plug into expression for $I(\nu)$:

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

when $f_\alpha = 0$ for all $\alpha \Rightarrow I(\nu) = 0$ (ESS)

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

$$\delta y_{n_1 n_0}^{(\alpha)} \approx \delta x_{n_1 n_0}^{(\alpha)} - k_B T\left(b_{n_1}^{(\alpha)} - b_{n_0}^{(\alpha)}\right)$$

used approx $\ln(1+\epsilon) \approx \epsilon$

$$\phi_\alpha = \frac{f_\alpha}{T} \Rightarrow I(\nu) = \sum_\alpha \phi_\alpha \, \delta y_{n_1 n_0}^{(\alpha)}$$

plug into Eq. (1):

$\langle e^{-I(\nu)/k_B} \rangle = 1 \Rightarrow$

IFT

$$\underbrace{\frac{\langle I(\nu)\rangle}{\delta t}}_{\sigma} = \frac{1}{2k_B\delta t}\langle I^2(\nu)\rangle$$

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

$$\parallel$$

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

Onsager coeff. matrix

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

$\Rightarrow$ recipe for calc. $L_{\alpha\gamma}$

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

Onsager reciprocity [1931 $\Rightarrow$ Nobel prize]

two loop circuit:

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

write out Eq. 2 in detail:

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

$$W_{n, n_0} p^s_{n_0} = W^{eq}_{n, n_0} p^{eq}_{n_0} \left(1 + \sum_{\alpha} f_\alpha c^{(\alpha)}_{n, n_0} + \cdots \right)$$

$$\Rightarrow L_{\alpha\gamma} = \frac{1}{2k_B \delta t} \sum_{n, n_0} W^{eq}_{n, n_0} p^{eq}_{n_0} \delta y^{(\alpha)}_{n, n_0} \delta y^{(\gamma)}_{n, n_0} + \cdots$$

$$\approx \frac{1}{2k_B \delta t} \left\langle \delta y^{(\alpha)} \delta y^{(\gamma)} \right\rangle_{eq}$$

fluctuation-dissipation theorem
(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.

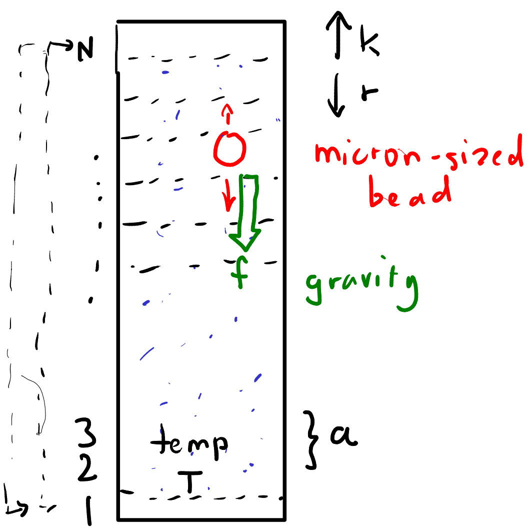
$$\sigma = \vec{\phi}^T L \vec{\phi} = \frac{I}{\delta t} = -\frac{Q}{\delta t}$$

heat per unit time dissip. into env. when out of equil.

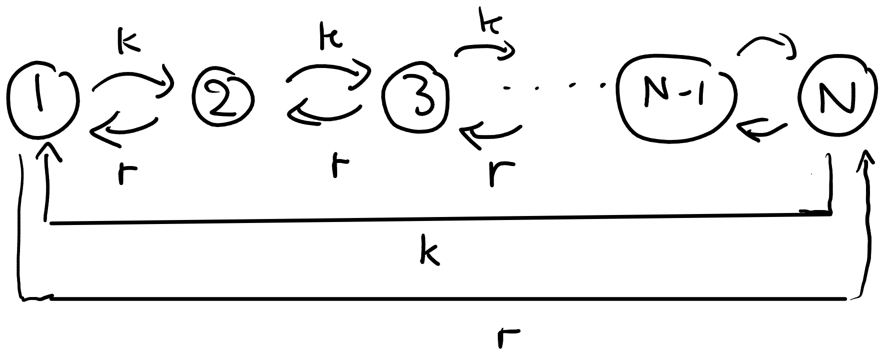
dissipation

Examples:

colloidal particle in water



state of bead:



internal energy of bead is same in all states:

$$\frac{k}{r} = e^{-\beta(\underbrace{E_{n+1} - E_n}_{0} + fa)}$$

$$= e^{-\beta fa}$$

coupling to one force $(M=1)$

we have periodic BC for convenience

$\Rightarrow$ stat. state $p_n^s = \frac{1}{N} = p_n^{eq}$

(indep. of f)

$$p_n^s(f) = p_n^{eq}\left(1 + \overset{0}{\cancel{b_n}} f + \ldots\right)$$

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

L is a 1×1 matrix (L is a scalar)

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

$$\frac{\langle \delta x \rangle}{\delta t} = \underset{\substack{\text{current} \\ \text{III} \\ \text{mean velocity of bead}}}{J} = L\phi = L\frac{f}{T}$$

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

$\gamma =$ drag friction coefficient

$\Rightarrow \quad \frac{L}{T} = \frac{1}{\gamma} \qquad$ rewrite FDT:

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

$$\langle \delta x^2 \rangle_{eq} = 2\frac{k_B T}{\gamma}\delta t$$

$$\Rightarrow \quad \boxed{D = \frac{k_B T}{\gamma}}$$

Einstein 1905

D diffusion constant