PHYS 414: 4-6-20

$$-T(t)\,\mathring{S}^{i} = \mathring{\bar{E}} - T(t)\,\mathring{S} + \sum_{\nu} f_{\nu}(t)\,\mathring{\bar{x}}_{\nu}$$

$$\downarrow$$

$$P(t)\,\mathring{\bar{V}}$$

$$T(t)\,\mathring{S} - T(t)\,\mathring{S}^{i} = \mathring{\bar{E}} + P(t)\,\mathring{\bar{V}}$$

$$T\,dS \qquad = \qquad dU + P\,dV$$

≈ 0 if we are changing slowly (quasistatic, reversible) near equilibrium

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ensemble picture of stat. mech. ⇝ Schröd. picture

prob. $p_n(t) \simeq$ frac. of our ensemble in state n at time t

$$\bar{E} = \sum_{n} E_n\, p_n(t)$$

$$\mathring{\bar{E}} = \frac{1}{2}\sum_{nm} J_{nm}\,(E_n - E_m)$$

$$\mathring{S}^{i} = \sim\sim$$

trajectory picture of stat. mech ⇝ Feynman path integ. picture

to make math easier we will return to discrete time formulation

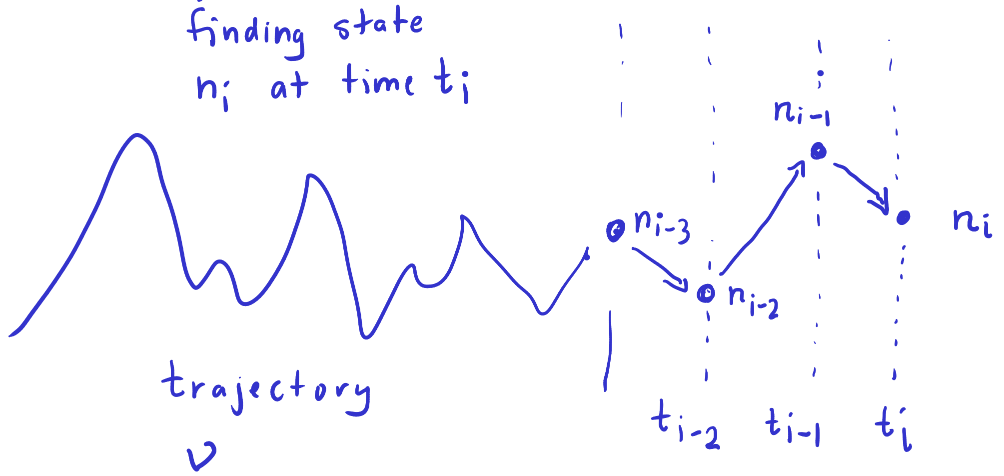
$$t_i = t_0 + i\,\delta t$$

$$p_n(t_i) = \sum_m W_{nm}\, p_m(t_{i-1})\,\delta t$$

$$\downarrow$$

$$p_{n_i} = \sum_{n_{i-1}=1}^{N} W_{n_i n_{i-1}}\, p_{n_{i-1}}\,\delta t \qquad (1)$$

prob. of finding state n_i at time t_i



trajectory ν

$= (n_0, n_1, \dots, n_i)$

$$p_{n_i} = \underbrace{\sum_{n_{i-1}} \sum_{n_{i-2}} \cdots \sum_{n_0}}_{\text{sum over all } (n_0, \dots, n_{i-1})} \overbrace{W_{n_i n_{i-1}} W_{n_{i-1} n_{i-2}} \cdots W_{n_1 n_0}\, p_{n_0}}^{\text{prob. of seq. } (n_0, \dots, n_i)} \cdot [\delta t]^i$$

$$\boxed{\bar{E}(t_\tau) = \sum_{n_\tau} p_{n_\tau} E_{n_\tau}}$$

$t = t_\tau$

$$= \underbrace{\sum_{n_\tau} \sum_{n_{\tau-1}} \cdots \sum_{n_0}}_{\equiv \sum_\nu} \overbrace{W_{n_\tau n_{\tau-1}} \cdots W_{n_1 n_0}\, p_{n_0} [\delta t]^\tau}^{\equiv \mathcal{P}(\nu) \text{ prob. of traj. } \nu = (n_0, \dots, n_\tau)} \underbrace{E_{n_\tau}}_{E(\nu, t)}$$

