Canonical Ensemble

Last time

m states with energies

in a system

$$\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_m = \{\varepsilon_m\}$$

make A copies of our system

N_1 = num systems in state 1

N_2 = # in 2 etc

Prob being in state i = $P_i = N_i / A$

$$P_i = \frac{e^{-\beta \varepsilon_i}}{\sum_{i=1}^{m} e^{-\beta \varepsilon_i}} \qquad Q(T) = \sum_{i=1}^{m} e^{-\beta \varepsilon_i}$$

$$\langle \varepsilon \rangle = \sum_{i=1}^{m} \varepsilon_i P_i = \frac{1}{Q} \underbrace{\sum_{i=1}^{m} \varepsilon_i e^{-\beta \varepsilon_i}}_{-\frac{\partial Q}{\partial \beta}}$$

$$= -\frac{1}{Q}\frac{\partial Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial \beta} \ast = U$$

$$U = -\frac{\partial \ln Q}{\partial \beta}$$

β is an unknown constant

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

Gibbs Entropy

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

$$dU = dq + dw = TdS - pdV$$

$$U(S,V) \Rightarrow dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

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

$$S = k_B \underline{\underline{\beta U}} + k_B \ln Q$$

$$\left(\frac{\partial S}{\partial \beta}\right)_V = k_B \left[\cancel{\underbrace{\left(\frac{\partial \beta}{\partial \beta}\right)_V}_{1} U +} \beta \left(\frac{\partial U}{\partial \beta}\right)_V \right] \cancel{+ k_B \overbrace{\left(\frac{\partial \ln Q}{\partial \beta}\right)_V}^{-U}}$$

$$= k_B \beta \left(\frac{\partial U}{\partial \beta}\right)_V$$

$$T = \frac{1}{k_B \beta} \Rightarrow \beta = \frac{1}{k_B T}$$

<u>Get rid of β's for now</u>

$$U = -\frac{\partial \ln Q}{\partial \beta} = -\left(\frac{\partial \ln Q}{\partial T}\right)\cdot\left(\frac{\partial T}{\partial \beta}\right)$$

$$\left(\frac{\partial T}{\partial \beta}\right) = \left(\frac{\partial \beta}{\partial T}\right)^{-1} = \frac{1}{k_B}\frac{\partial}{\partial T}\left(\frac{1}{T}\right) = -\frac{1}{k_B T^2}$$

$$\boxed{U = + k_B T^2 \frac{\partial \ln Q}{\partial T}}$$

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

$$\left[S = \underline{k_B \ln \omega} \right]$$

$$S = dq/T$$

$$= k_B \left[\frac{U}{k_B T} \right] + k_B \ln Q$$

$$= \frac{U}{T} + k_B \ln Q$$

Remember: thermodynamic potentials

Are $\underbrace{\text{maximized}}_{S\uparrow \text{ at eq for } NVE}$ or minimized at Eq.

$G \downarrow$ for n, P, T

$$A = U - TS$$

minimized @ eq
for const N, V, T
canonical ensemble

$$A = U - T\left[\frac{U}{T} + k_B \ln Q\right]$$

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

similar to
$$S = k_B \ln W$$

Another important quantity is C_V

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$ ← energy required to increase by 1°

$$= \left(\frac{\partial U}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial T}\right)_V = \frac{-1}{k_B T^2}\left(\frac{\partial U}{\partial \beta}\right)_V$$

$$U = -\frac{\partial \ln Q}{\partial \beta} \qquad C_V = \frac{1}{k_B T^2} \cdot \left(\frac{\partial^2 U}{\partial \beta^2}\right)_V$$

$$C_V = \frac{-1}{k_B T^2}\left(\frac{\partial u}{\partial \beta}\right)_V \qquad u = -\frac{\partial \ln Q}{\partial \beta}$$

