since

$$< Z^n >= \exp(\ln < Z^n >) =\simeq 1 + \ln < Z^n >$$

Then the free energy per component can be written in the form

$$f = - \lim_{n \to 0} \lim_{N \to \infty} \frac{\ln < Z^n >}{knN}$$

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2.6 Maximal Entropy Principle and Onsager Theory

According to the Second Principle of Thermodynamics there exists a state function Entropy that is maximal at the thermodynamic equilibrium (Maximum Entropy Principle). We assume that the system state is described by the macroscopic observables $E_1, ..., E_n$ (coarse grained description since many microstates corresponds to the same observables). There is no need to specify these quantities but according to the second Principle the equilibrium state is defined by a maximum of the Entropy with the constraints due to the observables. This approach is quite general in complex systems to define null models from a limited knowledge. We expand the Entropy in a neighborhood of the equilibrium state

$$S = S_0 - \frac{1}{2} \sum_{ij} G_{ij} \Delta E_i \Delta E_j$$

where ΔE_i are fluctuation near the equilibrium: G is a positive defined symmetric matrix since the equilibrium corresponds to a maximum point. Generalizing the first principle one writes

$$dS = \sum_i X_i dE_i$$

where X_i are generalized forces: e.g. form the firt principle we have

$$\frac{\partial S}{\partial E} = \frac{1}{T}$$

Remark: the fluctuations are not independent due to the observable constraints in the definition of the Entropy maximum. According to the definition the Boltzmann Entropy $S(E_1, ..., E_n)$ is the logarithm of the statistical weight $w(E_1, ..., E_n)$ (i.e. the probability to observe the macroscopic state); then the probability distribution of fluctuations ΔE reads

$$w(\Delta E) \propto \exp(S_0) \exp\left(-\frac{1}{2} \sum G_{ij} \Delta E_i \Delta E_j \right) \tag{2.48}$$

i.e. we have a Gaussian distribution centered at $\Delta E = 0$ and we have the covariance function

$$< \Delta E_i \Delta E_j >= K_{ij} = G_{ij}^{-1}$$

The Maximum Entropy Principle not only means that the equilibrium state is the maximum of Entropy, but it also implies that the dynamics of the system tends to relax toward the equilibrium state (time arrow). In other words, there should exist 'forces' that affect the value of any observable in order to increase the Entropy. These entropic forces can be apparent since they are related to the probability measure to observe a microstate of the system: i.e. since the system relaxes to an equilibrium distribution invariant for the microdynamics, the value of an observable that is the result of a measure, tends to the average value according to the equilibrium distribution. We can interpret this tendency as the result of an entropic force. The quadratic form

$$V = \frac{1}{2}\sum_{ij} G_{ij}\Delta E_i \Delta E_j$$

can be interpreted as the entropic potential which creates forces

$$X_i = -\frac{\partial V}{\partial E_i} = -\sum_j G_{ij}E_j$$

along the gradient of the Entropy. In the linear approximation we have the dynamical system

$$\dot{E}_i = \sum_j L_{ij}X_j$$

where L_{ij} are phenomenological coefficients that describes as the entropic forces act on the system according to the relaxation proces.The quantities $-L_{ij}X_j$ are related to the flows from the system: the previous equation can be considered a continuity equation for the observable Ei. We get the linear system

$$\dot{E} = -(LG)E \tag{2.49}$$

whose solution reads

$$E(t+\tau) = \exp(-LG\tau)E(t)$$

Remark: this approach can be applied in the case of an infinite dimension so that LG is a linear operator in a Hilbert space.
The stability of the equilibrium solution implies that the real part of the eigenvalues of the matrix LG should be positive. Since the Entropy is a Ljapunov function we have the relation

$$\frac{dS}{dt} = \sum_i X_i \frac{dE_i}{dt} = \sum_{ij} X_i L_{ik} X_j \geq 0$$

i.e. the symmetric part $L^S = (L+L^T)/2$ of$L$ is positive defined and the stability of the equilibrium solution follows from the positivity of the matrix G

$$\vec{v}LG\vec{v} = \vec{u}\sqrt{G^{-1}}L\sqrt{G}\vec{u} \geq 0$$

where $\vec{v} = \sqrt{G^{-1}}\vec{u}$. Therefore the matrix LG is a positive defined matrix. The Gaussian distribution for the fluctuation near the equilibrium state can be represented as the stationary solution of a linear stochastic equation whose average dynamic reduces to (2.49)

$$dE_i = -S_{ij}E_j dt + \sqrt{D_{ij}}dw_j \tag{2.50}$$

where $S_{ij} = (LG)_{ij}$. Eq. (2.50) understands the assumption that we restrict to the class of Markov systems to describe the system evolution. The stationary solution can be written in the form

$$E_i = \lim_{t\to\infty} \int_0^t \exp(-S_{ik}(t-s))\sqrt{D_{kj}}dw_j(s)$$

so that the covariance matrix among the fluctuations can be computed

$$\lim_{t\to\infty} < E_i(t+\tau)E_j(t) >= K_{ij}(\tau)$$

$$= \lim_{t\to\infty} \int_0^{t+\tau}\int_0^t \exp(-S_{ik}(t+\tau-s))\sqrt{D_{kj}}\exp(-S_{jl}(t-u))\sqrt{D_{lj}} < dw_j(u)dw_j(s) > \tag{2.51}$$

and we get

$$K_{ij}(\tau) = \lim_{t\to\infty} \int_0^t \exp(-S_{ik}(t+\tau-s))\sqrt{D_{kj}}exp(-S_{il}(t-s))\sqrt{D_{lj}}ds = \exp(-S_{ik}\tau)G^{-1}_{kj}$$

where we use the previous assumptions. In a similar way we compute the correlation for backward fluctuations

$$\begin{aligned} K(-\tau) &= \lim_{t\to\infty} < E_i(t-\tau)E_j(t) > \\ &= \lim_{t\to\infty} \int_0^{t-\tau} \exp(-S_{ik}(t-\tau-s))\sqrt{D_{kj}}\exp(-S_{il}(t-s))\sqrt{D_{lj}}ds \\ &= \lim_{t\to\infty} \int_0^{t} \exp(-S_{ik}(t-s))\sqrt{D_{kj}}\exp(-S_{jl}(t+\tau-s))\sqrt{D_{lj}}ds \end{aligned}$$

so that

$$K_{ij}(-\tau) = G^{-1}_{ik}\exp(-S^T_{kj}\tau) = K^T_{ji}(\tau)$$

The physical assumption by Onsager is that in an equilibrium state it is not possible to detect the time arrow, so that the following relation holds

$$K(-\tau) = K(\tau) \tag{2.52}$$

This is possible if

$$G^{-1}exp(-S^T\tau) = \exp(-S\tau)G^{-1}$$

then, since $S = LG$

$$L = L^T \tag{2.53}$$

i.e. the phenomenological matrix L_{ij} has to symmetric. The influence of the 'entropic force' X_j associated to the observable E_j on the relaxation process of another observable E_i is the same of the force X_i on the observable X_j. The Onsager relations describe the fluctuations of the observable so that they shed a first light on the non equilibrium thermodynamics.

For example, consider fluid systems described in terms of temperature, matter density, and pressure. In this class of systems, it is known that temperature differences lead to heat flows from the warmer to the colder parts of the system; similarly, pressure differences will lead to matter flow from high-pressure to low-pressure regions. What is remarkable is the observation that, when both pressure and temperature vary, temperature differences at constant pressure can cause matter flow (as in convection) and pressure differences at constant temperature can cause heat flow.