3,\ldots,x_n} > \frac{\partial y_1}{\partial x_1}\Big|_{y_2,\ldots,y_{n-1},x_n} > \frac{\partial y_1}{\partial x_1}\Big|_{y_2,\ldots,y_n} \tag{1}$$

$$\frac{\partial x_1}{\partial y_1}\Big|_{y_2,\ldots,y_n} > \frac{\partial x_1}{\partial y_1}\Big|_{x_2,y_3,\ldots,y_n} > \frac{\partial x_1}{\partial y_1}\Big|_{x_2,\ldots,x_{n-1},y_n} > \frac{\partial x_1}{\partial y_1}\Big|_{x_2,\ldots,x_n}, \tag{2}$$

which refer to the initial state of the perturbed system, where x_i are the extensive parameters and y_i the intensive ones. These are consequences of the entropy maximum principle.

We characterize the departure from equilibrium state with parameters α_i[4,5]

$$\alpha_i = \frac{x_i - x_{io}}{x_{n+1}}, \quad i = 1, 2 \ldots, n, \tag{3}$$

then the thermodynamic forces are:

$$X_i = \frac{\partial \alpha_s}{\partial \alpha_i} - \frac{\partial \alpha_s}{\partial \alpha_i}\Big|_0, \quad i = 1, 2 \ldots, n, \tag{4}$$

where α_s is the α parameter of the entropy as the function of the other α_i parameters.

By means of parameters α_i and forces X_i I. Kirschner gave another way to characterize the perturbed system initial state [6].

$$|X_1|_{\alpha_2,\ldots,\alpha_n} > |X_1|_{X_2,\alpha_3,\ldots,\alpha_n} > |X_1|_{X_2,X_3\alpha_4,\ldots,\alpha_n} > \cdots > |X_1|_{X_2,\ldots,X_n} \quad (5)$$

$$|\alpha_1|_{X_2,\ldots,X_n} > |\alpha_1|_{a_2,x_3,\ldots,X_n} > |\alpha_1|_{\alpha_2,\alpha_3,X_4,\ldots,X_n} > \cdots > |\alpha_1|_{\alpha_2,\ldots,\alpha_n} \quad (6)$$

and by fluxes: $\dot{\alpha}_i = \frac{d\alpha_i}{dt}$

$$|\dot{\alpha}_1|_{X_2,\ldots,X_n} > |\dot{\alpha}_1|_{\dot{\alpha}_2,X_3,\ldots,X_n} > |\dot{\alpha}_1|_{\dot{\alpha}_2,\dot{\alpha}_3,X_4,\ldots,X_n} > \cdots > |\dot{\alpha}_1|_{\dot{\alpha}_2,\ldots,\dot{\alpha}_n} \quad (7)$$

where $X_1 \neq 0$ and

$$|X_1|_{\dot{\alpha}_2,\ldots,\dot{\alpha}_n} > |X_1|_{X_2,\dot{\alpha}_3,\ldots,\dot{\alpha}_n} > |X_1|_{X_2,X_3\dot{\alpha}_4,\ldots,\dot{\alpha}_n}, > \cdots > |X_1|_{X_2,\ldots,X_n}, \quad (8)$$

where $\dot{\alpha}_1 \neq 0$.

2. Effect of perturbation to the thermodynamic system

The parameter α of the entropy is:

$$\alpha_s = \alpha_s(\alpha_1\alpha_2\ldots,\alpha_n). \quad (9)$$

We can expand α_s in powers of the parameters α_i

$$\alpha_s = \alpha_s(0) + \sum_i \frac{\partial\alpha_s}{\partial\alpha_i}\alpha_i + \frac{1}{2}\sum_{i,k}\frac{\partial^2\alpha_s}{\partial\alpha_i\partial\alpha_{k_0}}\alpha_i\alpha_k + \ldots. \quad (10)$$