$$= -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$$

$$= \frac{\pm 1}{k_B T^2}\underbrace{\frac{\partial}{\partial \beta}\left[\frac{1}{Q}\frac{\partial Q}{\partial \beta}\right]}_{\left[\frac{\partial\left(\frac{1}{Q}\right)}{\partial \beta}\frac{\partial Q}{\partial \beta} + \frac{1}{Q}\frac{\partial}{\partial \beta}\left[\frac{\partial Q}{\partial \beta}\right]\right]}$$

$$C_V = \frac{1}{k_B T^2}\left[\frac{\partial\left(\frac{1}{Q}\right)}{\partial\beta}\frac{\partial Q}{\partial\beta} + \frac{1}{Q}\frac{\partial}{\partial\beta}\left[\frac{\partial Q}{\partial\beta}\right]\right]$$

$$\left[\underbrace{\left(-\frac{1}{Q^2}\frac{\partial Q}{\partial\beta}\right)\left(\frac{\partial Q}{\partial\beta}\right)}_{\frac{1}{Q}\frac{\partial Q}{\partial\beta} = \frac{\partial \ln Q}{\partial\beta} = \langle\varepsilon\rangle} + \frac{1}{Q}\frac{\partial}{\partial\beta}\left[\frac{\partial Q}{\partial\beta}\right]\right)$$

$$C_V = \frac{1}{k_B T^2}\left[-\langle\varepsilon\rangle\langle\varepsilon\rangle + \frac{1}{Q}\frac{\partial}{\partial\beta}\frac{\partial}{\partial\beta}Q\right]$$

$$C_V = \frac{1}{k_B T^2}\left[-\langle\varepsilon\rangle\langle\varepsilon\rangle + \frac{1}{Q}\frac{\partial}{\partial\beta}\frac{\partial}{\partial\beta}Q\right]$$

$$\frac{\partial Q}{\partial\beta} = \sum_{i=1}^{m}(-\varepsilon_i)e^{-\beta\varepsilon_i}$$

$$\frac{1}{Q}\frac{\partial}{\partial\beta}\left[\frac{\partial Q}{\partial\beta}\right] = \frac{\sum_{i=1}^{m}\varepsilon_i^2 e^{-\beta\varepsilon_i}}{Q} = \langle\varepsilon^2\rangle$$

$$C_v = \frac{1}{k_B T^2}\left[\langle\varepsilon^2\rangle - \langle\varepsilon\rangle^2\right] = \frac{1}{k_B T^2}\mathrm{Var}(\varepsilon)$$

