12.B.1. Stability Conditions Near Equilibrium

Near equilibrium, we have [see (10.10.96)]

$$\mathcal{J}_i = -\sum_j L_{ij}\,\chi_j \tag{12.5}$$

where L_{ij} are transport coefficients satisfying [see §10.D.1.2]

$$L_{ij} = L_{ji} \qquad \text{[Onsager's relation]} \tag{12.5a}$$

Near equilibrium, we are in the linear regime so that all L_{ij} are independent of the forces χ_k.

Putting (12.5) into (12.4-a) gives

$$T\,\sigma_s = \sum_{i,j} L_{ij}\,\chi_j\,\chi_i \geq 0 \tag{12.6}$$

which means the symmetric matrix $\mathbb{L} = \{L_{ij}\}$ is positive semi-definite (or non-negative definite).

Consider now the case of 2 forces so that (12.6) becomes

$$T\,\sigma_s = \sum_{i,j=1}^{2} L_{ij}\,\chi_j\,\chi_i \geq 0 \tag{12.7}$$

Choosing χ_i as the independent variables, the conditions for extremum entropy production are [T is independent of χ_i even if $\chi_i = -\nabla_{\boldsymbol{r}} T$]

$$\begin{aligned} 0 = T\frac{\partial\,\sigma_s}{\partial\,\chi_1} &= \sum_i L_{i1}\,\chi_i + \sum_j L_{1j}\,\chi_j = 2\sum_i L_{i1}\,\chi_i \qquad \text{[(12.5a) used.]} \\ &= 2\,(L_{11}\,\chi_1 + L_{21}\,\chi_2) = 2\,(L_{11}\,\chi_1 + L_{12}\,\chi_2) \\ &= -2\,\mathcal{J}_1 \qquad \text{[(12.5) used.]} \end{aligned} \tag{12.8}$$

and

$$\begin{aligned} 0 = T\frac{\partial\,\sigma_s}{\partial\,\chi_2} &= \sum_i L_{i2}\,\chi_i + \sum_j L_{2j}\,\chi_j = 2\sum_i L_{i2}\,\chi_i \qquad \text{[(12.5a) used.]} \\ &= 2\,(L_{12}\,\chi_1 + L_{22}\,\chi_2) = 2\,(L_{21}\,\chi_1 + L_{22}\,\chi_2) \\ &= -2\,\mathcal{J}_2 \qquad \text{[(12.5) used.]} \end{aligned} \tag{12.9}$$

Since $\mathbb{L}$ is positive semi-definite,

$$\frac{\partial^2\,\sigma_s}{\partial\,\chi_i\,\partial\,\chi_j} = \frac{L_{ij}}{T} \geq 0 \tag{12.9a}$$

Therefore, the extrema given by (12.8-9) are all minima corresponding to minimal entropy production.

Thus, minimum entropy production occurs when

$$\mathcal{J}_1 = \mathcal{J}_2 = 0$$

which, when substituted into (12.5), gives

$$\chi_1 = \chi_2 = 0$$

On the other hand, if we keep χ_1 constant, the conditions for minimum entropy production reduce to a single criterion

$$0 = T\frac{\partial\,\sigma_s}{\partial\,\chi_2} = -2\,\mathcal{J}_2 \tag{12.10}$$

which turns (12.5) into

$$\mathcal{J}_1 = -(L_{11}\,\chi_1 + L_{12}\,\chi_2)$$
$$0 = -(L_{21}\,\chi_1 + L_{22}\,\chi_2)$$

with solutions

$$\chi_2 = -\frac{L_{21}}{L_{22}}\,\chi_1 = \text{const}$$
$$\mathcal{J}_1 = -\left(L_{11}\,\chi_1 - L_{12}\,\frac{L_{21}}{L_{22}}\,\chi_1\right) = -\frac{\det L}{L_{22}}\,\chi_1 = \text{const}$$

so that the state of minimum entropy production is stationary.

These results can be easily generalized to the case of n independent forces $\{\chi_i;\ i = 1, \ldots, n\}$. The entropy production (12.6) becomes

$$T\,\sigma_s = \sum_{i,j=1}^{n} L_{ij}\,\chi_j\,\chi_i \qquad (12.11)$$

If we hold the first k forces $\{\chi_i;\ i = 1, \ldots, k\}$ constant, the conditions for minimum entropy production are

$$0 = T\,\frac{\partial\,\sigma_s}{\partial\,\chi_i} = \sum_j L_{ji}\,\chi_j + \sum_j L_{ij}\,\chi_j = 2\,\mathcal{J}_i \qquad i = k+1, \ldots, n \qquad (12.12\text{-}3)$$

Thus, if the system is in a state of minimum entropy production, only fluxes conjugate to the forces being held constant exist.

Putting (12.13) into (12.5) gives

$$\mathcal{J}_i = -\sum_j L_{ij}\,\chi_j \qquad i = 1, \ldots, k \qquad (12.13\text{a})$$
$$0 = -\sum_j L_{ij}\,\chi_j \qquad i = k+1, \ldots, n \qquad (12.13\text{b})$$

(12.13b) can be solved for $\{\chi_i;\ i = k+1, \ldots, n\}$ in terms of the constants L_{ij} and $\{\chi_i;\ i = 1, \ldots, k\}$. This means $\{\chi_i;\ i = k+1, \ldots, n\}$ are also constants in the state of minimum entropy production. By (12.13a), the nonvanishing fluxes $\{\mathcal{J}_i;\ i = 1, \ldots, k\}$ are also constants. Such a state is called stationary to the k^{th} order.

