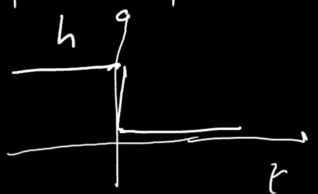
Generalized response function

$$\Xi_{ij}(t) = \epsilon_i \epsilon_j \Xi_{ji}(t)$$

$$\mathcal{T} X_i = \epsilon_i X_i \qquad \epsilon_i = \pm 1$$

$\Big(h(t)$  $\Big) \rightarrow \langle X_i(t) \rangle = \beta h \langle X_i(t) X_j(0) \rangle_0$

ONSAGER regression relation

ENTROPY PRODUCTION RATE

$$d\mathcal{S} = dS + dS_R \qquad d\mathcal{S} \geq 0$$

X_i extensive thermodynamic observable

affinity $\mathbb{F}_i = \dfrac{\partial \mathcal{S}}{\partial X_i} = F_i - F_i^{(R)}$

μ, T, P ensemble

$$T\,dS = dU + P\,dV - \sum_j \mu_j dN_j$$

$$\mathbb{F}_U = \frac{1}{T} - \frac{1}{T_R} \,; \quad \mathbb{F}_V = \frac{P}{T} - \frac{P_R}{T_R} \,; \quad \mathbb{F}_{N_j} = -\frac{\mu_j}{T} + \frac{\mu_j^{(R)}}{T_R}$$

fluxes: $J_i = \dfrac{dX_i}{dt}$

$$\frac{d\mathcal{S}}{dt} = \sum_i \mathbb{F}_i J_i \geq 0 \quad (2^{nd} \text{ Law})$$

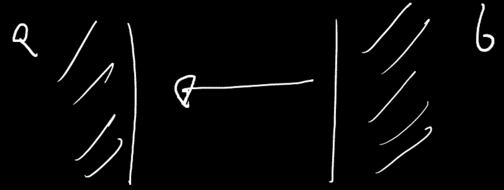
2 reservoirs (a, b)

$$\mathbb{X}_i = X_i + X_i^{(a)} + X_i^{(b)}$$

$\mathbb{X}_i$ conserved $\Rightarrow d\mathbb{X}_i = 0 = \cancel{dX_i} + dX_i^{(a)} + dX_i^{(b)} \simeq dX_i^{(a)} + dX_i^{(b)}$

$$\rightarrow dX_i^{(a)} = - dX_i^{(b)} \rightarrow J_i^{(a)} = -J_i^{(b)}$$

$$\frac{d\mathbb{S}}{dt} \approx \sum_i \underbrace{\left(\frac{\partial S_a}{\partial X_i^{(a)}} - \frac{\partial S_b}{\partial X_i^{(b)}} \right)}_{\mathbb{F}_i} J_i^{(a)}$$



$T^{(a)}$ $\qquad$ $T^{(b)}$ $\qquad$ $\underline{T^{(b)} > T^{(a)}}$

$$\frac{d\mathbb{S}}{dt} \approx \underbrace{\left(\frac{1}{T^{(a)}} - \frac{1}{T^{(b)}} \right)}_{\mathbb{F}_U > 0} \underbrace{J_U^{(a)}}_{> 0} \gtrless 0$$

$$J_U^{(b)} = -J_U^{(a)} < 0$$

ENTROPY PRODUCTION RATE FOR continuous system

$S(\vec{r})\ ;\ X_i(\vec{r})$ (assumption of local equilibrium)

$$dS = \sum_i F_i\, dX_i \qquad \left(F_i = \frac{\partial S}{\partial X_i} \right)$$

intensive quantities $s = S/V\ ;\ x_i = X_i/V \qquad F_i = \dfrac{\partial s}{\partial x_i}$

$$\underline{ds = \sum_i F_i\, dx_i}$$

current densities $\underbrace{\vec{j}_s}_{\text{current density for } S} = \underline{\sum_i F_i}\, \underbrace{\vec{j}_i}_{\text{current density for } x_i}$

entropy is not conserved: $\underline{\dfrac{dS}{dt} = \overbrace{\dfrac{\partial S}{\partial t}}^{\text{"volume" term}} + \overbrace{\vec{\nabla}\cdot\vec{j}_s}^{\text{"surface" term}}}$

x_i are conserved $\rightarrow$ $dx_i/dt = \underbrace{\dfrac{\partial x_i}{\partial t} + \vec{\nabla}\cdot\vec{j}_i = 0}_{\text{continuity equation}}$

$$\frac{\partial S}{\partial t} = \sum_i F_i \frac{\partial x_i}{\partial t}$$

$$\vec{\nabla}\cdot\vec{j}_s = \vec{\nabla}\cdot\left(\sum_i F_i \vec{j}_i\right) = \sum_i \left(\vec{\nabla} F_i \cdot \vec{j}_i + F_i \vec{\nabla}\cdot\vec{j}_i\right)$$

$$\frac{dS}{dt} = \frac{\partial S}{\partial t} + \vec{\nabla}\cdot\vec{j}_s = \sum_i F_i \underbrace{\left(\frac{\partial x_i}{\partial t} + \vec{\nabla}\cdot\vec{j}_i\right)}_{0} + \sum_i \vec{\nabla} F_i \cdot \vec{j}_i$$

$$\boxed{\frac{dS}{dt} = \sum_i \vec{\nabla} F_i \cdot \vec{j}_i}$$

continuous system

analog for $\boxed{\dfrac{dS}{dt} = \sum_i \mathbb{F}_i J_i}$

$\vec{\mathbb{F}}_i = \vec{\nabla} F_i(\vec{r})$ $\qquad$ $\mathbb{F}_i = F_i - F_i^{(0)}$