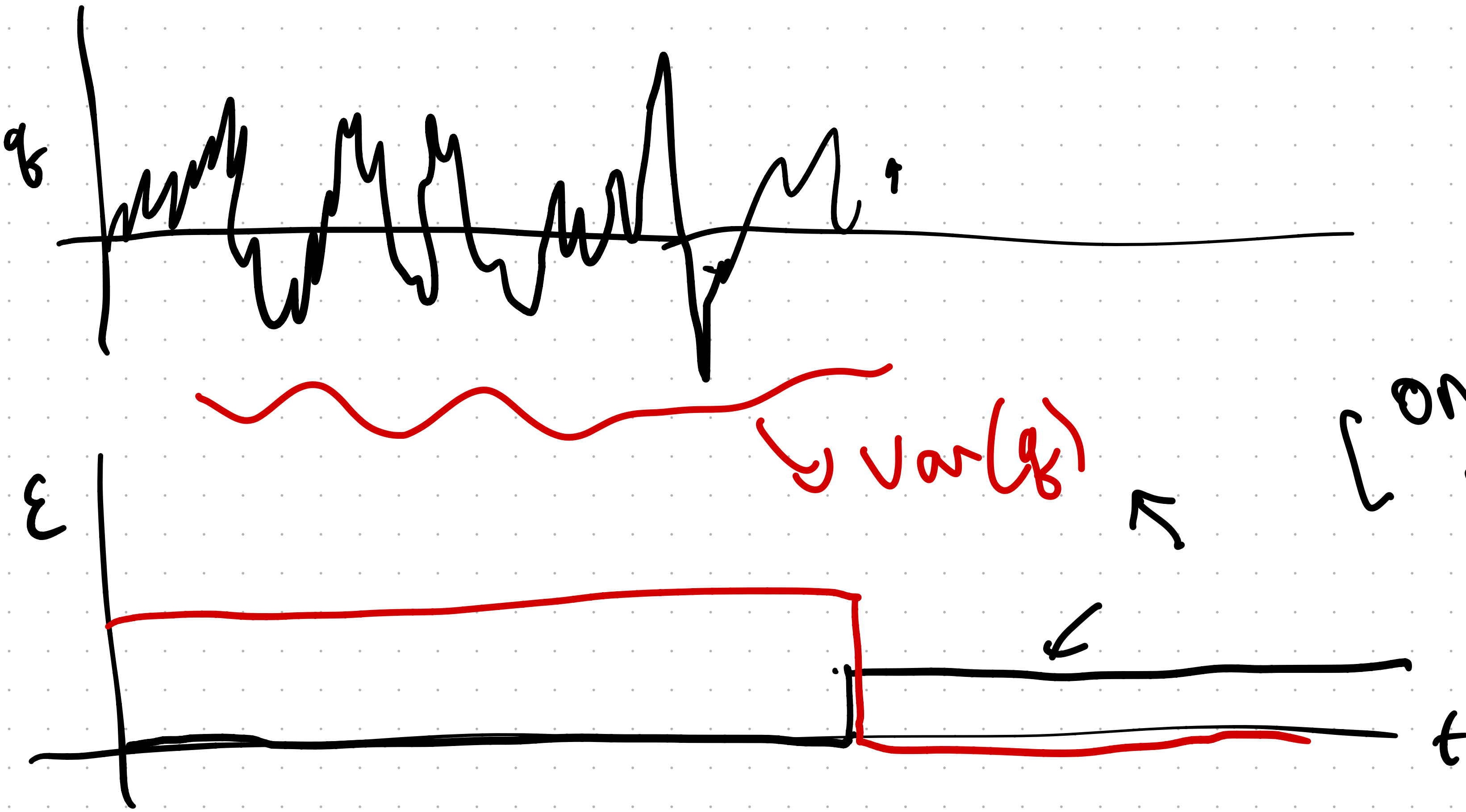
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{1}{k_B T^2} \mathrm{Var}(U(T))$$

Fundemental Points:

1) Linear response

a small change in a control parameter, results in a small response in a conjugate property

