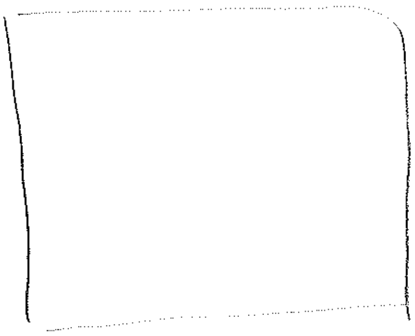
$\boxed{\text{Les Houches}}$

I Equilibrium versus non equilibrium

$\boxed{\text{ONE WAITS VERY LONG}}$ $t \to \infty$

Equilibrium at temperature T

T



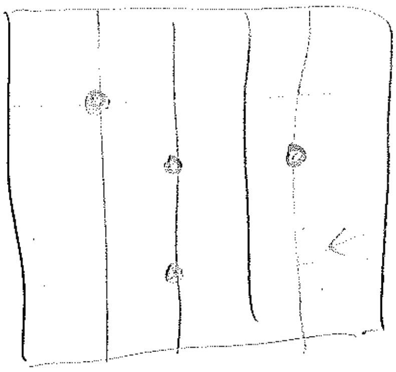
$\mathcal{C}$ = microscopic configuration

$\mathcal{C} = (\vec{r}_1, \dots \vec{r}_N, \vec{p}_1 \dots \vec{p}_N)$

gas

$$E(\mathcal{C}) = \sum_i \frac{p_i^2}{2m} + \sum V(\vec{r}_i - \vec{r}_j)$$

T



Lattice gas

$n_i = 0, 1$ (exclusion)

$n_i = 0, 1, 2 \dots k \dots$

nb of particles on site i

$$\mathcal{C} = \{ n_1, n_2 \dots n_V \}$$

$E(\mathcal{C})$ = energy of config. $\mathcal{C}$.

$= E(\{n_i\})$ $k, \dots$

<u>Equilibrium</u>

no need to care about the contacts with heat bath,

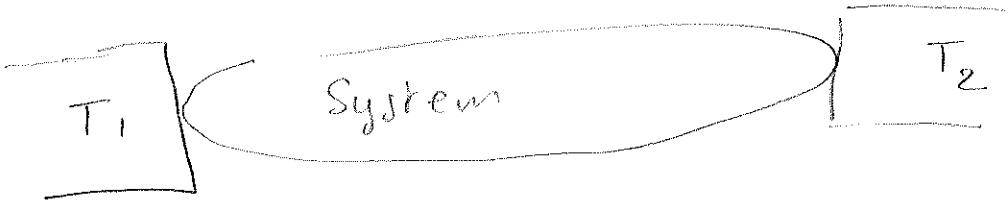
$$P(\mathcal{C}) = \frac{e^{-\beta E(\mathcal{C})}}{Z(\beta)}$$

$\uparrow$ normalization

$$\boxed{\beta = \frac{1}{kT}}$$

$\boxed{\text{here } k = 1}$

<u>Non equilibrium</u>: steady state



$\boxed{P(\mathcal{C}) = \, ?}$ except for very few models

. Certainly knowledge of T_1 and T_2 not sufficient

weak contact with T_1 $\quad P(\mathcal{C}) \simeq P_{eq \text{ at } T_2}(\mathcal{C})$

T_2 $\quad P(\mathcal{C}) = P_{eq. \text{ at } T_1}(\mathcal{C})$

$\boxed{\text{One needs to represent the heat baths}}$

A3

II Description of heat baths

(1) Deterministic Heat baths + deterministic dynamics

- Nosé . Hoover heat bath
- Coupling with a large number of harmonic oscillators
- gaussian heat bath

$m \ddot{q}_i = F_i$ is replaced by

minimising $\sum_{i=1}^{N} (m_i \ddot{q}_i - F_i)^2 A_i$

with the constraint

$$\frac{m_i \dot{q}_i^2}{2} = \frac{k_B T}{2}$$

$\Uparrow$

fixes the kinetic energy of the particle

for the particles i in contact with a heat bath

A4

No difficulty to have different particles in contact with heat baths at $\neq$ temperature

