The canonical Ensemble

We will begin with an assertion about how to do stat mech because it will allow us to do some interesting and important things. Later we will come back to motivating the approach better.

First: what is stat mech? In classical mechanics the goal is to compute the precise trajectories $\{\vec{r}_n(t), \vec{p}_n(t)\}$. Stat mech recognizes those are not the quantities typically measured in expt. Rather one looks at pressure, specific heat, etc. These are determined by the average positions and momenta.

Canonical Ensemble : System has degrees of freedom ϕ_n and an energy $E(\{\phi_n\})$

$$\text{probability } \{\phi_n\} = c\, e^{-E(\{\phi_n\})/k_B T}$$

2A

$$k_B = 1.37 \cdot 10^{-23} \ \text{J}/{}^\circ\text{K}$$

Constant c normalizes probability. We usually write

$$p = \frac{1}{Z} e^{-E/k_B T}$$

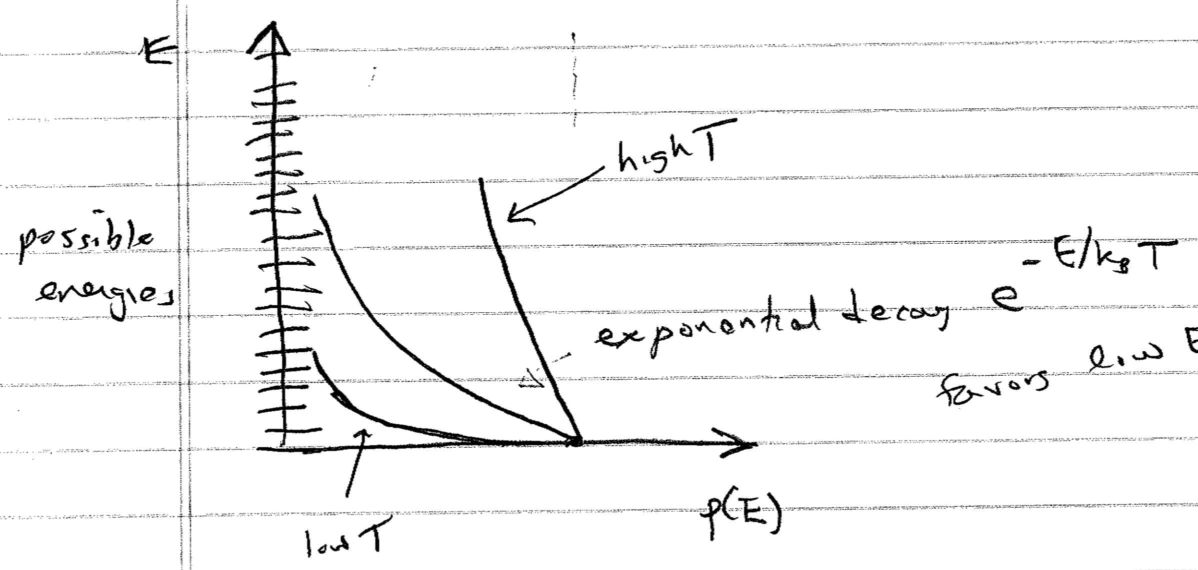
$$Z = \sum_{\{\phi_n\}} e^{-E/k_B T} \quad \text{"partition function"}$$

$$\beta = 1/k_B T \quad \text{useful abbreviation}$$

Question: What is temperature?! There are empirical definitions Construct a thermometer eg with mercury in class tube or resistor or expanding gas. For now let's go with that. Later we will see mathematical definitions of temperature.

CE-2A

Canonical Ensemble is intuitively reasonable



In fact, T is "control parameter" for fall-off of probability

Thus T determines how likely you are to occupy states above the lowest possible energy.

Aside: Does zero of E matter?

If $E(\{\phi_n\}) \to E(\{\phi_n\}) + E_{shift}$

will $\rho(\{\phi_n\})$ be altered

A digression on probability

Conduct expt and make list Ω of all possible outcomes

Suppose $x \in \Omega$ is one possible outcome. Frequency definition of probability: Conduct Expt N times

If get outcome x n times then $p(x) = n/N$

(N must be large!). Clearly from this definition

$$0 \le p(x) \le 1$$

and $$\sum_x p(x) = 1$$

If outcome is a continuous variable one counts up the number of times result is between x and $x + dx$

$$p(x) = n/N\,dx$$

"probability density"