- linear response is proportional to equilibrium fluactions

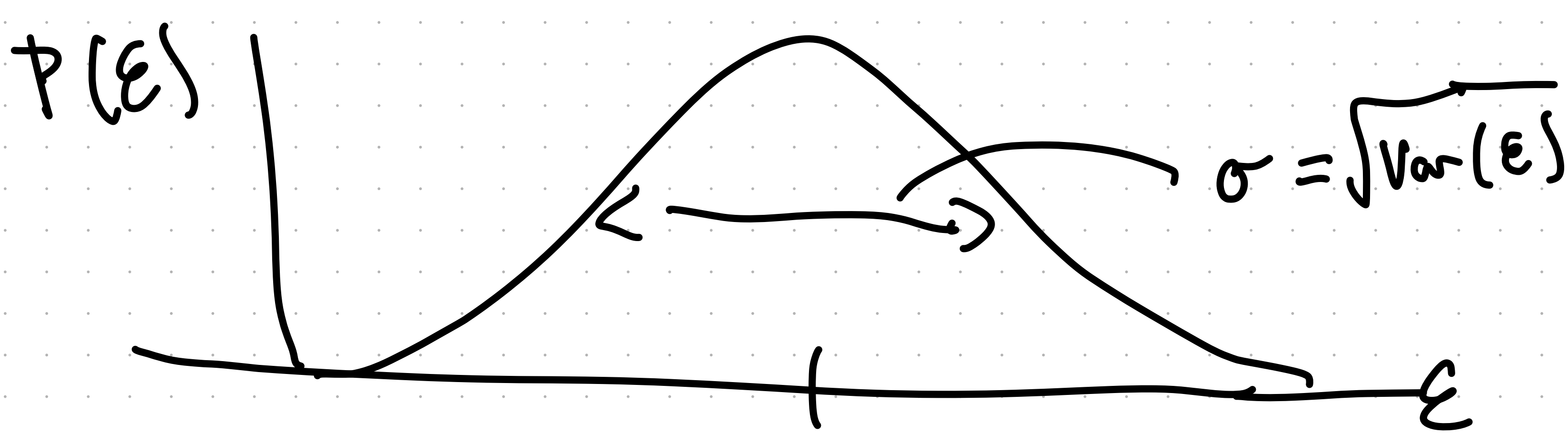


[Onsager regression hypothesis]

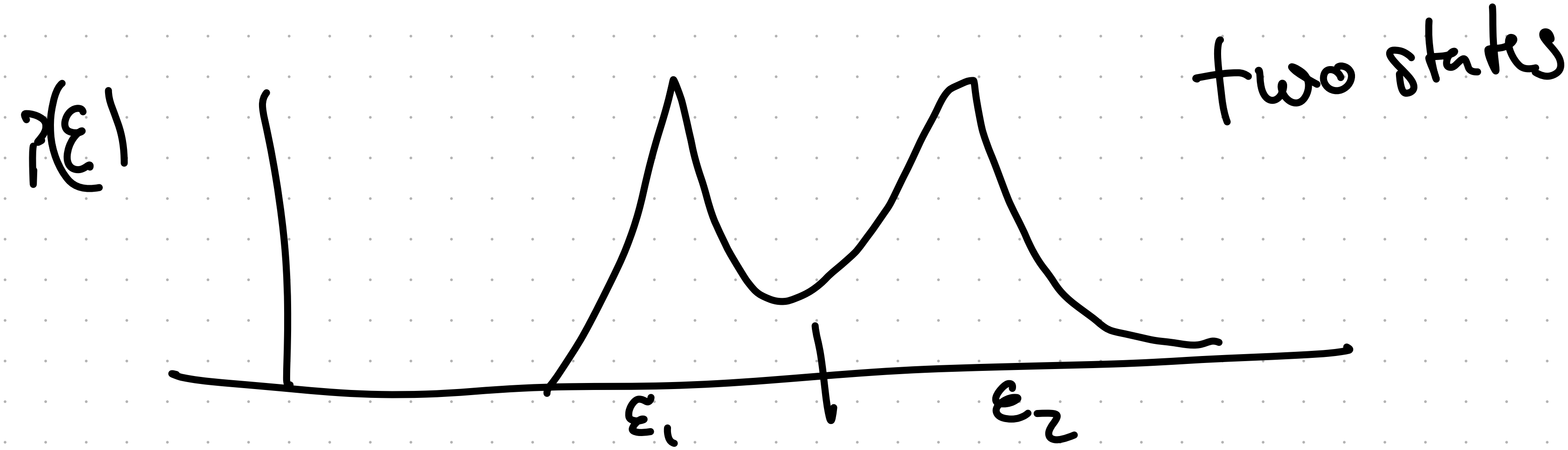
2) wide distribution of energies means you have a large heat capacity

