Canonical Ensemble continued

Many states, different energies $\{\varepsilon_i\}$

$$P_i = e^{-\beta\varepsilon_i} \Big/ \sum_{i=1}^{N} e^{-\beta\varepsilon_i}$$

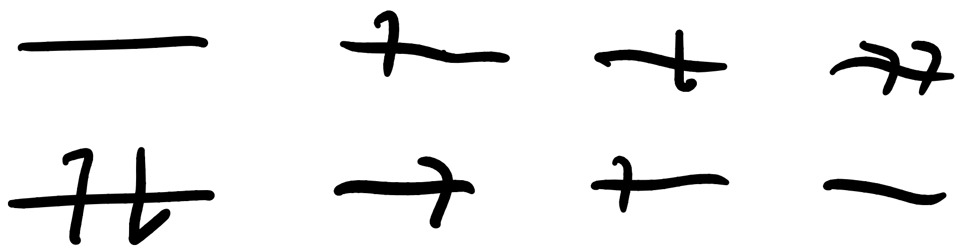
$$Q = \sum_{i=1}^{N} e^{-\beta\varepsilon_i} \quad \text{partition function}$$

like W in $S = k_B \ln W$

$$Q = \sum_{i=1}^{N_{states}} e^{-\beta \varepsilon_i} = \sum_{\{E\}} \omega(E)\, e^{-\beta E}$$

ε_2

ε_1



4 states

ε_{total}	$2\varepsilon_1$	$\varepsilon_1 + \varepsilon_2$	$\varepsilon_1 + \varepsilon_2$	$2\varepsilon_2$

$$Q = e^{-\beta(2\varepsilon_1)} + e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(2\varepsilon_2)}$$

$$= e^{-\beta(2\varepsilon_1)} + 2e^{-\beta(\varepsilon_1+\varepsilon_2)} + e^{-\beta(2\varepsilon_2)}$$

$$P_\varepsilon = \omega(\varepsilon)\, e^{-\beta\varepsilon} \Big/ \sum_\varepsilon \omega(\varepsilon) e^{-\beta\varepsilon}$$

degeneracy

"density of states"

$$Q = \sum_{i=1}^{N} e^{-\beta \varepsilon_i}$$

$$U = \langle \varepsilon \rangle = \sum_{i=1}^{N} P_i \varepsilon_i$$

$$= \sum_{i=1}^{N} \varepsilon_i e^{-\beta \varepsilon_i} \Big/ Q$$

$$= -\frac{\partial \ln Q}{\partial \beta} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{1}{Q}\left[\sum_{i=1}^{N} (-\varepsilon_i) e^{-\beta \varepsilon_i}\right]$$

Gibbs Entropy

$$S = -k_B \sum_{i=1}^{N} P_i \ln P_i \qquad \text{(more general)}$$

microcanonical ensemble

$$P_i = P_j = 1/\Omega$$

$$S = -k_B \sum_{i=1}^{\Omega} \underbrace{\frac{1}{\Omega} \ln \frac{1}{\Omega}}_{\text{const}} = k_B \Omega \cdot \frac{1}{\Omega} \ln \Omega$$

$$\ln(1/\Omega) = -\ln \Omega \qquad = k_B \ln \Omega$$

$$S = -k_B \sum_{i=1}^{N} p_i \ln p_i$$

$$p_i = e^{-\beta \epsilon_i} / Q$$

$$= -k_B \sum_{i=1}^{N} \left(e^{-\beta \epsilon_i} / Q \left[\ln \left(e^{-\beta \epsilon_i} / Q \right) \right] \right)$$

$$= -k_B \sum_{i=1}^{N} p_i \left[-\beta \epsilon_i - \ln Q \right]$$

$$= k_B \cdot \beta \langle \epsilon \rangle + k_B \ln Q \underbrace{\sum_{i=1}^{N} p_i}_{1}$$

$$= k_B \beta U + k_B \ln Q$$

$$S = k_B \beta U + k_B \ln Q \qquad (N, V, T)$$

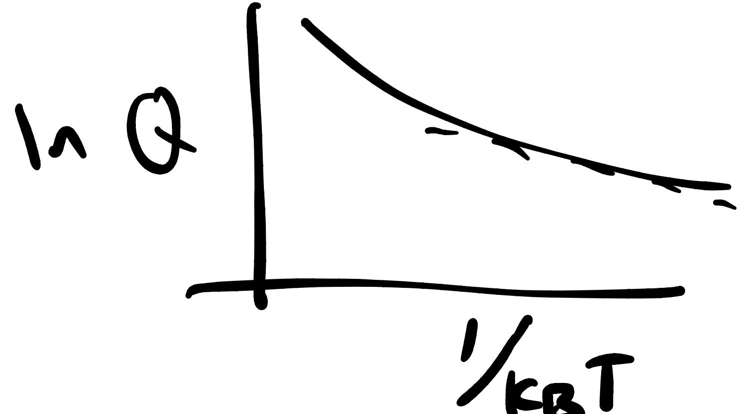
$$1/T = \left(\frac{\partial S}{\partial U}\right)_V$$

