Canonical Ensemble Continued

Last time:

M states of energy $\{\varepsilon_i\}$

make A copies so that

N_1 are in state 1, etc

$$P_i = \frac{N_i}{A} = \frac{e^{-\beta\varepsilon_i}}{\sum_{i=1}^{m} e^{-\beta\varepsilon_i}}$$

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

b/c $-\frac{\partial Q}{\partial \beta} = \sum_{i=1}^{m} \varepsilon_i e^{-\beta\varepsilon_i} = \langle\varepsilon\rangle \cdot Q$

saw $\langle\varepsilon\rangle = -\frac{\partial \ln Q}{\partial \beta} \equiv U$

Last, defined gibbs entropy as

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

which for canonical gave

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

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

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

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

$$\left(\frac{\partial S}{\partial \beta}\right)_V = k\left[1\,U + \beta\left(\frac{\partial U}{\partial \beta}\right)_V\right] + \underbrace{k\frac{\partial}{\partial \beta}\ln Q\Big|_V}_{-U}$$

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

So $\quad T = (k\beta)^{-1} \Rightarrow \beta = \dfrac{1}{k_B T}$ ✓

<u>Lets get rid of β's from prev formulas</u>

$$U = -\frac{\partial \ln Q}{\partial \beta} = -\frac{\partial \ln Q}{\partial T}\left(\frac{\partial T}{\partial \beta}\right) = -\left(\frac{\partial \beta}{\partial T}\right)^{-1}\frac{\partial \ln Q}{\partial T}$$

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

So $\quad U = k_B T^2 \dfrac{\partial \ln Q}{\partial T}$ ☆

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

$$\Rightarrow S = \frac{U}{T} + k \ln Q$$

Remember, defined

$$A = U - TS$$

where $U(S, V) \Rightarrow A(T, V)$

helmholz free energy is thermo potential that is minimized for chemical reactions / processes @ const V, T

$$A = U - T\left(\frac{U}{T} + k \ln Q\right)$$

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

(similar to $S = k \ln W$)

One other quantity we didn't consider is C_v (but you did on the exam)

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v$$ ⇐ energy change required to increase temp 1°

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

$$U = -\left(\frac{\partial \ln Q}{\partial \beta}\right) = -\frac{1}{Q}\frac{\partial Q}{\partial \beta}$$

$$\frac{\partial U}{\partial \beta} = \left[-\frac{\partial}{\partial \beta}\left(\frac{1}{Q}\right)\frac{\partial Q}{\partial \beta} - \frac{1}{Q}\frac{\partial^2 Q}{\partial \beta^2}\right]$$

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

$$\frac{\partial Q}{\partial \beta} = \sum \varepsilon e^{-\beta \varepsilon_i} \Rightarrow \frac{\partial}{\partial \beta}\left(\frac{\partial Q}{\partial \beta}\right) = \frac{\partial}{\partial \beta}\sum \varepsilon_i^2 e^{-\beta \varepsilon_i}$$

so $$\frac{\partial U}{\partial \beta} = \langle \varepsilon \rangle^2 - \langle \varepsilon^2 \rangle$$
$$= -\mathrm{Var}(U)$$

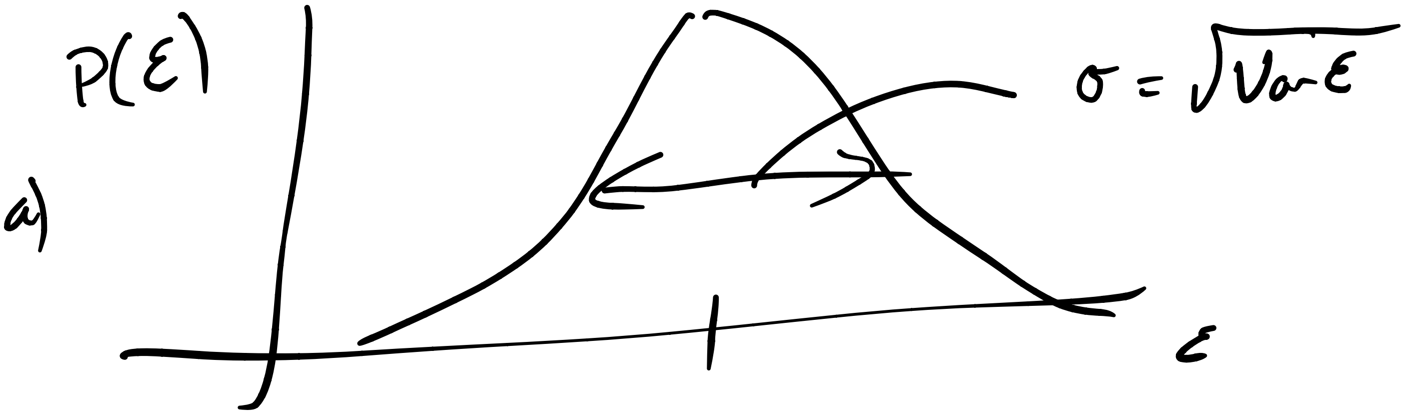
and $$\frac{\partial U}{\partial T} = +\frac{1}{k_B T^2} \mathrm{Var}(U) = C_v$$

