

case : 2) allow heat from env.  $Q \neq 0$

but no coupling to work:  $W = 0$

1st:  $Q = \Delta E$

2nd:  $T I = T \Delta S - \Delta E = -\Delta F \geq 0$

recall:

$$F = E - TS$$

↑  
avg.  
energy

↑  
entropy

$$\Delta F \leq 0$$

for any length traj. ensemble

Helmholtz free energy  
is non-increasing

Similar argument:  $F(t)$  cannot decrease forever

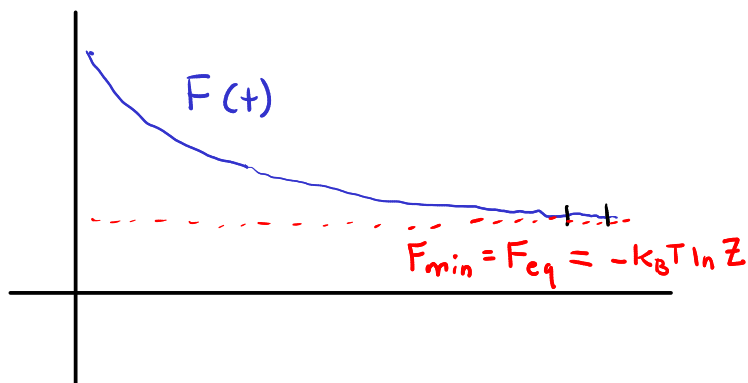
b/c  $F(t) = E(t) - TS(t)$

$$S(t): 0 \leq S(t) \leq k_B \ln N$$

$$E(t) = \sum_n p_n(t) E_n: E_{\min} \leq E(t) \leq E_{\max}$$

smallest  
sys. state  
energy

largest  
" "



look at ensemble of  
trajectories at long  
times (plateau):

$$\Delta F \approx 0 \Rightarrow I = 0$$

$$I = 0 \Rightarrow I(\mu_i) = 0 = k_B \ln \frac{W_{n_{i+1}n_i} P_{n_i}(t_i)}{W_{n_i n_{i+1}} P_{n_{i+1}}(t_{i+1})}$$

$$\frac{W_{n_{i+1}n_i}}{W_{n_i n_{i+1}}} = e^{-\beta(E_{n_{i+1}} - E_{n_i} + \cancel{W_{n_{i+1}n_i}}^0)}$$

numerator = denominator

$$e^{\beta E_{n_i}} \underbrace{P_{n_i}(t_i)}_{p_{n_i}^s} = e^{\beta E_{n_{i+1}}} \underbrace{P_{n_{i+1}}(t_{i+1})}_{p_{n_{i+1}}^s}$$

$$Z = \sum_{n=1}^N e^{-\beta E_n}$$

$$\Rightarrow \text{satisfied when: } p_n^s = \frac{e^{-\beta E_n}}{Z}$$

$$\text{as } t \rightarrow \infty \quad p_n(t) \rightarrow \frac{e^{-\beta E_n}}{Z} \quad \text{Boltz. equil. distrib.}$$

$$F(t) = E(t) - TS(t)$$

$$\text{plug in } p_n^s \Rightarrow F_{\text{eq}} = -k_B T \ln Z$$

$$E(t \rightarrow \infty) = \sum_n p_n^s E_n = \frac{1}{Z} \sum_n e^{-\beta E_n} E_n$$

$$S(t \rightarrow \infty) = -k_B \sum_n p_n^s \ln p_n^s = -k_B \sum_n \frac{e^{-\beta E_n}}{Z} (-\beta E_n - \ln Z)$$

$$\Rightarrow F(t \rightarrow \infty) = -k_B T \ln Z$$

Interpretation of entropy as information:

Shannon source coding theorem

surprisal:  $-k_B \ln p_n(t)$

entropy: avg. surprisal  $S(t) = -k_B \sum_n p_n(t) \ln p_n(t)$

imagine scenario: Alice (A) is a prof.  
Bob (B) is a grad. student

experiment: system  $N=4$  states  
(stochastic)

one run:

repeat  
many  
times

- B prepares sys. in init. dist.  $\vec{p}(0)$
- B lets it evolve for time  $t$
- B takes measurement, records state

output: series of state measurements

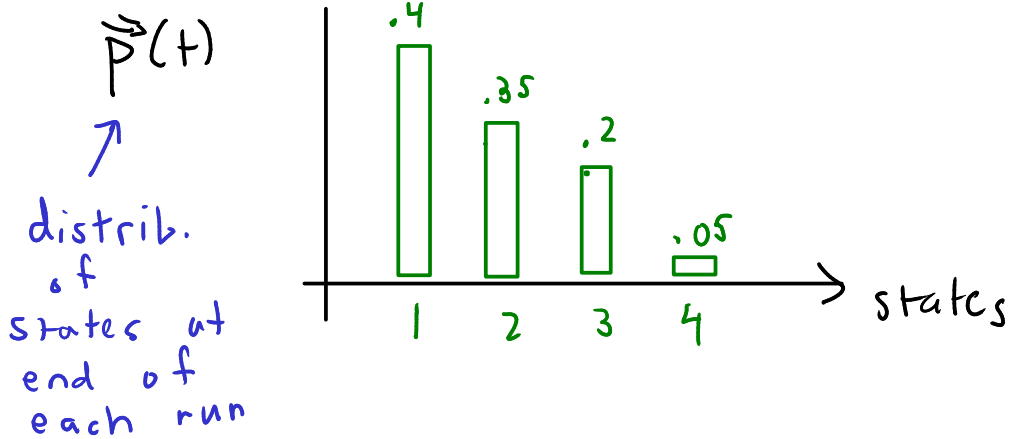
i.e. 2, 4, 1, 3, 2, ...

A + B know: sys. trans. matrix  $W$   
prob.  $\vec{p}(0)$

hence  $\vec{p}(t) = W^t \vec{p}(0)$

A doesn't know seq. of measurements

GOAL: Bob has to encode seq. + send it w/ fewest bits possible



case I: Bob is lazy

<u>state</u>	<u>code</u>	easy to read
1	00	(every 2 bits is a state)
2	01	
3	10	if there were
4	11	N states in general

mean message length per state  
 $= \log_2 N$