

$$I(v) = -k_B \ln \left[\frac{1 + \sum_{\alpha=1}^M f_{\alpha} b_{n_1}^{(\alpha)}}{1 + \sum_{\alpha} f_{\alpha} b_{n_0}^{(\alpha)}} \right] + \frac{1}{T} \sum_{\alpha} f_{\alpha} \delta x_{n_1, n_0}^{(\alpha)}$$

$$v = (n_1, n_0)$$

Simplify notation: $I(v) = \frac{1}{T} \sum_{\alpha} f_{\alpha} \delta y_{n_1, n_0}^{(\alpha)}$

in small f_{α} limit: $\delta y_{n_1, n_0}^{(\alpha)} \approx \delta x_{n_1, n_0}^{(\alpha)} - k_B T (b_{n_1}^{(\alpha)} - b_{n_0}^{(\alpha)})$

$\ln(1+\epsilon) \approx \epsilon$ $\phi_{\alpha} = \frac{f_{\alpha}}{T} \Rightarrow I(v) = \sum_{\alpha} \phi_{\alpha} \delta y_{n_1, n_0}^{(\alpha)}$

Eq. 1: $\underbrace{\langle I(v) \rangle}_{\sigma} \approx \frac{1}{2k_B} \frac{\langle I^2(v) \rangle}{\delta t}$ from $1/T$

$$\sigma = \vec{\phi}^T L \vec{\phi}$$

$$= \frac{1}{2k_B \delta t} \left\langle \sum_{\alpha \neq \gamma} \phi_{\alpha} \phi_{\gamma} \delta y^{(\alpha)} \delta y^{(\gamma)} \right\rangle$$

$$\sum_{\alpha \neq \gamma} \phi_{\alpha} \phi_{\gamma} L_{\alpha \gamma}$$

$$\Rightarrow L_{\alpha \gamma} = \frac{1}{2k_B \delta t} \langle \delta y^{(\alpha)} \delta y^{(\gamma)} \rangle \quad [\text{Eq. 3}]$$

recipe for calculating $L_{\alpha \gamma}$

\Rightarrow shows that $L_{\alpha \gamma} = L_{\gamma \alpha}$ for any $\alpha \neq \gamma$

\Rightarrow Onsager reciprocity
[1931 Nobel prize]

two loop circuit:

$$\begin{pmatrix} J_1 \\ J_2 \end{pmatrix} = L \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} \quad L = \begin{pmatrix} \frac{T}{R} + \frac{T}{R'} & \frac{-T}{R'} \\ \frac{-T}{R'} & \frac{T}{R'} \end{pmatrix}$$

write out Eq. 3 in detail:

$$L_{\alpha\gamma} = \frac{1}{2k_B\delta t} \sum_{n, n_0} \underbrace{W_{n, n_0} p_{n_0}^s}_{\mathcal{P}(\mu_0)} \delta y_{n, n_0}^{(\alpha)} \delta y_{n, n_0}^{(\gamma)}$$

$$W_{n, n_0} p_{n_0}^s = W_{n, n_0}^{eq} p_{n_0}^{eq} \left(1 + \sum_{\alpha} f_{\alpha} C_{n, n_0}^{(\alpha)} + \dots \right)$$

$$L_{\alpha\gamma} \approx \frac{1}{2k_B\delta t} \sum_{n, n_0} W_{n, n_0}^{eq} p_{n_0}^{eq} \delta y_{n, n_0}^{(\alpha)} \delta y_{n, n_0}^{(\gamma)} + \dots$$

$$L_{\alpha\gamma} \approx \frac{1}{2k_B\delta t} \left\langle \delta y^{(\alpha)} \delta y^{(\gamma)} \right\rangle_{eq} \quad \leftarrow \text{avg. in ESS}$$

fluctuation-dissipation theorem [FDT]
(Callen, Welton, Kubo, etc. 1950's)

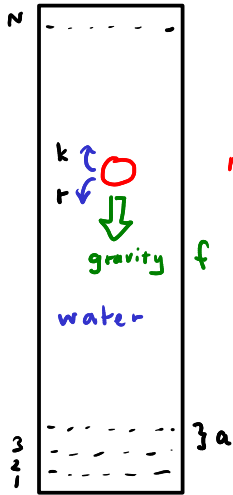
RHS: can be evaluated using equil. trajectories (fluctuations in equil.)