② Stochastic Heat baths

- Langevin Force

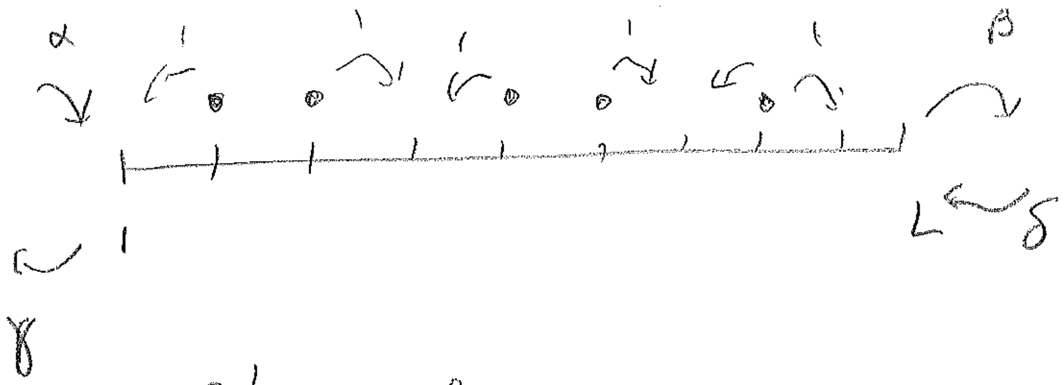
$$m_i \ddot{q}_i = F_i - \gamma \dot{q}_i + \eta_i(t)$$

$$\langle \eta_i(t) \eta_i(t') \rangle = 2 \gamma T_i$$

Changing $\gamma \Longleftrightarrow$ changing the strength of the contacts

③ Markov process

Ex: exclusion process SSEP



2^L configurations

• : a particle : transport of particles

• : a quantum of energy →

transport of heat

<u>Continuous time</u>

$\alpha\, dt$ site 1 becomes occupied

if site 1 was empty

$$\mathcal{C} = \{\tau_1 \cdots\cdots \tau_n\}$$

$$\tau_i = 0, 1$$

$$\boxed{\begin{aligned} \frac{dP_t(\mathcal{C})}{dt} &= \sum_{\mathcal{C}'} M(\mathcal{C},\mathcal{C}')P_t(\mathcal{C}') \\ P_{t+\Delta t}(\mathcal{C}) &= P_t(\mathcal{C}) + \Delta t \sum_{\mathcal{C}'} M(\mathcal{C},\mathcal{C}')P_t(\mathcal{C}') \end{aligned}}$$

<u>Discrete time, Markov Process</u>

$$\mathcal{C}_{-1} \quad \mathcal{C}_0 \quad \mathcal{C}_1 \quad \cdots \quad \mathcal{C}_t$$

$$M(\mathcal{C}', \mathcal{C}) \equiv M(\mathcal{C}' \leftarrow \mathcal{C})$$

prob in one time step of jumping from $\mathcal{C}$ to $\mathcal{C}'$

$$\boxed{P_{t+1}(\mathcal{C}) = \sum_{\mathcal{C}'} M(\mathcal{C},\mathcal{C}')\, P_t(\mathcal{C})}$$

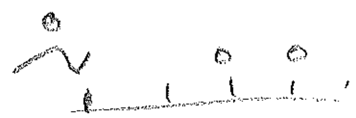
$$\Rightarrow \quad P_t(\mathcal{C} \mid \mathcal{C}_0) = M^t(\mathcal{C}, \mathcal{C}_0)$$

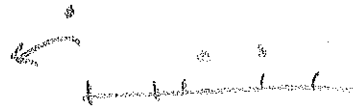
III Large deviations of the current

Ex 

$\overrightarrow{Q_t}$ number of particles which entered from the left
− nb of particles with exit to the left during time t

$\mathcal{C} \to \mathcal{C}'$: $q(\mathcal{C}' \leftarrow \mathcal{C}) = q(\mathcal{C}', \mathcal{C})$

one particle enters $\quad 1$ 

one particle exits $\quad -1$ 

no particle exchange with the left $\quad 0$ 

$$\boxed{Q_t = \sum_{\tau=0}^{t-1} q(\mathcal{C}_{\tau+1}, \mathcal{C}_\tau)}$$

(17)

$$\text{Prob}(\mathcal{C}_t, Q_t) = P(\mathcal{C}_t, Q_t)$$

$$\boxed{P(\mathcal{C}_{t+1}, Q_{t+1}) = \sum_{Q_t} \sum_{\mathcal{C}_t} M(\mathcal{C}_{t+1}, \mathcal{C}_t)\, P(\mathcal{C}_t, Q_t - q(\mathcal{C}_{t+1}, \mathcal{C}_t))}$$

$\mathcal{C}$: finite number of conf.