2 ways to have a large variance

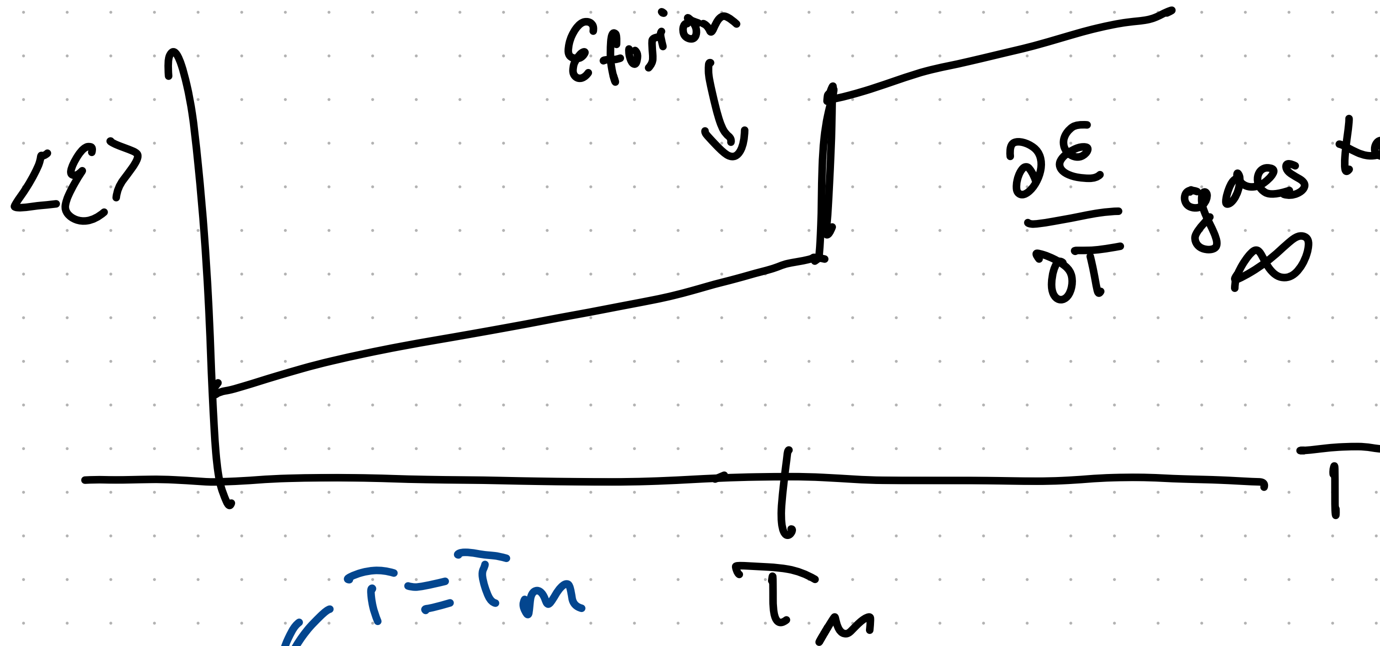
a)



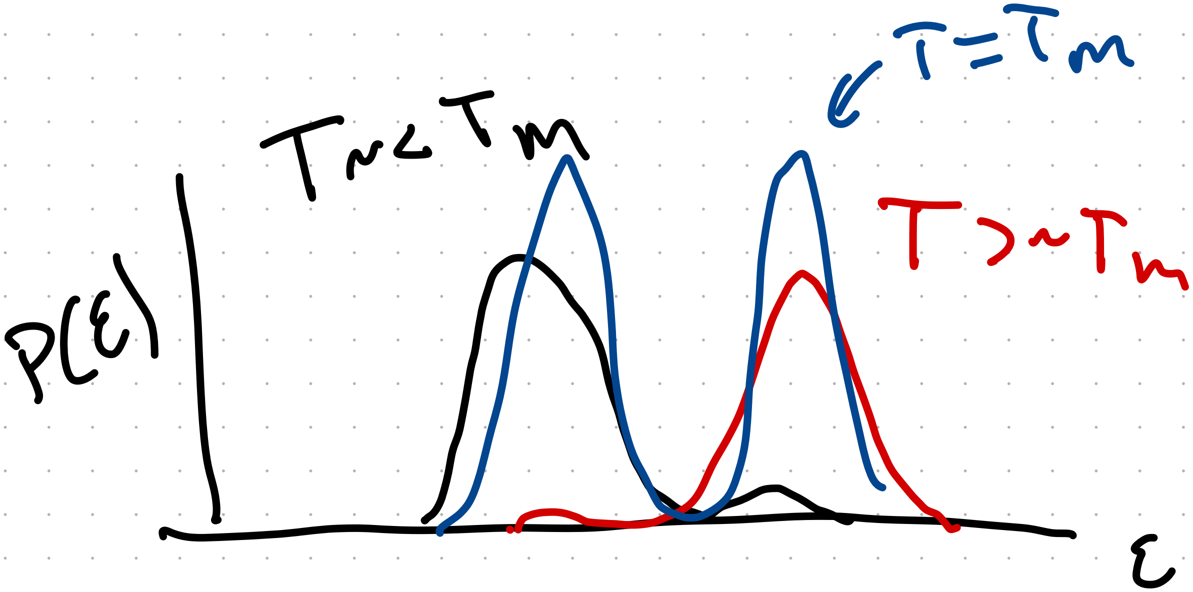
b)