Phenomenological equations involving transport kinetic coefficients

$(\Pi_{ij}\ ;\ \underline{\underline{L_{ij}}} \longrightarrow$ Onsager kinetic coefficients$)$

(linear response theory)

Definition of M coefficients:

$$\left[\langle J_i \rangle = \frac{d}{dt} \langle X_i \rangle = - \sum_k M_{ik} \langle X_k(t) \rangle \right] \alpha$$

(non equilibrium averages)

$$\left(\cancel{\#} \text{ observable } \quad \frac{d}{dt} \langle x_i \rangle = - M_{ii} \langle x_k(t) \rangle \right)$$

$$\left(\langle X_i \rangle_0 = 0 \right) \quad \to \text{ exponential decay of } \langle x_i(t) \rangle$$

Onsager regr. relation $\quad \langle X_i(t) \rangle \propto \langle x_i(t)\, x_j(0) \rangle_0$

$$\underline{\frac{d}{dt} \langle X_i(t)\, X_j(0) \rangle_0 = - \sum_k M_{ik} \langle X_k(t)\, X_j(0) \rangle_0}$$

if $\tau_i = \tau_j = 1 \to \underbrace{\langle x_i(t)\, x_j(0) \rangle_0 = \langle x_j(t)\, x_i(0) \rangle_0}$

$$\frac{d}{dt} \cdots \qquad \downarrow$$

$$\sum_k M_{ik} \langle x_k(t)\, x_j(0) \rangle_0 = \sum_k M_{jk} \langle x_k(t)\, x_i(0) \rangle_0$$

define $\underline{L_{ij} = \sum_k M_{ik} \langle x_k x_j \rangle_0}$ $\quad \langle x_k(0)\, x_j(0) \rangle_0$ (+)

$$t = 0 \to \underline{L_{ij} = L_{ji}} \quad \left(\begin{array}{l} \text{Symmetric Onsager} \\ \text{matrix } (\tau_i = \tau_j = 1) \end{array} \right)$$

$$\Rightarrow \boxed{\langle J_i \rangle = \frac{d}{dt} \langle X_i \rangle = \sum_k L_{ik} \langle F_k \rangle} \quad \alpha$$

(*) $\quad (+ \mathcal{O}(F_k^2))$

general definition for L_{ij}

$$\boxed{L_{ik} = \left.\frac{\partial \langle J_i \rangle}{\partial \mathbb{F}_k}\right|_{\mathbb{F}_k = 0 \ \forall k}}$$

Start from (*) to recover (+)

Onsager regr. rel.: $\frac{d}{dt}\langle x_i(t)\, x_j(0)\rangle_0 = \sum_k L_{ik} \langle \mathbb{F}_k(t) X_j(0)\rangle_0$

$$\frac{d}{dt}\langle x_i(t)\, x_j(0)\rangle_0 = - \sum_k M_{ik} \langle x_k(t)\, x_j(0)\rangle_0$$

$$\sum_k M_{ik} \langle x_k(t)\, x_j(0)\rangle_0 = - \sum_k L_{ik} \langle \mathbb{F}_k(t) X_j(0)\rangle_0$$

$$\langle \mathbb{F}_k(0) X_j(0)\rangle_0 = -\delta_{kj}$$

$$\Rightarrow \boxed{\sum_k M_{ik} \langle x_k x_j \rangle_0 = L_{ij}} \quad (+)$$

(*) $$\frac{dS}{dt} = \sum_i J_i \mathbb{F}_i = \sum_{ij} L_{ij} \mathbb{F}_i \mathbb{F}_j$$

a bilinear form in $\mathbb{F}_i, \mathbb{F}_j$

$dS/dt > 0$ at $\mathbb{F}_i > 0$ (at least one i)

$\Rightarrow \underline{L_{ii} > 0 \text{ and } \det L > 0}$

$$\frac{d^2 S}{dt^2} = 2 \sum_{i,j} L_{ij} \underbrace{\sum_k \frac{\partial F_i}{\partial x_k} \underbrace{\frac{d x_k}{dt}}_{J_k}}_{dF_i/dt} F_j$$