$$1/T = k_B \beta \Rightarrow \beta = 1/k_B T$$

$$\boxed{S = U/T + k_B \ln Q}$$

$$\boxed{A = U - TS = -k_B T \ln Q}$$

$$\boxed{\begin{aligned} U &= -\frac{\partial}{\partial \beta} \ln Q \\ U &= k_B T^2 \frac{\partial \ln Q}{\partial T} \end{aligned}}$$



$$\frac{\partial}{\partial T} = \left(\frac{\partial}{\partial \beta}\right)\left(\frac{\partial \beta}{\partial T}\right)$$

$$-\frac{1}{k_B T^2}$$

$$\beta = 1/k_B T = \frac{1}{k_B} T^{-1}$$

$$\partial \beta/\partial T = \frac{1}{k_B} -1\, T^{-2}$$

$$= -\frac{1}{k_B T^2}$$

$$\frac{\partial}{\partial \beta} = -k_B T^2 \frac{\partial}{\partial T}$$

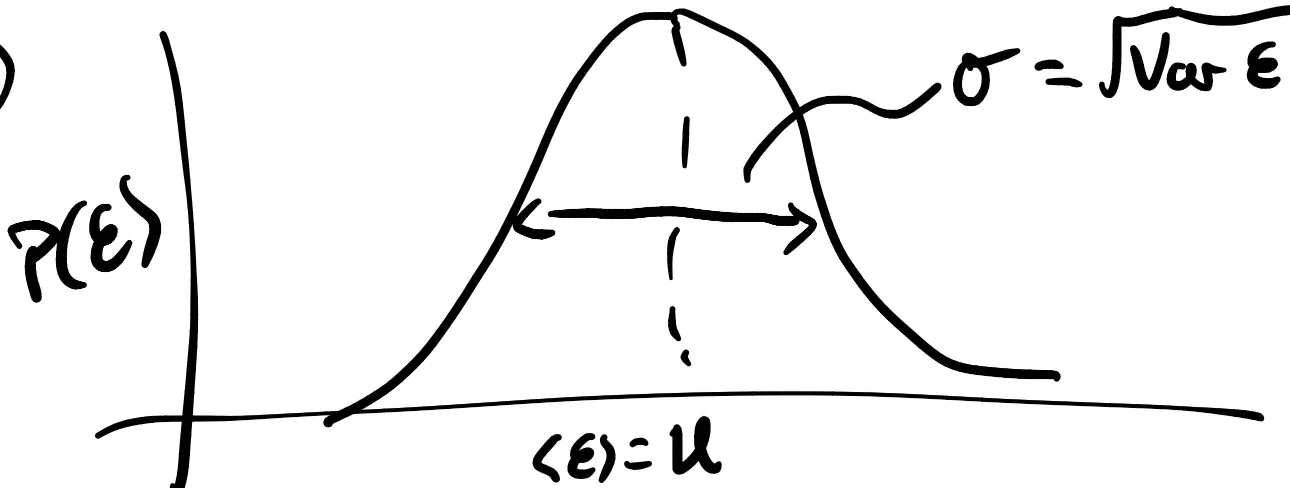
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$= -k_B \left(\frac{\partial}{\partial T}\left[k_B T^2 \frac{\partial \ln Q}{\partial T}\right]\right)$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{k_B T^2}\left[\overbrace{\langle \varepsilon^2 \rangle - \langle \varepsilon \rangle^2}^{\text{fluctuations in } \varepsilon}\right]$$