$\sum_\nu$: sum over all poss. traj. b/t t_0 + t_τ

$E(\nu, t)$: energy of traj. ν at time t

$$\Rightarrow \boxed{\bar{E}(t) = \sum_\nu \mathcal{P}(\nu)\, E(\nu, t)} \qquad \sum_\nu \mathcal{P}(\nu) = 1$$

$$\bar{\dot{E}}(t) = \frac{1}{2} \sum_{n_\tau, n_{\tau-1}} J_{n_\tau, n_{\tau-1}} (E_{n_\tau} - E_{n_{\tau-1}})$$

$$= \frac{1}{2} \sum_{n_\tau, n_{\tau-1}} (W_{n_\tau n_{\tau-1}} p_{n_{\tau-1}} - W_{n_{\tau-1} n_\tau} p_{n_\tau})(E_{n_\tau} - E_{n_{\tau-1}})$$

$$= \sum_{n_\tau, n_{\tau-1}} W_{n_\tau n_{\tau-1}} \underbrace{p_{n_{\tau-1}}}_{\text{expand thru iter. of Eq. (1)}} (E_{n_\tau} - E_{n_{\tau-1}})$$

$$\equiv \sum_\nu \mathcal{P}(\nu) \dot{E}(\nu, t)$$

$$\dot{E}(\nu, t) \equiv \frac{E_{n_\tau} - E_{n_{\tau-1}}}{\delta t}$$

"deriv." of E in the ν traj.

check consistency:

$$\Delta \bar{E} = \bar{E}(t) - E(0)$$

change in energy from beg. to end of traj.

$$= \int_0^t \bar{\dot{E}}(t)\, dt$$

$$= \sum_{i=1}^{\tau} \delta t \sum_\nu \mathcal{P}(\nu) \dot{E}(\nu, t_i)$$

$$E_5 - E_4 + E_4 - E_3 + \cdots E_2 - E_1$$

$$= \sum_\nu \mathcal{P}(\nu) \sum_{i=1}^{\tau} \delta t \frac{(E_{n_\tau} - E_{n_{\tau-1}})}{\delta t}$$

$$= \sum_\nu \mathcal{P}(\nu) [E_{n_\tau} - E_{n_0}]$$

$E_{n_\tau} \to E(\nu, t)$, $E_{n_0} \to E(\nu, 0)$

in brackets is the energy change of traj. ν $= E(\nu, t) - E(\nu, 0)$

$$= \bar{E}(t) - \bar{E}(0)$$

Use this notion to construct traj-specific versions of any thermodyn. quantity

$$\dot{S}^i(t) = \frac{k_B}{2} \sum_{n_\tau n_{\tau-1}} J_{n_\tau n_{\tau-1}} \ln \frac{W_{n_\tau n_{\tau-1}} p_{n_{\tau-1}}}{W_{n_{\tau-1} n_\tau} p_{n_\tau}}$$

$$= \circ \circ \circ = \sum_\nu \mathcal{P}(\nu)\, \dot{S}^i(\nu, t)$$

$$\dot{S}^i(\nu, t) = \frac{k_B}{\delta t} \ln \frac{W_{n_\tau n_{\tau-1}} p_{n_{\tau-1}}}{W_{n_{\tau-1} n_\tau} p_{n_\tau}}$$

instantaneous entropy prod. assoc. w/ traj. ν
rate

$$\Delta S^i(\nu) = \int_0^t dt\, \dot{S}^i(\nu, t)$$

int. entropy produced over whole traj. ν

$$= \sum_{i=1}^{\tau} \delta t \left[\frac{k_B}{\delta t} \ln \frac{W_{n_\tau n_{\tau-1}} p_{n_{\tau-1}}}{W_{n_{\tau-1} n_\tau} p_{n_\tau}} \right]$$

$$= k_B \ln \left[\frac{W_{n_\tau n_{\tau-1}} p_{n_{\tau-1}} \cdots\cdots W_{n_2 n_1} p_{n_1} W_{n_1 n_0} p_{n_0}}{W_{n_0 n_1} p_{n_1} W_{n_1 n_2} p_{n_2} \cdots\cdots W_{n_{\tau-1} n_\tau} p_{n_\tau}} \right]$$

all prob. cancel in num / den except p_{n_0} + p_{n_τ}

$$\boxed{\Delta S^i(\nu) = k_B \ln \frac{\mathcal{P}(\nu)}{\mathcal{P}(\tilde{\nu})}}$$

where $\tilde{\nu} \equiv$ traj. w/ reverse order of states from ν

$$= (\tilde{n}_0, \tilde{n}_1, \ldots, \tilde{n}_\tau)$$

where $\tilde{n}_0 = n_\tau$
$\tilde{n}_1 = n_{\tau-1}$
$\vdots$
$\tilde{n}_\tau = n_0$

$$S = -k_B \sum_n p_n \ln p_n$$

$$\dot{S} = \underset{\begin{array}{c}\downarrow\\ \frac{\dot{Q}}{T}\end{array}}{\dot{S}^e} + \underset{\begin{array}{c}\searrow\\ \geq 0\end{array}}{\dot{S}^i}$$