CE-2C

Toss coin 3 times

Ω

HHH

HHT

HTH

THH

TTH

THT

HTT

TTT

If coin is fair all these have probability $1/8$

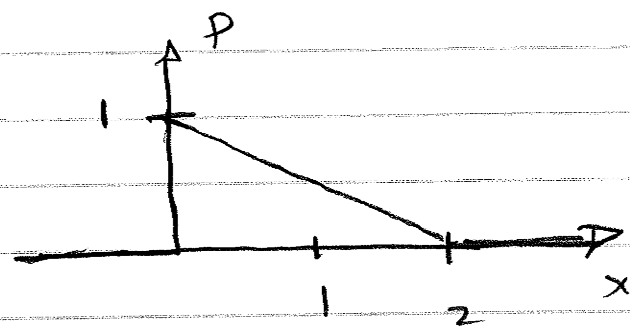
$$p(2H) = 3/8$$

"measurements"

$$\langle \#H \rangle = 3\left(\tfrac{1}{8}\right) + 2\left(\tfrac{1}{8}\right) + 2\left(\tfrac{1}{8}\right) + 2\left(\tfrac{1}{8}\right) + \ldots = \frac{12}{8} = 1.5$$

probabilities

Continuous distribution



$$p(x) = \begin{cases} 0 & x < 0 \\ 1 - x/2 & 0 < x < 2 \\ 0 & x > 2 \end{cases}$$

$$\langle x \rangle = \int dx\, x\, p(x) = \int_0^2 x\left(1 - \frac{x}{2}\right) dx = \frac{x^2}{2} - \frac{x^3}{6}\Big|_0^2 = \frac{2}{3}$$

$$\langle A(x) \rangle = \int dx\, A(x)\, p(x)$$

general "observable"

CE-3

Note however that empirical definitions obey certain important rules (laws of thermodynamics)

① eg if two systems S_1 + S_2 brought into contact with $T_1 > T_2$: heat will flow from S_1 to S_2 and eventually they will come to same T_* with $T_1 < T_* < T_2$.

meaning same Temp T_*

② if S_1 and S_2 in equilibrium and S_2 + S_3 in equilibrium then S_1 and S_3 in equilibrium

CE-~~3~~4

One ~~gas~~ atom in a box of dim $0 < x, y, z < L$

$$E = p_x^2/2m + p_y^2/2m + p_z^2/2m$$

$$Z = \underbrace{\int dx \int dy \int dz}_{L^3 = V} \int dp_x \int dp_y \int dp_z \; e^{-\beta E}$$

$$\int dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$$

How proven? $\longrightarrow \int dx\, x^2 e^{-ax^2} = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

$$1 + x + x^2 + \ldots = \sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

analogy

$$1 + 2x + 3x^2 + \ldots \quad \sum n x^{n-1} = \frac{1}{(1-x)^2}$$

binomial distrib. HW problem

3 independent integrals

$$Z = V\left(2m\pi/\beta\right)^{3/2}$$

$$\langle p_x^2 \rangle = \int dx \int dy \int dz \int dp_x \int dp_y \int dp_z \; p_x^2 \, P(\ldots)$$

observable

Usual expectation value definition eg in QM

$$\langle x \rangle = \int dx \; x \underbrace{|\psi(x)|^2}_{P(x)}$$

$$= Z^{-1} L^3 \left(\frac{2m\pi}{\beta}\right)^{3/2} \frac{1}{2\,\beta/2m} = m k_B T$$

$$\langle E \rangle = \frac{1}{2m}\left(\langle p_x^2\rangle + \langle p_y^2\rangle + \langle p_z^2\rangle\right) = \frac{1}{2m}\, 3\, m k_B T$$

$$\langle E \rangle = \tfrac{3}{2} k_B T$$

a famous result!

<u>Useful trick!</u>

$$\langle E \rangle = -\frac{\partial}{\partial \beta} \ln Z$$

$$Z = \sum_{\{\phi\}} e^{-\beta E(\{\phi\})}$$

$$-\frac{\partial}{\partial \beta} \ln Z = \frac{1}{Z} \sum_{\{\phi\}} E(\{\phi\})\, e^{-\beta E(\{\phi\})}$$

$$= \sum_{\{\phi\}} E(\{\phi\})\, \rho(\{\phi\}) \equiv \langle E \rangle$$

We will come back to this later but it is also true that

$$P = +\frac{\partial}{\partial V} k_B T \ln Z$$

For N ideal gas atoms $Z = \left[V\left(\frac{2m\pi}{\beta}\right)^{3/2}\right]^N$

$$\ln Z = N \ln V + \frac{3}{2} N \ln\left(\frac{2m\pi}{\beta}\right)$$

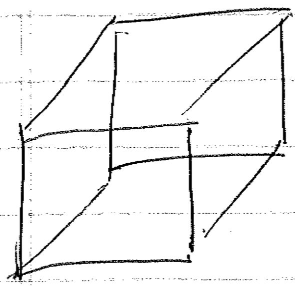
$$\frac{\partial}{\partial V} \ln Z = N \frac{1}{V} \qquad P = k_B T \frac{N}{V} \quad \leftarrow \text{Ideal gas law}$$