Q_t : ∞ number of values

$$\hat{P}_t(\mathcal{C}_t) = \sum P(\mathcal{C}_t, Q_t)\, e^{\lambda Q_t}$$

$$\Rightarrow \boxed{\hat{P}_{t+1}(\mathcal{C}) = \sum_{\mathcal{C}'} \underbrace{M(\mathcal{C}, \mathcal{C}')\, e^{\lambda q(\mathcal{C}, \mathcal{C}')}}_{\text{tilted matrix } M_\lambda(\mathcal{C}, \mathcal{C}')} \hat{P}_t(\mathcal{C}')}$$

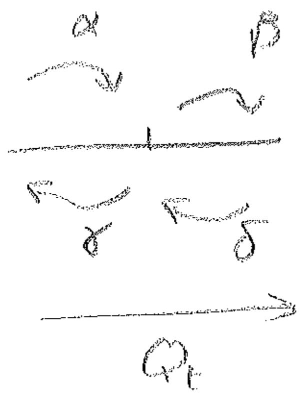
Long time

$$\hat{P}_t(\mathcal{C}) \sim e^{\mu(\lambda) t}$$

$$\boxed{e^{\mu(\lambda)} = \text{largest eigenvalue of } M_\lambda}$$

Example continuous time

SSEP $L = 1$



$$\frac{dP_1}{dt} = -(\beta+\gamma)P_1 + (\alpha+\delta)P_0$$

$$\frac{dP_0}{dt} = (\beta+\gamma)P_1 - (\alpha+\delta)P_0$$

$$M = \begin{pmatrix} -(\beta+\gamma) & \alpha+\delta \\ \beta+\gamma & -(\alpha+\delta) \end{pmatrix}$$

$$M_\lambda = \begin{pmatrix} -(\beta+\gamma) & \alpha e^{\lambda}+\delta \\ \beta+\gamma e^{-\lambda} & -(\alpha+\delta) \end{pmatrix}$$ tilted matrix

$\mu(\lambda)$ = largest eigenvalue of M_λ

$$M_{\text{discrete}} = I + \Delta t \, M_{\text{continuous}}$$

$$e^{\mu_d} = 1 + \Delta t \, \mu_{\text{continuous}}$$

A 8a

<u>Remark</u>

Here $M = M_1 + M_2$

$$\begin{pmatrix} -\gamma & \alpha \\ \gamma & -\alpha \end{pmatrix} + \begin{pmatrix} -\beta & \delta \\ \beta & -\delta \end{pmatrix}$$

Reservoir 1 reservoir 2

$$\tilde{M} = \tilde{M}_1 + M_2$$

$$\begin{pmatrix} -\gamma & \alpha e^{\lambda} \\ \gamma e^{-\lambda} & -\alpha \end{pmatrix} \qquad \begin{pmatrix} \; \end{pmatrix}$$

$$\mu(\lambda) = \mu(\lambda')$$

$$\boxed{e^{\lambda'} = \frac{\gamma\delta}{\alpha\beta}\, e^{-\lambda}}$$

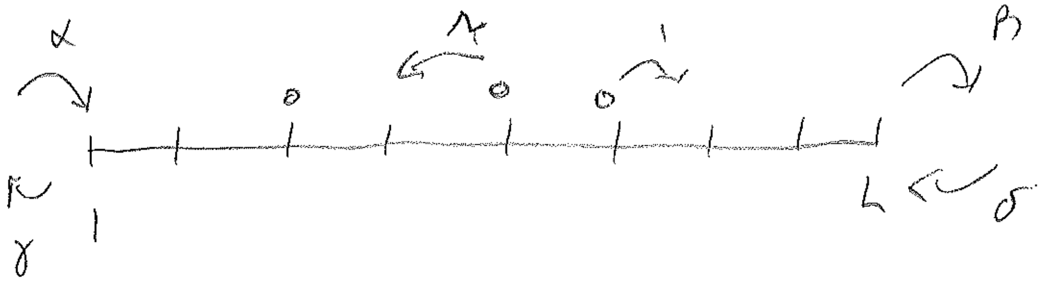
$$\mu(\lambda) = \mu\left(-\lambda + \log\frac{\gamma\delta}{\alpha\beta}\right)$$

$$\Rightarrow \quad P\left(\frac{Q_t}{t} = q\right) \sim e^{-t\, I(q)}$$

$$\boxed{I(-q) = I(q) + q\log\left(\frac{\alpha\beta}{\gamma\delta}\right)}$$

SSEP true for all L !