Next, we consider the stability of a stationary state of the general (non-linear) entropy production.

As described in Appendix C.3, a stationary state at point $\bar{\boldsymbol{y}}$ in phase space is stable if there exists a Liapounov function $V(\boldsymbol{y})$ in a neighborhood $\mathcal{N}$ of $\bar{\boldsymbol{y}}$ such that for all $\boldsymbol{y} \in \mathcal{N}$,

1. $V(\boldsymbol{y}) \geq 0$ with $V = 0$ only at $\boldsymbol{y} = \bar{\boldsymbol{y}}$ (12.13c)
2. $\dfrac{dV}{dt} \leq 0$ (12.13d)

Consider again a system of n independent forces $\{\chi_i;\ i = 1, \ldots, n\}$ with the first k forces $\{\chi_i;\ i = 1, \ldots, k\}$ being held constant. Let the properties of the stationary state be denoted by a superscript 0. The entropy production near the stationary state can be expanded as a Taylor series

$$\sigma_s(\chi_{k+1}, \ldots, \chi_n) = \sigma_s(\chi_{k+1}^0, \ldots, \chi_n^0) + \sum_{i=k+1}^{n} \left(\frac{\partial \sigma_s}{\partial \chi_i}\right)^0 \delta\chi_i \qquad [\,\delta\chi_i = \chi_i - \chi_i^0\,]$$

$$+\frac{1}{2} \sum_{i,j=k+1}^{n} \left(\frac{\partial^2 \sigma_s}{\partial \chi_i \partial \chi_j}\right)^0 \delta\chi_i\,\delta\chi_j + \ldots$$

$$= \sigma_s(\chi_{k+1}^0, \ldots, \chi_n^0) - \frac{1}{2T} \sum_{i,j=k+1}^{n} L_{ij}\,\delta\chi_i\,\delta\chi_j + \ldots \qquad (12.14)$$

where, from (12.9a) was used.

The quantity

$$\Delta P = \int d^3r\; T\left[\,\sigma_s(\chi_{k+1}, \ldots, \chi_n) - \sigma_s(\chi_{k+1}^0, \ldots, \chi_n^0)\,\right]$$

$$= \frac{1}{2}\int d^3r \sum_{i,j=k+1}^{n} L_{ij}\,\delta\chi_i\,\delta\chi_j \qquad (12.15)$$

$$\geq 0 \qquad [\,(12.6)\text{ used.}\,]$$

is called the excess entropy production. Taking the time derivative gives

$$\frac{d\Delta P}{dt} = \frac{1}{2}\int d^3r \sum_{i,j=k+1}^{n} L_{ij}\left(\frac{d\,\delta\chi_i}{dt}\,\delta\chi_j + \delta\chi_i\,\frac{d\,\delta\chi_j}{dt}\right)$$

$$= -\frac{1}{2}\int d^3r \left(\sum_{j=k+1}^{n} \frac{d\,\delta\chi_j}{dt}\,\delta\mathcal{J}_j + \sum_{i=k+1}^{n} \delta\mathcal{J}_i\,\frac{d\,\delta\chi_i}{dt}\right) \qquad [\,(12.5)\text{ used.}\,]$$

$$= -\int d^3r \sum_{j=k+1}^{n} \frac{d\,\delta\chi_j}{dt}\,\delta\mathcal{J}_j \qquad (12.16a)$$

From (10.79) of §10.D.1, we have

$$\boldsymbol{\chi} = T\,\mathbb{g}\cdot\boldsymbol{\alpha}$$

$$\rightarrow \qquad \delta\boldsymbol{\chi} = T\,\mathbb{g}\cdot\delta\boldsymbol{\alpha}$$

$$\frac{d\delta\boldsymbol{\chi}}{dt} = T\,\mathbb{g}\cdot\frac{d\,\delta\boldsymbol{\alpha}}{dt} = T\,\mathbb{g}\cdot\delta\boldsymbol{\mathcal{J}} \qquad [\,(10.80)\text{ used.}\,]$$

$$\therefore \qquad \frac{d\delta\chi_j}{dt} = T\sum_i g_{ji}\,\delta\mathcal{J}_i$$

(12.16a) thus becomes

$$\frac{d\Delta P}{dt} = -T\int d^3r \sum_{i,j=k+1}^{n} g_{ji}\,\delta\mathcal{J}_i\,\delta\mathcal{J}_j$$

$$\leq 0 \qquad [\,\mathbb{g}\text{ is positive definite.}\,] \qquad (12.16)$$

ΔP is therefore a Lyapunov function and the stationary state is stable in the linear regime.

In the nonlinear regime, (12.5) no longer holds so that $\frac{d\Delta P}{dt}$ cannot be put into the form (12.16), i.e., ΔP may not be a Lyapunov function and the stability of the stationary state is not guaranteed. Phase transition far from equilibrium is then a possibility.