

Onsager reciprocity relations

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(Lars Onsager, Awarded Nobel prize for this in chemistry 1968)

entropy close to equilibrium

$$S = -\frac{1}{2} X_i A_{ij} X_j \quad \text{Einstein summation conv. is understood. (} k_B=1 \text{)}$$

Where $X_i = 0$ $\bar{x}_i$ are the equil. values, so X_i 's are deviations from equil. Typical X 's are different densities, (charge density, mass density, magnetization density), energy density)
 A_{ij} is symmetric in its indices

If the system starts away from equilibrium at $t=0$ (i.e. finite $X_i(0)$ values for at least one i), then it will move towards equilibrium as time goes on. On average

$$\dot{\bar{X}}_i = -\lambda_{ik} \bar{X}_k \quad \text{where } \lambda_{ik} \text{ determines the relaxation towards equil.}$$

We can also introduce the thermodynamic conjugate variables; forces:

$$F_j \equiv + \frac{\partial S}{\partial X_j} = -A_{je} X_e \quad \left(S = S(E, V, N, X) \quad \frac{\partial S}{\partial E} = \frac{1}{T} \dots \right)$$

In stat. mech the TD variables are averages:

$$\bar{F}_j = -A_{je} \bar{X}_e \quad \text{multiplying by } A'_{kj} \text{ we find}$$

$$\bar{X}_k = -A'^{-1}_{kj} \bar{F}_j$$

$$\dot{\bar{X}}_i = + \underbrace{L_{ik} A_{kj}}_{L_{ij}} \bar{F}_j$$

$L_{ij} \leftarrow$ Onsager kinetic coefficients

Onsager reciprocity relations:

$$L_{ij} = L_{ji}$$

Proof:

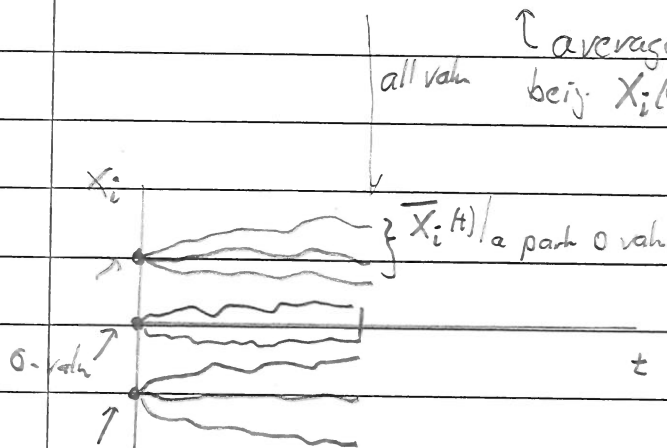
for a system obeying time-reversal symmetry

$$\langle X_i(t) X_j(0) \rangle = \langle X_i(-t) X_j(0) \rangle \xrightarrow{\text{Time-transit}} \langle X_i(0) X_j(t) \rangle$$

average over all values at $t=0$

$$\langle X_i(t) X_j(0) \rangle = \langle \bar{X}_i(t) X_j(0) \rangle_0$$

$\uparrow$ average over all trajectories that starts out being $X_i(0) = X_i \leftarrow$ a particular value



So

$$\langle \bar{X}_i(t) X_j(0) \rangle_0 = \langle X_i(0) \bar{X}_j(t) \rangle_0$$

subtract $\langle X_i(0) X_j(0) \rangle$
and divide by t

$$\left\langle \left(\frac{\bar{X}_i(t) - X_i(0)}{t} \right) X_j(0) \right\rangle_0 = \left\langle X_i(0) \left(\frac{\bar{X}_j(t) - X_j(0)}{t} \right) \right\rangle_0$$

for $t=0$: $\bar{X}_i(0) = X_i(0)$ so for t larger than microscopic fluctuation times but smaller than macroscopic relaxation times, we get

$$\left\langle \dot{\bar{X}}_i(t) X_j(0) \right\rangle_0 = \left\langle X_i(0) \dot{\bar{X}}_j(t) \right\rangle_0$$

$$L_{ik} \left\langle \bar{F}_k(t) X_j(0) \right\rangle_0 = \left\langle X_i(0) \bar{F}_k(t) \right\rangle_0 L_{jk}$$