We introduce the positive definite symmetric matrix g_{ik}

$$g_{ik} = -\frac{\partial^2\alpha_s}{\partial\alpha_k\partial\alpha_i} \quad (11)$$

and by inserting Eq. (10) in Eq. (4), we find in second-order approximation

$$x_i = -\sum_k g_{ik}\alpha_k, \qquad i = 1,2,\ldots,n. \quad (12)$$

From Eq. (4) it follows in second-order approximation

$$\Delta\alpha_s = -\frac{1}{2}\sum_{i,k} g_{ik}\alpha_i\alpha_k = -\frac{1}{2}\hat{g}\underline{\alpha\alpha}. \quad (13)$$

The entropy production is the sum of products of each force with its conjugated affinity [7, 8] and in this case, we have

$$\sigma = \Delta\dot{\alpha}_s = \sum_{i,k} g_{ik}\dot{\alpha}_i\alpha_k = \sum_i \dot{\alpha}_i X_i = \underline{\dot{\alpha}}\mathbf{X}. \tag{14}$$

Differentiating the entropy production σ with respect to the time, we have:

$$\dot{\sigma} = \underline{\ddot{\alpha}}\mathbf{X} + \underline{\dot{\alpha}}\dot{\mathbf{X}}, \tag{15}$$

$$\underline{\dot{\alpha}} = \hat{L}\mathbf{X}, \tag{16}$$

where the Onsager theorem states that L_{ik} is a positive definite symmetric matrix [9].

Assuming that $\hat{L}$ is constant the acceleration can be written as follows

$$\underline{\ddot{\alpha}} = \hat{L}\dot{\mathbf{X}}. \tag{17}$$

Inserting this Eq. (15), we obtain

$$\dot{\sigma} = \hat{L}\dot{\mathbf{X}}\mathbf{X} + \hat{L}\mathbf{X}\dot{\mathbf{X}}, \tag{18}$$

where the two terms on the right hand side are equal. Thus

$$\dot{\sigma} = 2\hat{\mathbf{L}}\mathbf{X}\dot{\mathbf{X}} = 2\underline{\dot{\alpha}}\dot{\mathbf{X}}. \tag{19}$$

It is remarkable that this result was obtained already in 1963 by Gyarmati and Oláh, however, in a different way [10]. From Table I substituting any initial condition into Eq. (19) we find

$$\dot{\sigma} = 2\dot{X}_1\dot{\alpha}_1 \tag{20}$$

and substituting the K-th initial condition into Eqs. (12) we have

$$\begin{aligned} X_1 &= -g_{11}\dot{\alpha}_1 - g_{22}\dot{\alpha}_2 - \cdots - g_{1,n-k}\dot{\alpha}_{n-k}, \\ 0 &= -g_{21}\dot{\alpha}_1 - g_{22}\dot{\alpha}_2 - \cdots - g_{2,n-k}\dot{\alpha}_{n-k}, \\ 0 &= -g_{31}\dot{\alpha}_1 - g_{32}\dot{\alpha}_2 - \cdots - g_{n-k,n-k}\dot{\alpha}_{n-k}, \\ &\;\;\vdots \\ 0 &= -g_{n-k,1}\dot{\alpha}_1 - g_{n-k,2}\dot{\alpha}_2 - \cdots - g_{3,n-k}\dot{\alpha}_{n-k}, \end{aligned} \tag{21}$$

Table I

Perturbation possibility		Parameters equal to zero	Parameters unequal to zero
	1.	$x_2, x_3, \ldots, x_{k-1}, x_k, \ldots, x_{n-1}, x_n$	$\alpha_1, \alpha_2, \alpha_3, \ldots, \alpha_{k-1}, \alpha_k, \ldots, \alpha_{n-1}, \alpha_n$
	2.	$x_2, x_3, \ldots, x_{k-1}, x_k, \ldots, x_{n-1}, \alpha_n$	$\alpha_1, \alpha_2, \ldots, \alpha_{k-1}, \alpha_k, \ldots, \alpha_{n-1}, x_n$
	3.	$x_2, x_3, \ldots, x_{k-1}, \ldots, x_{n-2}, \alpha_{n-1}, \alpha_n$	$\alpha_1, \alpha_2, \ldots, \alpha_{k-1}, \ldots, \alpha_{n-2}, x_{n-1}, x_n$
	.		
$x_1 \neq 0$	.		
	.		
	/k+1/	$x_2, x_3, \ldots, x_{n-k}, \alpha_{n-k+1}, \alpha_{n-k+2}, \ldots, \alpha_n$	$\alpha_1, \alpha_2, \ldots, \alpha_{n-k}, x_{n-k+1}, x_{n-k+2}, \ldots, x_n$
	.		
	.		
	.		
	n	$\alpha_2, \alpha_3, \ldots, \alpha_{k-1}, \ldots, \alpha_{n-1}, \alpha_n$	$\alpha_1, x_2, x_3, \ldots, x_{n-k}, x_{n-k+1}, \ldots, x_n$