CE-5A

can get ideal gas law from classical mechanics

$$P_x = \frac{F_x}{A} = \frac{dp_x/dt}{A} = \frac{N\, 2mv_x / 2L/v_x}{L^2}$$

$$= \frac{N\, m v_x^2}{L^3}$$



$$PV = N m v_x^2 = N m \frac{1}{3} \langle v^2 \rangle$$

$$= N \frac{2}{3} \frac{1}{2} m \langle v^2 \rangle$$

$$= N \frac{2}{3} \langle E \rangle$$

Same as $PV = N k_B T \rightarrow \frac{2}{3} N \langle E \rangle$

$$\langle E \rangle = \frac{3}{2} k_B T$$

CE-~~4~~6

Harmonic oscillator

$$E(x,p) = \tfrac{1}{2} m\omega^2 x^2 + p^2/2m$$

$$Z = \int dx \int dp \; e^{-\beta E}$$

$\int dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$

$$= \sqrt{\frac{2\pi}{m\omega^2\beta}} \sqrt{\frac{2m\pi}{\beta}}$$

$\int dx\, e^{-ax^2} x^2 = \frac{1}{2a}\sqrt{\frac{\pi}{a}}$

$$= 2\pi/\omega\beta$$

Q: How proven?

$$P(x,p) = Z^{-1} e^{-\beta E}$$

$$\langle x^2 \rangle = \int dx\,dp \; \underbrace{x^2}_{\text{observable}} \; \underbrace{P(x,p)}_{\text{probability}}$$

$$= Z^{-1} \int dx\,dp \; x^2 e^{-\beta E}$$

$$= Z^{-1} Z \; 1/2(\tfrac{1}{2} m\omega^2\beta) = \frac{1}{m\omega^2\beta} = \frac{k_B T}{m\omega^2}$$

$$\frac{1}{2} m\omega^2 \langle x^2 \rangle = \frac{1}{2} k_B T$$

Similarly $\frac{1}{2m}\langle p^2 \rangle = \frac{1}{2} k_B T$

$$\langle E \rangle = k_B T$$

CE-87

In 3-D

$$E(x, y, z, p_x, p_y, p_z) = \left(\frac{2\pi}{\omega\beta}\right)^3$$

Integrals factorize if E = sum of independent contributions

$$\langle E \rangle = 3k_B T$$

~~[illegible]~~

CE-8

Two level system E_1 E_2

ie $\phi = \phi_1, \phi_2$ with

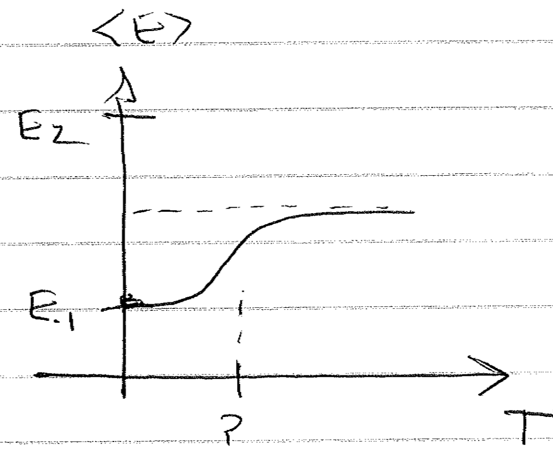
$$Z = e^{-\beta E_1} + e^{-\beta E_2}$$

$$\left.\begin{aligned} P_1 &= e^{-\beta E_1}/Z \\ P_2 &= e^{-\beta E_2}/Z \end{aligned}\right\} \text{ evidently } P_1 + P_2 = 1$$

$$\langle E \rangle = P_1 E_1 + P_2 E_2$$

Q: $\langle E \rangle$ at $T=0$

$T=\infty$?



Q: $\frac{E_2 - E_1}{k_B}$

other quantities

Free energy $F = -k_B T \ln Z$

Entropy $\cancel{E}$ $F = \langle E \rangle - TS$

For two level system

$$S = \frac{1}{T}\left(\langle E \rangle - F\right)$$

$$= \frac{1}{T} \frac{E_1 e^{-\beta E_1} + E_2 e^{-\beta E_2}}{e^{-\beta E_1} + e^{-\beta E_2}} + k_B \ln\left(e^{-\beta E_1} + e^{-\beta E_2}\right)$$

$$\Delta = E_2 - E_1$$

$$= \frac{1}{T} \frac{E_1 + E_2 e^{-\beta \Delta}}{1 + e^{\beta \Delta}} - \frac{\cancel{k_B} E_1}{T} + k_B \ln\left(1 + e^{-\beta \Delta}\right)$$

$T \to \infty$ $(\beta \to 0)$

$$S \to \phi - \phi + k_B \ln 2$$

"$S = k_B \ln \left\{ \begin{matrix} \text{\# accessible} \\ \text{states} \end{matrix} \right\}$"