$L_{ij} = L_{ji}$

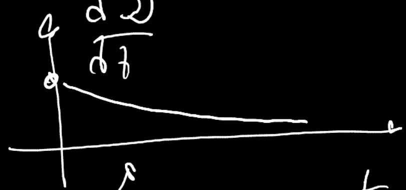
$$= 2 \sum_{i,k} \frac{\partial F_i}{\partial x_k} J_i J_k = 2 \sum_{i,k} \frac{\partial^2 S}{\partial x_i \partial x_k} J_i J_k$$

$J_i = \sum_j L_{ij} F_j$ $\qquad$ $F_i = \frac{\partial S}{\partial x_i}$

$S(\{X_i\})$ is a concave function of $\{X_i\}$

$\partial^2 S / \partial x_i \partial x_j$ is a <u>negative</u> form

$\frac{d^2 S}{dt^2} \leq 0 \rightarrow dS/dt$ always decreases



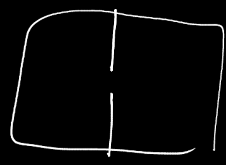
2 possible scenarios:

- relaxation to equilibrium $\qquad dS/dt \xrightarrow[t \to \infty]{} 0$
- relaxation to a stationary non-equilibrium state (NESS)

$\frac{dS}{dt} \xrightarrow[t \to \infty]{}$ finite positive value

Mechanothermal effect (fixed Volume)

(coupled transport)



$T \quad T(2)$

energy and particle fluxes coupled

$$dS = \frac{dU}{T} - \frac{\mu}{T}\, dN$$

$$\mathbb{F}_U = \frac{1}{T} - \frac{1}{T_2} \; ; \; \mathbb{F}_N = -\frac{\mu}{T} + \frac{\mu_2}{T_2} \quad (\text{observables}, U, N)$$

$$J_U = dU/dt \; ; \; J_N = dN/dt$$

ONSAGER MATRIX

$$\begin{cases} J_U = L_{UU}\,\mathbb{F}_U + L_{UN}\,\mathbb{F}_N \\ J_N = L_{NU}\,\mathbb{F}_U + L_{NN}\,\mathbb{F}_N \end{cases}$$

1) Thermal equilibrium: $\mathbb{F}_U = 0 \quad (T = T_2)$

$$J_U = L_{UN}\left(\frac{\mu_2 - \mu}{T}\right) \qquad (\text{for } \mathbb{F}_N \neq 0)$$

$\mu_2 \neq \mu$

$$J_U / J_N = \frac{L_{UN}}{L_{NN}}$$

2) Thermomechanical effect:

stationary state with $J_N = 0$

$$\mathbb{F}_N / \mathbb{F}_U = -\frac{L_{UN}}{L_{NN}} \; ; \; J_U = \mathbb{F}_U\left[L_{UU} - \frac{L_{UN}^2}{L_{NN}}\right] = \frac{\det L}{L_{NN}}\,\mathbb{F}_U$$

$\mathbb{F}_N, \mathbb{F}_U \neq 0$

APPENDIX: $\langle \mathbb{F}_k \, X_j \rangle_0 = -\delta_{kj}$

$$\left(L_{ij} = \sum_k \Gamma_{ik} \langle x_k \, x_j \rangle_0 \iff \langle J_i \rangle = \sum_k L_{ik} \langle \mathbb{F}_k \rangle \right)$$

$$\langle \mathbb{F}_x \, X_j \rangle_0 = \frac{\int \prod_k dx_k \, \mathbb{F}_x \, X_j \exp\left(S(\{x_n\}) \right)}{\int \prod_k dx_k \exp\left(S(\{x_n\}) \right)}$$

$(x_k^* =$ equilibrium values$)$

$$S(\{x_\lambda\}) \simeq S(\{x_n^*\}) + \frac{1}{2} \sum_{ij} \frac{\partial^2 S}{\partial x_i \partial x_j}\Bigg|_{x_k = x_k^* \, \forall k} \Delta x_i \, \Delta x_j$$

$\Delta x_i = x_i - x_i^*$; $\dfrac{\partial^2 S}{\partial x_i \partial x_j}$ is a negative form

$$\mathbb{F}_k = \frac{\partial S}{\partial x_k} \simeq \sum_i \frac{\partial^2 S}{\partial x_k \partial x_i}\Bigg|_{x_j = x_j^* \, \forall j} \Delta x_i \qquad x_j^* = \langle x_j \rangle_0$$

$$\langle \mathbb{F}_k \, X_j \rangle_0 \simeq \sum_i \frac{\partial^2 S}{\partial x_k \partial x_i}\Bigg|_{x_\ell = x_\ell^* \, \forall \ell} \underbrace{\langle \Delta x_i \, \Delta x_j \rangle_0}$$

$(X_j = \Delta X_j \quad (x_j^* = 0))$

$$\simeq \sum_i \frac{\partial^2 S}{\partial x_k \partial x_i}\Bigg|_{x_\ell = x_\ell^* \, \forall \ell} \cdot \left(- \left(\frac{\partial^2 S}{\partial x^2} \right)^{-1}_{ij} \Bigg|_{x_\ell = x_\ell^* \, , \forall \ell} \right)$$

$$\simeq -\left(\mathbb{1} \right)_{kj} = -\delta_{kj}$$