Now set $t=0$ and use the fact that $\bar{F}_k(0) = F_k(0)$

$$\left\langle F_k X_j \right\rangle_0 = \frac{\int D\mathbf{x} F_k X_j e^{+\frac{\partial S}{\partial x_k} \mathbf{x}}}{\int D\mathbf{x} e^S} \quad \begin{array}{l} S \leftarrow \# \text{ microstates.} \\ \text{Prob of a fluct: } \frac{\# \text{ microstates}}{\# \text{ microstates in eq.}} \\ S = k_B \ln W \\ \uparrow \\ \text{Prob. of microstate} \end{array}$$

$\leftarrow \text{equil.}$

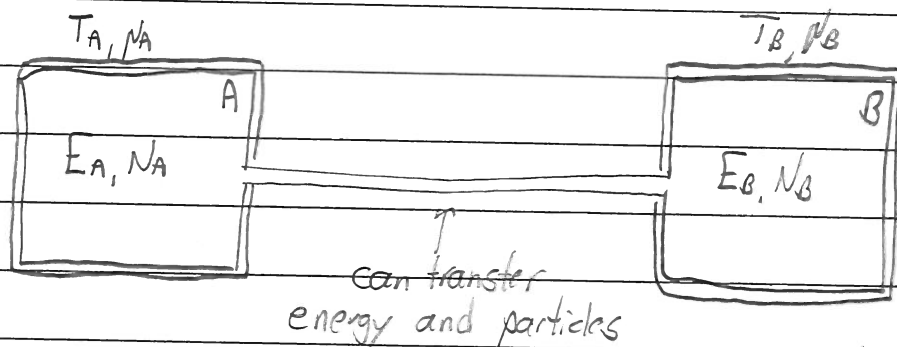
$$= \frac{1}{\int D\mathbf{x} e^S} \left(\int D\mathbf{x} \left[\frac{\partial}{\partial x_k} \left(X_j e^S \right) - \frac{\partial X_j}{\partial x_k} e^S \right] \right) = -\delta_{kj}$$

$\underbrace{+ \frac{\partial X_j}{\partial x_k} e^S + X_j \frac{\partial S}{\partial x_k} e^S}_{+ X_j e^S / \text{Boundary} = 0 \text{ as } e^S \rightarrow 0} \quad \delta_{kj}$

$$\text{So } L_{ik} \underbrace{\left\langle F_k X_j \right\rangle_0}_{-\delta_{kj}} = L_{jk} \underbrace{\left\langle X_i F_k \right\rangle_0}_{-\delta_{ik}}$$

$$\Rightarrow L_{ij} = L_{ji} \quad \text{g.c.d.}$$

Example: Two subsystems at different T 's and μ 's



Total system is thermally insulated and closed.

$$E_A + E_B = E, \quad N_A + N_B = N$$

$$E_B = E - E_A, \quad N_B = N - N_A$$

$$S = S_A(E_A, N_A) + S_B(E_B, N_B)$$

const.

$$\text{Let } X = \left\{ \overbrace{E_A - E_A^0}^{\delta E_A}, \overbrace{N_A - N_A^0}^{\delta N_A} \right\}$$

↖ eq. vals ↗

$$\delta E_A = E_A - E_A^0$$

Then the conjugate variables (forces) are

$$\frac{\partial S}{\partial \delta E_A} = \frac{\partial S}{\partial E_A} = \frac{\partial S_A}{\partial E_A} + \frac{\partial S_B}{\partial E_B} \frac{\partial E_B}{\partial \delta E_A} = \frac{1}{T_A} - \frac{1}{T_B} = F_E$$

-1

$$\frac{\partial S}{\partial \delta N_A} = \frac{\partial S}{\partial N_A} = \frac{\partial S_A}{\partial N_A} + \frac{\partial S_B}{\partial N_B} \frac{\partial N_B}{\partial \delta N_A} = -\frac{\mu_A}{T_A} + \frac{\mu_B}{T_B} = F_N$$

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$$\dot{\delta E_A} = \dot{E_A}$$

$$\dot{\delta N_A} = \dot{N_A}$$

$$\begin{aligned} \dot{E_A} &= L_{EE} F_E + L_{EN} F_N \\ \dot{N_A} &= L_{NE} F_E + L_{NN} F_N \end{aligned}$$

$$L_{NE} = L_{EN}$$