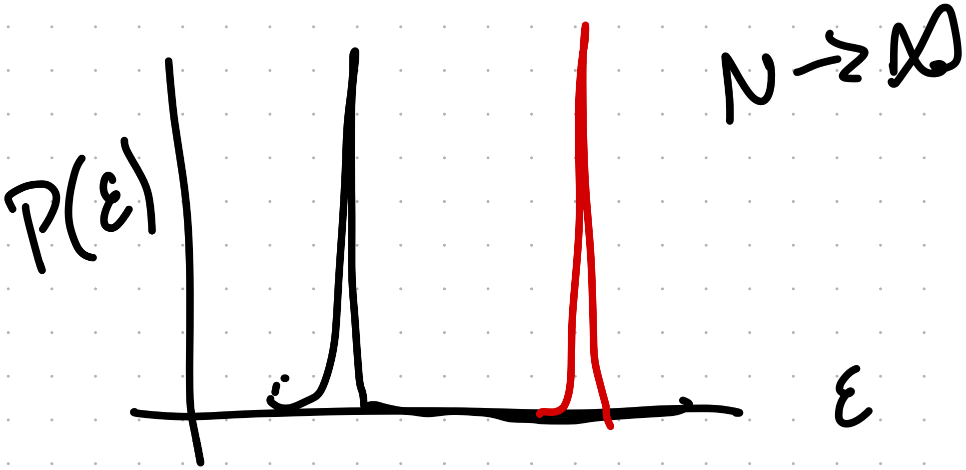
phase transition
1st order

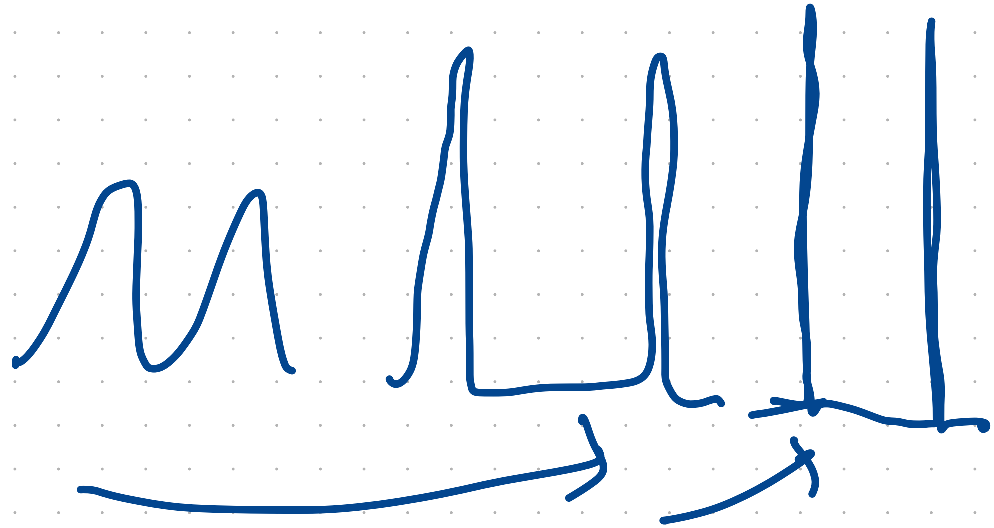


$\frac{\partial E}{\partial T}$ goes to ∞



for small N





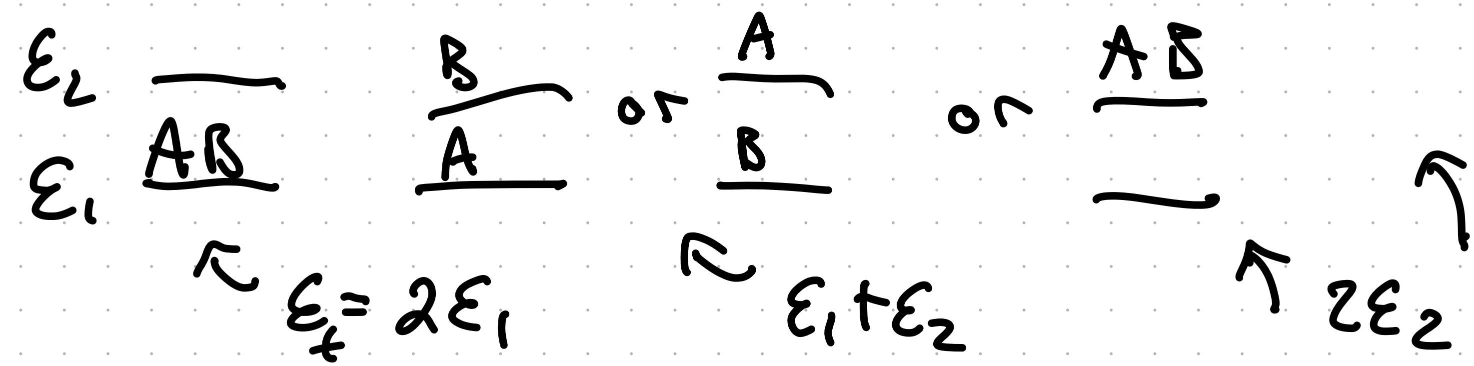
$\mathrm{Var}(\varepsilon) \longrightarrow \varepsilon$ as $N \to \infty$ @ T_m