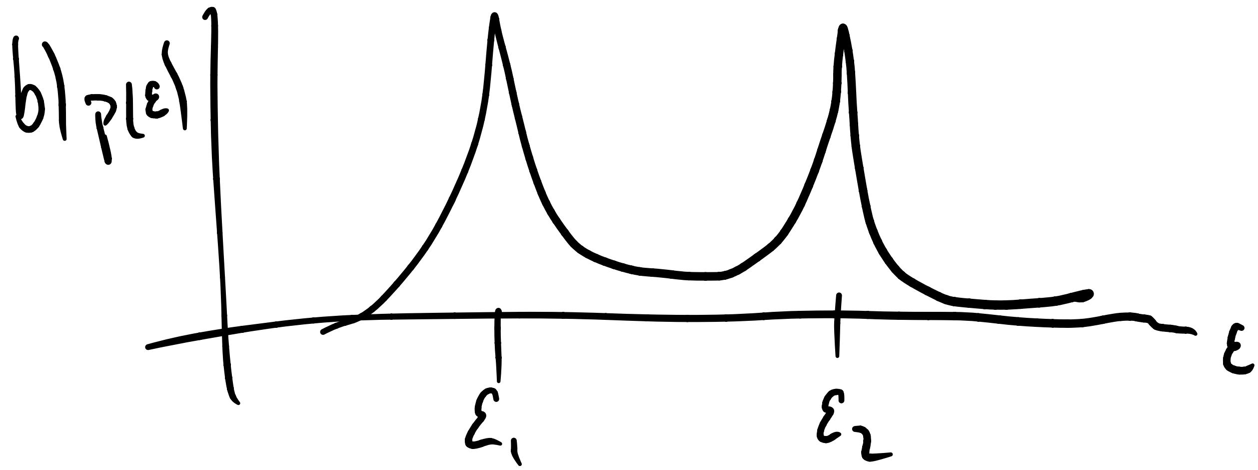
Spread of energies at a given temp is proportional to heat capacity

Fundamental:

1) linear response: small change in control (temp) produces a small change in response (U)
how small: proportional to equilibrium fluctuations!

2) wide distribution leads to large heat capacity → 2 ways

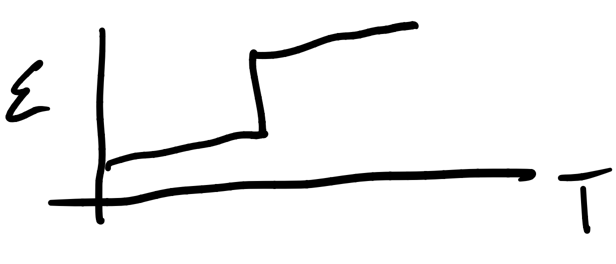




two states

one time this can happen is at phase transitions, 1st order

small system



$\frac{\partial \varepsilon}{\partial T} \to +\infty$ at T_m

So far, talked about a system of states with discrete energy levels. This could actually represent 1 particle w/ discrete levels (harmonic oscillator, particle in box) or a combination.

We will discuss multi particle later (note, not quite order in book)

2 level system is a very important example for 1 particle (like spin)

State 1 ε_1 State 2 ε_2

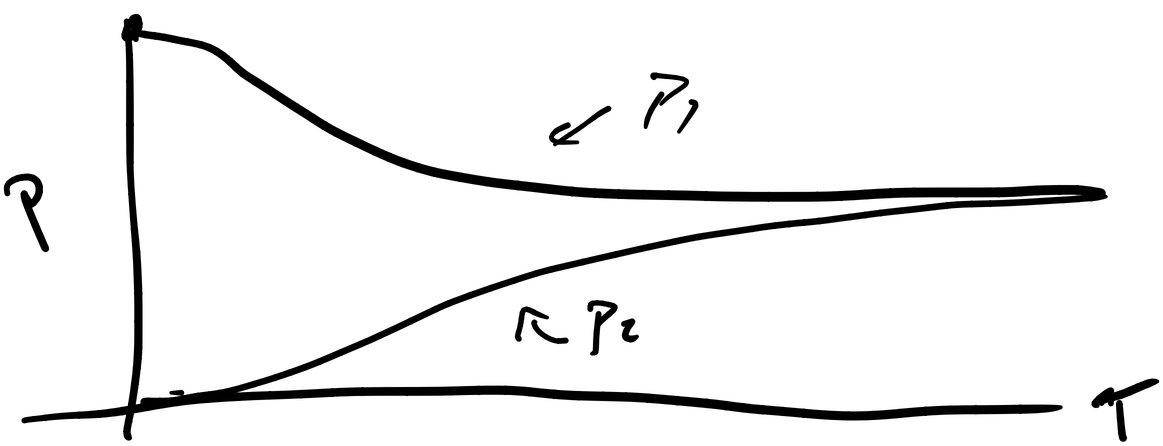
$$Q = e^{-\beta\varepsilon_1} + e^{-\beta\varepsilon_2}$$

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

$$p_i = \frac{1}{1+e^{-\beta \Delta \varepsilon}}$$ all that matters is the gap

Could say $\varepsilon_1 = 0$ and $\varepsilon_2 = \Delta\varepsilon$

$$p_2 = \frac{e^{-\beta\Delta\varepsilon}}{1+e^{-\beta\Delta\varepsilon}} = \frac{1}{1+e^{+\beta\Delta\varepsilon}}$$



gap is only relative to temp!

all ground state at low T

Could get temp ε_1?

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

$\rightarrow$ ε_1 at $T=0$ $\quad \frac{\varepsilon_1+\varepsilon_2}{2}$ @ low T