Fluctuation theorem



Field

A10

$$\boxed{e^{\lambda'} = r^{L-1} \frac{\gamma\delta}{\alpha\beta} e^{-\lambda}}$$

$$I(-q) = I(q) + \left(\log \frac{\alpha\beta}{\gamma\delta} - (L-1)\log r\right) q$$

Exercices ① Q sortie / entrée

② $L = 2$ vérifier

IV Fluctuation Theorem

- Evans ~93
- Gallavotti Cohen
- Lebowitz Spohn
- Kurchan ~99

⋮

Discrete Markov Process

$M(\mathcal{C}', \mathcal{C})$ = prob $\mathcal{C} \to \mathcal{C}'$ 1 time step

$$\boxed{s(\mathcal{C}', \mathcal{C}) = \log\left[\frac{M(\mathcal{C}', \mathcal{C})}{M(\mathcal{C}, \mathcal{C}')}\right]}$$

$$S_t = \sum_{\tau=0}^{t-1} \log \left[\frac{M(\mathcal{C}_{\tau+1}, \mathcal{C}_\tau)}{M(\mathcal{C}_\tau, \mathcal{C}_{\tau+1})} \right]$$ (A11)

$$\langle e^{\lambda S_t} \rangle \sim e^{t\,\mu(\lambda)}$$

$e^{\mu(\lambda)}$ largest eigenvalue of

$$M_\lambda(\mathcal{C}', \mathcal{C}) = M(\mathcal{C}', \mathcal{C})\, e^{\lambda S(\mathcal{C}', \mathcal{C})}$$

$$M_\lambda(\mathcal{C}', \mathcal{C}) = M(\mathcal{C}', \mathcal{C})^{1+\lambda} \left[M(\mathcal{C}, \mathcal{C}') \right]^{-\lambda}$$

$$M_{-1-\lambda}(\mathcal{C}', \mathcal{C}) = M(\mathcal{C}', \mathcal{C})^{-\lambda} \left[M(\mathcal{C}, \mathcal{C}') \right]^{1+\lambda}$$

$$M_\lambda^{\,t}$$

No problem if finite nb of states $\mathcal{C}$

$$\Rightarrow \boxed{\mu(\lambda) = \mu(-1-\lambda)}$$

Fluctuation Theorem

$$\boxed{\tilde{I}(s) = \tilde{I}(-s) - s}$$

check:

$$\mu(\lambda) = \max_s \left[\lambda s - \tilde{I}(s) \right] = \max_s \left[\lambda s + s - \tilde{I}(-s) \right]$$

$$= \max_s \left[-(\lambda+1)s - \tilde{I}(s) \right]$$

V Physical interpretation

$$S_t = \sum_{\tau=0}^{t-1} s(\mathcal{C}_{\tau+1}, \mathcal{C}_\tau)$$

$s(\mathcal{C}_{\tau+1}, \mathcal{C}_\tau)$ = creation of entropy in outside world

detailed balance at equilibrium

$E(\mathcal{C})$ = energy of system in $\mathcal{C}$

$$M(\mathcal{C}', \mathcal{C})\, e^{-\beta E(\mathcal{C})} = M(\mathcal{C}, \mathcal{C}')\, e^{-\beta E(\mathcal{C}')}$$

$\Rightarrow$ syst. $\rightarrow$ equilibrium
(finite number of states
M irreducible)

System
$\mathcal{C} \rightarrow \mathcal{C}'$

$E(\mathcal{C}) \rightarrow E(\mathcal{C}')$ $\Rightarrow$ ΔE outside world $= E(\mathcal{C}) - E(\mathcal{C}')$

ΔS outside world $= \beta(E(\mathcal{C}) - E(\mathcal{C}'))$

A13

because the entropy S of a heat bath

$$S_{\text{heat bath}} = \beta E_{\text{heat bath}}$$

$$\Rightarrow \quad \Delta S_{0.w} = \beta \left[E(\mathcal{C}) - E(\mathcal{C}') \right]$$
$$= \log \left(\frac{M(\mathcal{C}', \mathcal{C})}{M(\mathcal{C}, \mathcal{C}')} \right)$$