$\mathrm{Var}\,\varepsilon$

1



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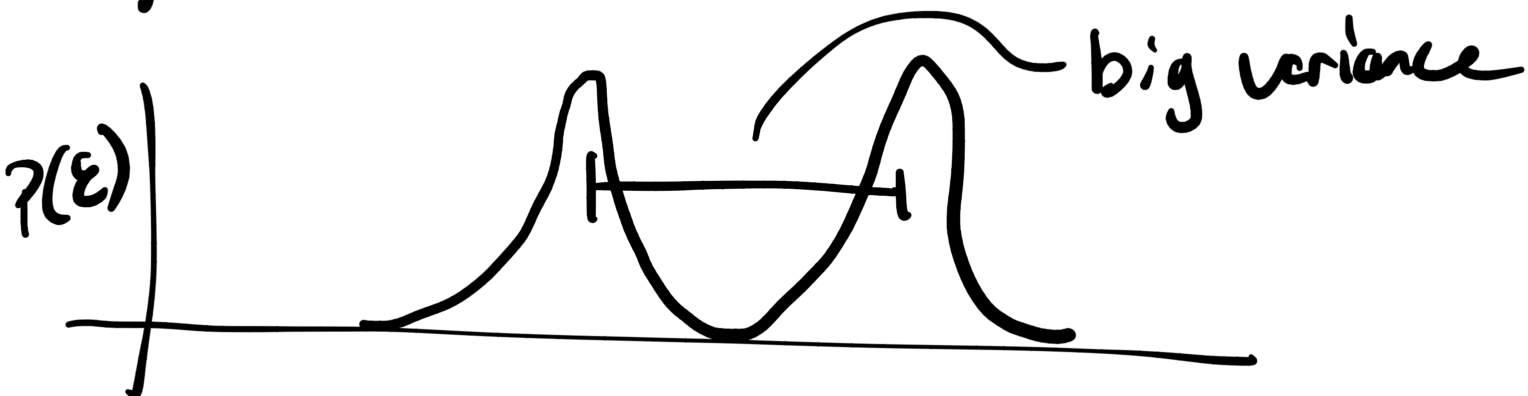
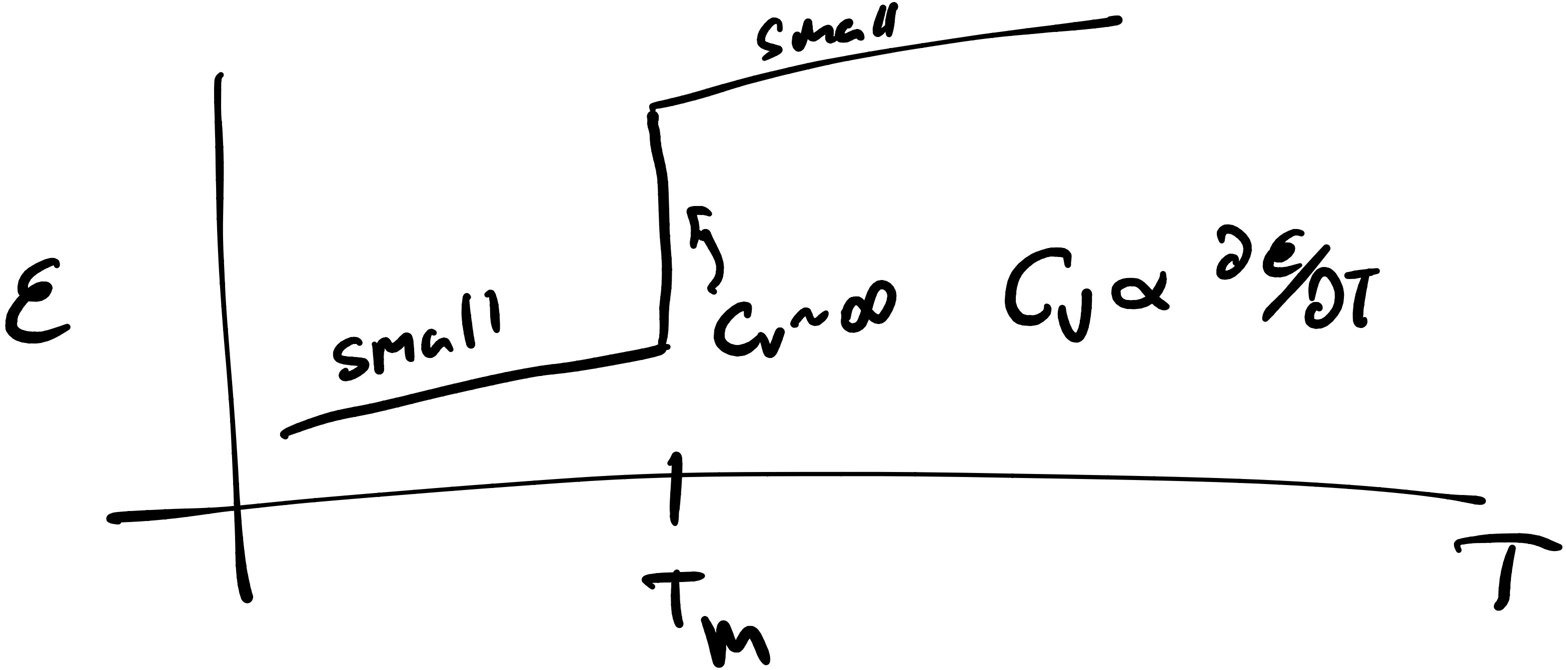



small
small
$\mathcal{E}$
$C_v \sim \infty$
$C_V \propto \partial \mathcal{E} / \partial T$
T_m
T