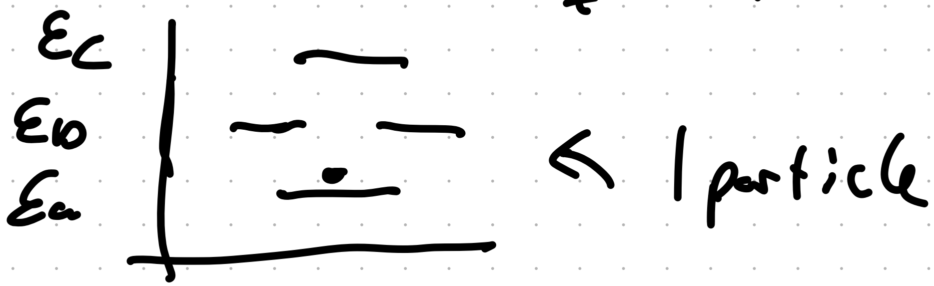
Systems w/ discrete Energy levels
& continuous energy

Example discrete system

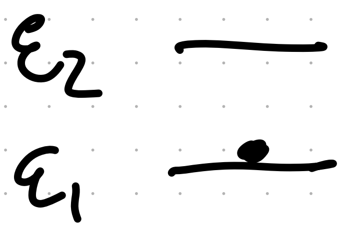
Previously: we discussed Energies $\varepsilon_1, \varepsilon_2, \ldots \varepsilon_n$