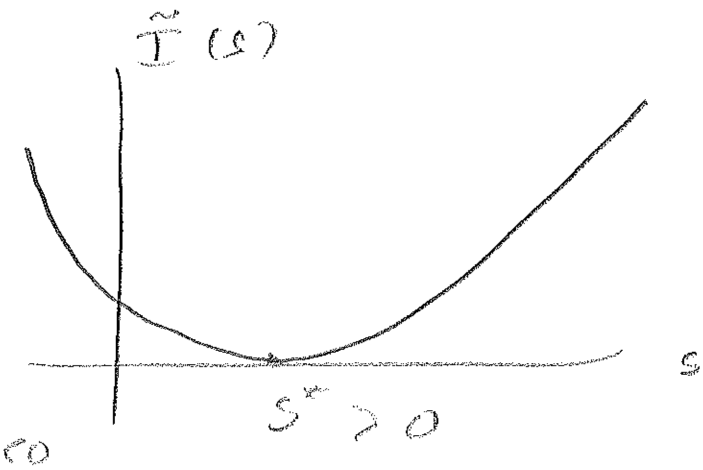
$$P\left(\frac{S_t}{t} = s \right) \sim e^{-t \tilde{I}(s)}$$

$$\boxed{\tilde{I}(-s) = \tilde{I}(s) + s}$$

Fluctuation Theorem

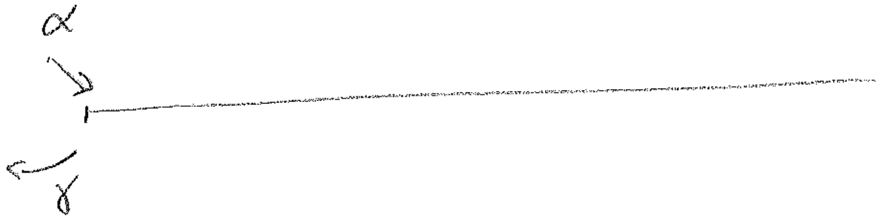
<u>Remark</u> $s > 0$ $\quad \tilde{I}(-s) > \tilde{I}(s)$

- <u>Second law</u>



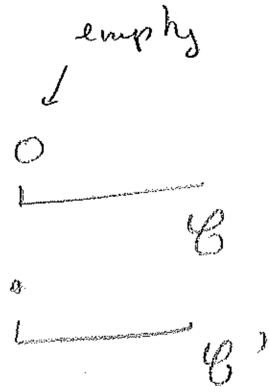
- <u>Possible events with $s < 0$</u>

Events $\boxed{\tilde{I}(-s^*) = s^*} > 0$ $\boxed{\text{rare}}$



- Unit energy

$$\frac{\alpha}{\gamma} = \frac{M(\mathcal{C}', \mathcal{C})}{M(\mathcal{C}, \mathcal{C}')} = e^{\frac{E(\mathcal{C}) - E(\mathcal{C}')}{kT}}$$



$$\frac{\alpha}{\gamma} = e^{-\frac{1}{kT_1}}$$

$$\frac{\delta}{\beta} = e^{-\frac{1}{kT_2}}$$

$$\tilde{I}(s) = I(q) = \tilde{I}(-s) - s$$
$$= I(-q) - q\left(\frac{1}{kT_2} - \frac{1}{kT_1}\right)$$

$$\boxed{I(q) = I(-q) - q\left(\frac{1}{kT_2} - \frac{1}{kT_1}\right)}$$

energy

$T_2 < T_1 \Rightarrow q > 0$ $\quad$ 2nd law

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<u>Remark</u> : The Markov matrix could depend on time:

