Then we have

$$\frac{\partial}{\partial \alpha_i} P(\alpha_1, \dots, \alpha_n) = \frac{1}{k_B} \frac{\partial \Delta S}{\partial \alpha_i} P = \frac{1}{k_B} X_i P$$

$$\Rightarrow \quad \langle \alpha_i X_j \rangle = \frac{1}{W} \int d\alpha_1 \dots d\alpha_n \, \alpha_i \, k_B \frac{\partial P}{\partial \alpha_j} =$$

$$= \left\{ \begin{array}{ll} 0 & i \neq j \\ -k_B & i = j \end{array} \right\} \text{ by partial integration}$$

$$\Rightarrow \quad \langle \alpha_i X_j \rangle = -k_B \delta_{ij} .$$

Moreover

$$\sum_k g_{ik} \langle \alpha_k \alpha_j \rangle = - \langle X_i \alpha_j \rangle = k_B \delta_{ij}$$

$$\Rightarrow \quad \underline{\langle \alpha_i \alpha_j \rangle = k_B (g^{-1})_{ij}}$$

and similarly $\langle X_i X_j \rangle = k_B g_{ij}$.

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b) <u>Microscopic reversibility</u>

In an equilibrium state the deviations α_i are random functions of time.

Microscopic reversibility implies that their correlation functions are invariant under time reversal $t \to -t$:

$$\langle \alpha_i(t)\, \alpha_j(t+\Delta t)\rangle = \langle \alpha_i(t)\, \alpha_j(t-\Delta t)\rangle$$

$$= \langle \alpha_j(t)\, \alpha_i(t+\Delta t)\rangle$$

by time translation invariance

$$\Rightarrow \quad \underline{\langle \alpha_i \dot{\alpha}_j\rangle = \langle \alpha_j \dot{\alpha}_i\rangle} \qquad (\Delta t \to 0)$$

The <u>Onsager regression hypothesis</u> now assumes that the microscopic fluctuations can be described by macroscopic transport laws:

$$\dot{\alpha}_i = \sum_k L_{ik} X_k$$

$$\Rightarrow \quad \langle \alpha_i \dot{\alpha}_j\rangle = \sum_k L_{jk} \langle \alpha_i X_k\rangle = -k_B L_{ji}$$

$$\Rightarrow \quad \underline{L_{ij} = L_{ji}} \qquad \square$$

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c) <u>Application to thermoelectricity</u>

First law: $\quad dE = dQ + dW = T\,dS + \varphi\, dq$

q: charge on capacitor

$$\Rightarrow \quad \underline{dS = \frac{1}{T}\, dE - \frac{\phi}{T}\, dq}$$

- transfer of energy (heat) from 2 to 1:

$$dS = -\frac{dE}{T+\Delta T} + \frac{dE}{T} \simeq \frac{\Delta T}{T^2}\, dE$$

- transfer of charge across potential difference $\Delta\phi$:

$$dS = dS_1 + dS_2 = -\frac{\phi_1}{T}\, dq + \frac{\phi_2}{T}\, dq = \frac{\Delta\phi}{T}\, dq$$

$$\Rightarrow \quad \sigma = \frac{dS}{dt} = \frac{\Delta T}{T^2} \underbrace{\frac{dE}{dt}}_{= J_Q \text{ heat current}} + \frac{\Delta\phi}{T} \underbrace{\frac{dq}{dt}}_{= I \text{ electric current}}$$

$\Rightarrow$ generalized forces are $\Delta T / T^2$, $\Delta\phi / T$.

<u>Transport laws:</u>

$$\left.\begin{aligned} I &= L_{11} \frac{\Delta\phi}{T} + L_{12} \frac{\Delta T}{T^2} \\ J_Q &= L_{22} \frac{\Delta T}{T^2} + L_{21} \frac{\Delta\phi}{T} \end{aligned}\right\}$$

<u>Seebeck effect:</u> $\quad I = 0 \quad \Rightarrow \quad L_{11} \frac{\Delta\phi}{T} = -L_{12} \frac{\Delta T}{T^2}$

$$\Rightarrow \quad \underline{\Delta\phi = -\frac{1}{T} \cdot \frac{L_{12}}{L_{11}}\, \Delta T}$$

$$\Rightarrow \quad \underline{K_S = \frac{1}{T} \frac{L_{12}}{L_{11}}}$$

Peltier effect: $\Delta T = 0$

$$\Rightarrow \quad I = L_{11} \frac{\Delta \varphi}{T}, \quad J_\alpha = L_{21} \frac{\Delta \varphi}{T}$$

$$\Rightarrow \quad J_\alpha = \frac{L_{21}}{L_{11}} I \quad \Rightarrow \quad \underline{\Pi = \frac{L_{21}}{L_{11}}}$$

Onsager: $L_{12} = L_{21} \Rightarrow \underline{\Pi = T K_S}$ □

4° The principle of minimal entropy production

Question: Is there an analog of the principle of entropy maximization for nonequilibrium stationary states (NESS)?