Single particles or multiple





1 particle in a two level system



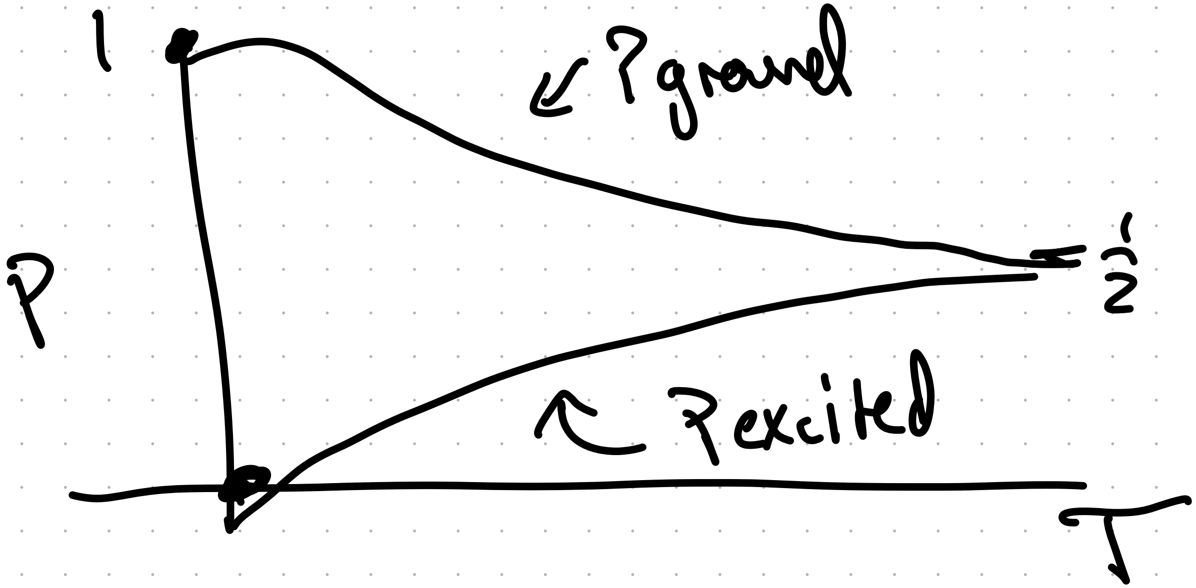
$$Q = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}$$

$$p_1 = \frac{e^{-\beta\varepsilon_1}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}} \qquad p_2 = \frac{e^{-\beta\varepsilon_2}}{e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}}$$

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

all that matters here is the gap

could say $\varepsilon_1 = 0 \quad \varepsilon_2 = \Delta\varepsilon$



$$P_1 = \frac{1}{1+e^{-\Delta\varepsilon/k_B T}}$$

$$P_2 = \frac{e^{-\Delta\varepsilon/k_B T}}{1+e^{-\Delta\varepsilon/k_B T}}$$

$$= \frac{1}{e^{+\Delta\varepsilon/k_B T}+1}$$

$T=\infty$, $\beta = \frac{1}{k_B T} = 0$

$$e^{\pm 0} = 1$$

$$P_1 = P_2 = \frac{1}{2}$$

$T=0$ $\quad e^{-\infty} = 0$

$e^{\infty} = \infty$

$$\langle \varepsilon \rangle = \sum_{i=1}^{m} \varepsilon_i p_i = \frac{\varepsilon_1}{1+e^{-\beta\Delta\varepsilon}} + \frac{\varepsilon_2 e^{-\beta\Delta\varepsilon}}{1+e^{-\beta\Delta\varepsilon}}$$

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

$T \to \infty$ $$\langle \varepsilon \rangle = \frac{\varepsilon_1 + \varepsilon_2 \cdot 1}{1+1} = \frac{\varepsilon_1+\varepsilon_2}{2}$$

$T \to 0$ $$\langle \varepsilon \rangle = \frac{\varepsilon_1 + 0}{1+0} = \varepsilon_1$$

Next time:

consider n states $\to \infty$

continuous equivalent of

Q, for position & velocity states

also multiple particles