2 level system – 1 particle

$$\overline{}\ \varepsilon_2$$

$$\overline{}\ \varepsilon_1$$

$$Q = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}$$

$$P_1 = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_1}+e^{-\beta\varepsilon_2}} = \frac{1}{1+e^{-\beta(\varepsilon_2-\varepsilon_1)}} = \frac{1}{1+e^{-\beta\Delta\varepsilon}}$$

$$P_2 = \frac{e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1}+e^{-\beta\varepsilon_2}} = \frac{1}{e^{+\beta(\varepsilon_2-\varepsilon_1)}+1} = \frac{1}{1+e^{\beta\Delta\varepsilon}}$$

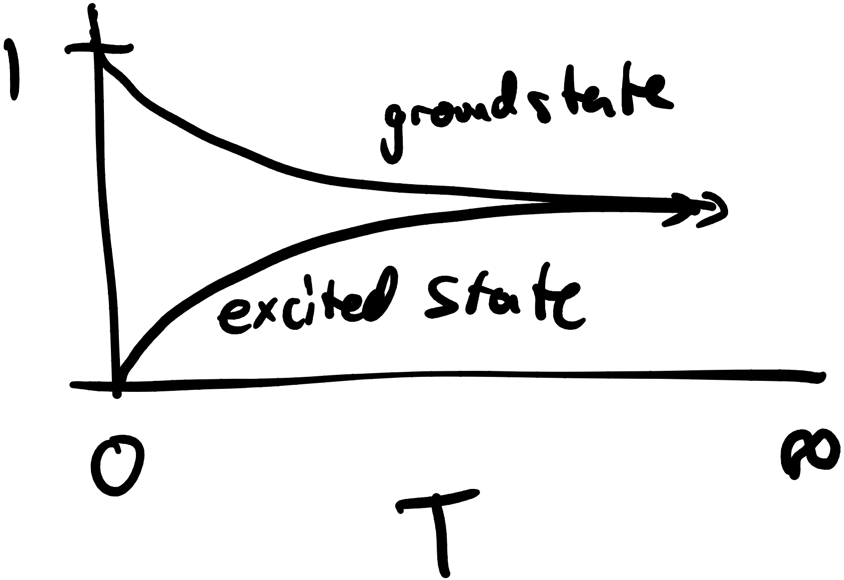
$— \cancel{\varepsilon_2}\ \epsilon \qquad P_1 = (1+e^{-\beta\Delta\epsilon})^{-1}$

$— \cancel{\varepsilon_1}\ 0 \qquad P_2 = (1+e^{\beta\Delta\epsilon})^{-1}$

$$Q = e^{-\beta(0)} + e^{-\beta\epsilon} = 1+e^{-\beta\epsilon}$$

$$P_1 = 1/Q$$

$$P_2 = e^{-\beta\epsilon}/Q$$



Gap is always relative to $k_B T$

$$P_1 = (1 + e^{-\beta \epsilon})^{-1}$$

$$P_2 = (1 + e^{\beta \epsilon})^{-1}$$

$$\beta = 1/k_B T$$

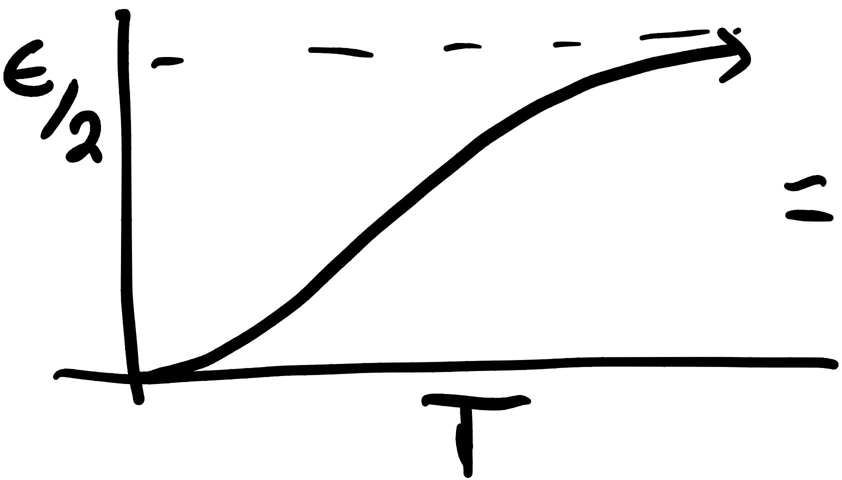
T	β	$1+e^{-\beta\epsilon}$	$1+e^{\beta\epsilon}$
0	∞	1	∞
∞	0	1	1