Prigogine (1945, Nobel prize 1977):

At least in certain cases (in particular, near equilibrium) NESS minimize entropy production (subject to the constraints that impose the nonequilibrium condition).

We illustrate the principle for some simple cases.

a) Heat conduction in a continuous system

Fourier's law: $\vec{J}_\alpha = -\lambda \nabla T = L_{qq} \nabla \left(\frac{1}{T}\right)$

since the thermodynamic driving force is $1/T$, not T; clearly $L_{qq} = \lambda T^2$.

Thus the entropy production is

$$\sigma = \int dV \, \vec{J}_\alpha \cdot \nabla\left(\frac{1}{T}\right) = \underline{\int dV \, L_{qq} \left(\nabla\left(\frac{1}{T}\right)\right)^2}$$

We now show: (i) $\dfrac{d\sigma}{dt} \leq 0$

(ii) The NESS minimizes σ

(i) $$\frac{d\sigma}{dt} = 2 \int dV \, \underbrace{L_{qq} \nabla\left(\frac{1}{T}\right)}_{\vec{J}_\alpha} \cdot \nabla \underbrace{\left(\frac{\partial}{\partial t} \frac{1}{T}\right)}_{= -\frac{1}{T^2}\dot{T}}$$

$$= -2 \int dV \, \vec{J}_\alpha \cdot \nabla\left(\frac{1}{T^2} \dot{T}\right) =$$

$$= 2 \int dV \, (\nabla \cdot \vec{J}_\alpha) \frac{1}{T^2} \frac{\partial T}{dt}$$

part. integration with time-independent b.c.

Now we use energy conservation:

$$\nabla \cdot \vec{J}_\alpha = -\frac{dq}{dt} = -c_V \frac{\partial T}{\partial t}$$ c_V: specific heat

$$\Rightarrow \frac{d\sigma}{dt} = -2 \int dV \, \frac{c_V}{T^2} \left(\frac{\partial T}{\partial t}\right)^2 \leq 0$$

because $c_V > 0$ (thermodynamic stability).

(ii) We look for the temperature distribution $T(\vec{r})$ that minimizes the functional

$$\sigma = \int dV \, L_{qq} \left(\nabla\left(\frac{1}{T}\right)\right)^2 = L_{qq} \int dV \left(\nabla \frac{1}{T}\right)^2$$

assuming L_{qq} = const. :

$$\frac{\delta \sigma}{\delta T} = 0 \quad \Rightarrow \quad \nabla^2\left(\frac{1}{T}\right) = 0 \quad \text{(Euler-Lagrange)}$$

$$\Rightarrow \quad \nabla \cdot \vec{J}_\alpha = 0 \quad \Rightarrow \quad \text{NESS} \quad \square$$

In particular, in one dimension this implies that $\frac{1}{T}$ is a linear function of x; for small gradients this implies linearity of T also.

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b) <u>Discrete systems with interference effects</u>

$$\sigma = \sum_{i=1}^{n} J_i X_i, \quad J_i = \sum_{k=1}^{n} L_{ik} X_k$$

$$\Rightarrow \quad \underline{\sigma = \sum_{i,j} L_{ij} X_i X_j}$$

We fix the generalized forces $X_1, \ldots, X_m$ and minimize σ with respect to the remaining $X_{m+1}, \ldots, X_n$:

$$\frac{\partial \sigma}{\partial X_k} = \sum_{j=1}^{n} (L_{jk} + L_{kj}) X_j \overset{\text{Onsager}}{=} 2 \sum_{j=1} L_{kj} X_j =$$

$$= 2 J_k = 0$$

$\Rightarrow$ all unconstrained fluxes vanish, which seems like a reasonable, general property of NESS.

5° Outlook: Nonequilibrium thermodynamics of small systems

(based on Bustamante et al., 2005)

- In small systems thermodynamic variables such as energy and force are fluctuating quantities.

  Examples:
  - Colloidal particles in a fluid (e.g., Brownian motion)
  - Single biomolecules
  - Molecular motors in living cells
  - Nanomachines

- Fluctuation theorems and work relations are precise, quantitative statements about the probability distributions of fluctuating thermodynamic quantities that hold universally for large classes of nonequilibrium processes and systems.

- They generally rely on a comparison of the process with its time reversed version.