$T \to 0$ $(\beta \to \infty)$

$$S \to \frac{E_1}{T} - \frac{E_1}{T} + k_B \ln 1 = \phi$$

In general $T \to \emptyset$ $\quad S \to k_B \ln g$

$g = \#$ states of lowest energy

$S \to 0$ if nondegenerate

If finite # of states N $\quad S \to k_B \ln N$ @ $T \to \infty$

<u>Specific heat</u>

$$C = \frac{d\langle E\rangle}{dT} \qquad d\langle E\rangle = C\,dT$$

C is "response function"

How does $\langle E\rangle$ respond to dT ?

$$\frac{d\langle E\rangle}{dT} = \frac{d}{dT} Z^{-1} \sum E e^{-\beta E}$$

drop ($\{\phi\}$)

$$\frac{d}{dT} = \frac{d\beta}{dT}\frac{d}{d\beta} = -\beta^2$$

$$= Z^{-1}(-\beta^2) \sum -E^2 e^{-\beta E}$$

$$-\beta^2(-Z^{-2})\left(\sum E e^{-\beta E}\right)^2(-1)$$

$$= \beta^2\left[\langle E^2\rangle - \langle E\rangle^2\right]$$

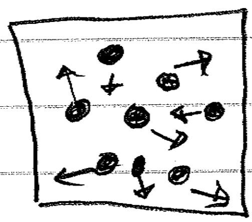
"Fluctuation dissipation theorem"

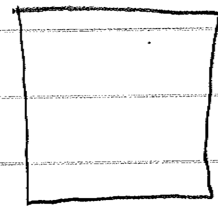
Amazing result!! Response of system to change in T

is related to fluctuations of energy at <u>fixed</u> T.

Other Examples of fluctuation-dissipation theorem

① Brownian motion (Einstein)





$\langle V \rangle = 0$

But $\langle v^2 \rangle - \langle v \rangle^2 \neq 0$

apply E field (charged particles)

$d\langle V \rangle = \mu dE$

"Mobility"

$\mu = \dfrac{d\langle V \rangle}{dE}$ response of V to E

but $\mu \sim \langle V^2 \rangle - \langle V \rangle^2$

@ $E = 0$ as well

② Magnetic moments with random orientations $\langle M \rangle = 0$

$d\langle M \rangle = \chi dB$ $\qquad \chi = d\langle M \rangle / dB$

response

$\chi = \beta \left[\langle M^2 \rangle - \langle M \rangle^2 \right]$ @ $B = 0$.

We considered two level system. Discrete levels can exist in classical physics, but naturally arise in QM.

Basic Principle of Quantum Stat Mech

$$\mathcal{H} \longrightarrow E_n \longrightarrow Z = \sum_n e^{-\beta E_n}$$

QM Hamiltonian — solve for energy levels — just as in classical!

Thus could ask for specific heat of 2 site Heisenberg model

$$\mathcal{H} = J\vec{S}_1 \cdot \vec{S}_2 \longrightarrow \begin{array}{l} E_n = -\frac{3}{4}J \\ E_n = +\frac{1}{4}J \quad \Leftarrow \text{3 fold degenerate} \end{array}$$

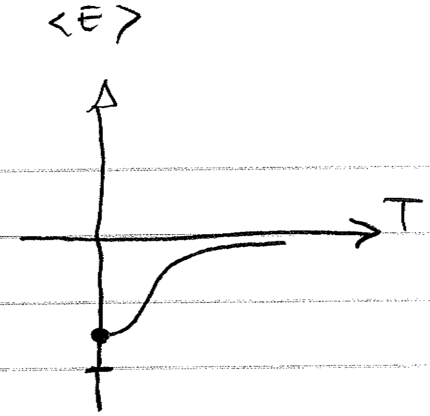
$$= \frac{J}{2}\left[\underbrace{(S_1+S_2)^2}_{0,1} - \underbrace{S_1^2}_{\frac{3}{4}} - \underbrace{S_2^2}_{\frac{3}{4}}\right]$$

$$Z = 3e^{-\frac{1}{4}\beta J} + e^{\frac{3}{4}\beta J}$$

$$\langle E \rangle = -\frac{\partial}{\partial\beta}\ln Z = \frac{-\frac{3}{4}J e^{\frac{3}{4}\beta J} + 3\left(\frac{1}{4}J\right)e^{-\frac{1}{4}\beta J}}{e^{\frac{3}{4}\beta J} + 3e^{-\frac{1}{4}\beta J}}$$

QE-13

$$\langle E \rangle = \frac{3J}{4}\left[\frac{-e^{\beta J}+1}{e^{\beta J}+3}\right]$$



$T \to 0 \quad \beta \to \infty \qquad E \to -3J/4$

$T \to \infty \quad \beta \to 0 \qquad E \to 0$ why?