- changing T_1 or T_2 with time
- changing $E_t(\mathcal{C})$

Work

$\boxed{\text{Stochastic Thermodynamics}}$

Terms of particles

$S_{reservoir} = -\frac{\mu}{k T_1} N_{reservoir}$

$$\boxed{I(q) = I(-q) - q\left(\frac{\mu_1}{k T_1} - \frac{\mu_2}{k T_2}\right)}$$

chemical potential

VI Einstein Relation

$$I(q) = I(-q) - q\left(\frac{1}{k T_2} - \frac{1}{k T_1}\right)$$

$$\langle e^{\lambda Q_t} \rangle \simeq e^{\mu(\lambda) t}$$

$$\mu(\lambda) = \mu\left(-\lambda - \left(\frac{1}{k T_2} - \frac{1}{k T_1}\right)\right)$$

$$\frac{\langle Q_t \rangle}{t} = \mu'(0)$$

$$\frac{\langle Q_t^2 \rangle - \langle Q_t \rangle^2}{t} = \mu''(0)$$

$$T_1 = T_2 + \Delta T$$

$$\mu(\lambda) = \mu\left(-\lambda - \frac{\Delta T}{k T^2}\right)$$

$$\mu'(0) = -\mu'\left(-\frac{\Delta T}{k T^2}\right) = -\mu'(0) + \frac{\Delta T}{k T^2}\,\mu''(0)$$

<u>ΔT small</u>

$$\frac{\langle Q_t \rangle}{t} = \mu'(0) = \frac{\mu''(0)}{2 k T^2}\,\Delta T \qquad \Delta T \text{ small}$$

$$\frac{\langle Q_t^2 \rangle}{t} = \mu''(0) \qquad \Delta T = 0$$

ΔT small $\qquad \dfrac{\langle Q_t \rangle}{t} = \tilde{D}\,\Delta T$

$\Delta T = 0 \qquad \dfrac{\langle Q_t^2 \rangle}{t} = \underbrace{2 k T^2 \tilde{D}}_{\gamma}$

$$\boxed{\text{variance} = k \quad \text{Response}}$$

$$\gamma = 2 k T^2 \tilde{D}$$

Particles

$$\mu(\lambda) \longrightarrow \nu(\lambda)$$

$$\mu_1 = \mu_2 + \Delta\mu \qquad T_1 = T_2 = T$$

$$\frac{\langle Q \rangle}{t} = \frac{1}{2kT}\nu''(0)\,\Delta\mu = \underbrace{\left(\frac{1}{2kT}\nu''(0)\frac{\Delta\mu}{\Delta\rho}\right)}_{\tilde{D}}\Delta\rho$$

$$\frac{\langle Q^2 \rangle}{t} = \nu''(0) \longleftarrow \tilde{\sigma}$$

$$F = V f\left(\frac{N}{V}\right)$$

free energy / unit volume

$$\mu = \frac{dF}{dV} = f'(\rho)$$

$$\frac{d\mu}{d\rho} = f''(\rho)$$

$$\boxed{\frac{\tilde{D}}{\tilde{\sigma}} = \frac{1}{2kT} f''(\rho)}$$

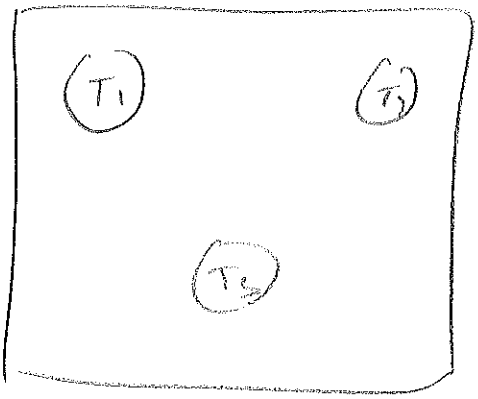
here $T = 1$

$k = 1$

$\tilde{D}$ hard to know!

but $\tilde{\sigma}$ related to $\tilde{D}$

VII Onsager relations



$$\langle e^{\lambda_1 Q_1 + \lambda_2 Q_2} \rangle$$

$$Q_3 = -Q_1 - Q_2$$

$$\mu(\lambda_1, \lambda_2) = \mu\left(-\lambda_1 - \left(\frac{1}{kT_3} - \frac{1}{kT_1}\right), -\lambda_2 - \left(\frac{1}{kT_3} - \frac{1}{kT_2}\right)\right)$$

$T_1 - T_3$ small $= \Delta T_1$

$T_2 - T_3$ small $= \Delta T_2$

$$\frac{\langle Q_1 \rangle}{t} = M_{11} \, \Delta T_1 + M_{12} \, \Delta T_2$$

$$\frac{\langle Q_2 \rangle}{t} = M_{21} \, \Delta T_1 + M_{22} \, \Delta T_2$$

$$\boxed{M_{21} = M_{12}}$$

Relation d' Onsager