$$Q = 1 + e^{-\beta \epsilon}$$

$$\langle \varepsilon \rangle = \sum_{i=1}^{2} \varepsilon_i P_i = \frac{0 e^{-\beta}}{Q} + \frac{\epsilon e^{-\beta \epsilon}}{Q}$$

$$= \frac{\epsilon e^{-\beta \epsilon}}{1 + e^{-\beta \epsilon}}$$

$$= \frac{\epsilon}{\left(e^{\beta \epsilon} + 1\right)}$$



$$Q = 1 + e^{-\beta\epsilon} \qquad (e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2})$$

$$\langle\epsilon\rangle = -\frac{\partial \ln Q}{\partial \beta} = -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$$

$$= -\frac{1}{1+e^{-\beta\epsilon}} \cdot -\epsilon e^{-\beta\epsilon}$$

$$= \epsilon \cdot \frac{1}{e^{\beta\epsilon}+1} \quad \checkmark$$

(HW C_v)

2 state models

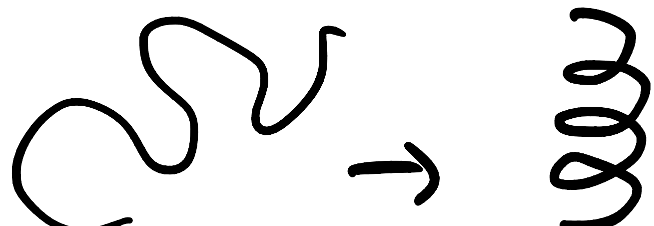
- magnets $\boxed{\uparrow\downarrow\uparrow\uparrow\downarrow} \rightarrow \boxed{\uparrow\uparrow\uparrow\uparrow\uparrow}$

- 

  $A \rightleftarrows B$

  $P + L \rightleftarrows PL$

- Protein folding



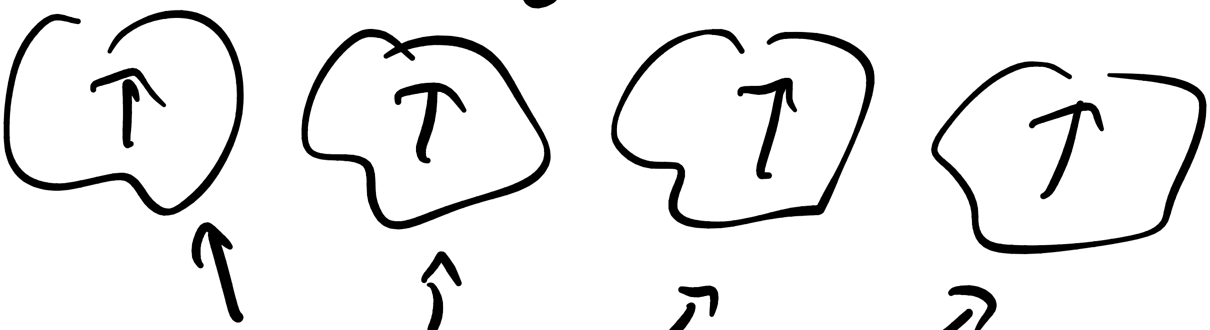
C	C	C	C	C	C

$\rightarrow$

H	H	H	H	H

....

if N independent 2 level systems



$$Q = q \cdot q \cdot q \cdot q$$

$$= q^N / N!$$

$$Q = q^N / N!$$

$$(1+e^{-\beta\epsilon})^{-1}$$

$$\langle \varepsilon \rangle = -\frac{\partial \ln Q}{\partial \beta} = -N \frac{\partial \ln q}{\partial \beta}$$

$$= N\epsilon \cdot \frac{1}{1+e^{-\beta\epsilon}}$$ fraction excited

$$= \epsilon \cdot N_{excited}$$