LHS: $L_{\alpha\gamma}$ tell you about entropy prod.
 $\sigma = \vec{\phi}^T L \vec{\phi} = \frac{I}{\delta t} = -\frac{Q}{\delta t}$ heat per unit time dissipated

dissipation

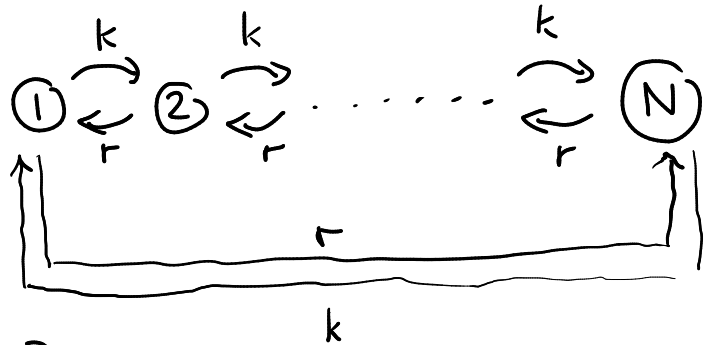
into environ.
when out of
equilibrium

Example: Brownian motion



micron-sized
bead

for
math
simplicity
assume
periodic BC



don't matter if cylinder
is big + bead starts
in middle

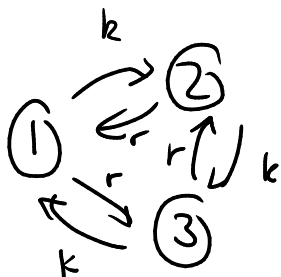
$$E_n = \text{const. for all } n$$

$$\begin{aligned} \text{LDB: } \frac{k}{r} &= e^{-\beta (E_{n+1} - E_n + fa)} \\ &= e^{-\beta fa} \end{aligned}$$

coupling to one force ($M = 1$)

$$\text{stat. state } p_n^s(f) = \frac{1}{N} = p_n^{\text{eq}}$$

Special
case
where
 $p_n^s(f)$ is
 f indep.
by
symmetry



$$W \vec{p}^s = \vec{p}^s \Rightarrow \vec{p}^s = \begin{pmatrix} 1/3 \\ 1/3 \\ 1/3 \end{pmatrix}$$

$$p_n^s(f) = p_n^{\text{eq}} \left(1 + b_n^{\text{red}} f + \dots \right)$$

$$\Rightarrow \delta y_{n,n_0} = \delta x_{n,n_0} = \begin{cases} a & \text{if } n_1 = n_0 + 1 \\ -a & \text{if } n_1 = n_0 - 1 \end{cases}$$

L is 1×1 matrix (L is scalar)

$$\text{FDT: } 2k_B \delta t L = \langle \delta x^2 \rangle_{eq}$$

$$\frac{\langle \delta x \rangle}{\delta t} = J = L \phi = L \frac{f}{T}$$

current
mean vel.
of bead

from fluid mechanics $J = \frac{1}{\gamma} f$

γ drag friction
coeff.

$$\frac{L}{T} = \frac{1}{\gamma}$$

\Rightarrow rewrite FDT

$$\langle \delta x^2 \rangle_{eq} = 2k_B L \delta t$$

$$= 2 \underbrace{\frac{k_B T}{\gamma}}_{D} \delta t$$

$$D = \frac{k_B T}{\gamma}$$

Einstein
1905

D diffusion
const.