where we have written out the first $n-k$ equations explicitly.

$$\alpha_1 = \frac{D^1_{n-k}}{D_{n-k}} X_1, \tag{22}$$

where notation D_{n-k} stands for the principal minor of the g_{ik} matrix with $n-k$ rows and columns and D^1_{n-k} is obtainable from D_{n-k} omitting the first row and column. Because:

$$\frac{D_k}{D^1_k} = \frac{D_{k-1}}{D^1_{k-1}} - \frac{D^1_{k-1}}{D^1_k} DD', \tag{23}$$

where

$$DD' = \begin{vmatrix} g_{1,1} & g_{1,2} & \cdots & g_{1,k-1} \\ g_{2,k} & & & \\ \cdot & & & \\ \cdot & & D^1_{k-1} & \\ g_{k-1,k} & & & \end{vmatrix} \begin{vmatrix} & & g_{k,2} \\ & & g_{k,3} \\ & D^1_{k-1} & \cdot \\ & & \cdot \\ & & g_{k,k-1} \\ g_{k-2}\cdot & --- \cdot g_{k,k} & g_{k,1} \end{vmatrix}. \tag{24}$$

Thus by the help of positive definitivity of matrix g_{ik} from Eq. (22) it follows:

$$|\dot\alpha_1|_{\dot X_2,\ldots,\dot X_n} > |\dot\alpha_1|_{\dot X_2,\ldots,\dot X_{n-1},\dot\alpha_n} > |\dot\alpha_1|_{\dot X_2,\ldots,\dot X_{n-2},\dot\alpha_{n-1},\dot\alpha_n} > \cdots > |\dot\alpha_1|_{\dot\alpha_2,\ldots,\dot\alpha_n}. \tag{25}$$

Inserting this in Eq. (19), we have:

$$|\dot\sigma|_{\dot X_2,\ldots,\dot X_n} > |\dot\sigma|_{\dot X_2,\ldots,\dot X_{n-1},\dot\alpha_n} > |\dot\sigma|_{\dot X_2,\ldots,\dot X_{n-2},\dot\alpha_{n-1},\dot\alpha_n} > \cdots > |\dot\sigma|_{\dot\alpha_2,\ldots,\dot\alpha_n}. \tag{26}$$

Similarly, if the initial state is $\alpha_1 \neq 0$ and the bound conditions are as in Table I, we obtain:

$$|\dot X_1|_{\dot\alpha_2,\ldots,\dot\alpha_n} > |\dot X_1|_{\dot X_2,\dot\alpha_3,\ldots,\dot\alpha_n} > |\dot X_1|_{\dot X_2,\dot X_3\dot\alpha_4,\ldots,\dot\alpha_n} > \cdots > |\dot X_1|_{\dot X_2,\ldots,\dot X_n} \tag{27}$$

and from Eq. (19) it follows:

$$|\dot\sigma|_{\dot\alpha_2,\ldots,\dot\alpha_n} > |\dot\sigma|_{\dot X_2\dot\alpha_3,\ldots,\dot\alpha_n} > |\dot\sigma|_{\dot X_2\dot X_3\dot\alpha_4,\ldots,\dot\alpha_n} > \cdots > |\dot\sigma|_{\dot X_2\ldots,\dot X_n}. \tag{28}$$

We would like to state that the inequality series (25), (26), (27) and (28) refer to the initial state of the perturbed system, and give information about the velocity of decrease of the deviation from equilibrium.

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