Introduction to Statistical + Quantum Mechanics

One of the first places we saw a failure of classical physics was in statistical (or average) behaviors of systems

- Statistical Physics

When we have lots of particles (or waves), it's not practical to list the behavior of each one.

- Distribution Functions
  - Instead of labeling the state of each particle, (for example $\vec{x}_1, \vec{p}_1; \vec{x}_2, \vec{p}_2; \ldots \vec{x}_N, \vec{p}_N$), we give the number of particles in each state
    - + For example, $f(\vec{x},\vec{p})\,d^3\vec{x}\,d^3\vec{p}$ = # of particles in box of volume $d^3\vec{x}$ at $\vec{x}$ and "momentum space" volume $d^3\vec{p}$ at $\vec{p}$.
    - + As you will learn, quantum systems often have discrete states, so you have a set of numbers f_n = # particles in state n.
    - + We'll assume the total # of particles is fixed to N

$$\int d^3\vec{x}\, d^3\vec{p}\, f = N \quad , \text{etc}$$

    - + That means you can have the probability that a selected particle is in a given state $P = f/N$.
- This lets us determine average values of quantities Q

$$\langle Q \rangle = \frac{1}{N}\int d^3\vec{x}\, d^3\vec{p}\; Q f = \int d^3\vec{x}\, d^3\vec{p}\; Q P$$

etc.

- An example we'll come back to: free particles in a box. Start in 1D
  - + Consider $f(x,p) = \frac{N}{L}\sqrt{\frac{a}{\pi}}\, e^{-ap^2}$ ⇐ like an ideal gas.
  - + Then

$$\langle K \rangle = \frac{1}{2m}\langle p^2 \rangle = \frac{1}{2m}\sqrt{\frac{a}{\pi}}\int_{-\infty}^{\infty} dp\; p^2 e^{-ap^2} = \frac{1}{4ma}$$

  - + Can you do that calculation?

— We want to write things in terms of energies often

- Density of States

  + Each energy value can have different states
  + For example, momenta with the same $|\vec{p}|$ have same K.E.

  So

$$\left(\text{avg. \# particles of energy } E\right) = \left(\overset{\text{1-particle}}{\text{\# states of energy } E}\right) \times \left(\text{avg. \# of particles in a state of energy } E\right)$$

  + We call $\Omega(E)\,dE$ = # states with energy $E \to E + dE$.

  This is called the <u>density of states</u>.

  + Example: A free particle (no potential) in volume V

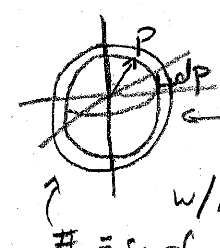
  A state is a little unit "volume" $d^3\vec{x}\, d^3\vec{p}$, so

$$\int \Omega(E)\,dE \propto \int d^3\vec{x}\, d^3\vec{p} = V \int p^2 \sin\theta\, dp\, d\theta\, d\phi = 4\pi V \int dp\, p^2$$

  Now use $p^2/2m = E \Rightarrow dE = p\,dp/m$

  So

$$\int \Omega(E)\,dE \propto V \int dE\, m\sqrt{2mE}$$



  This implies $\Omega(E) \propto V\sqrt{E}$.

- Temperature

  + The density of states for many particles is similar but is the surface area of a many-dimensional sphere.

$$\Omega_N(E) \propto E^{\frac{3}{2}N} \text{ for large } N. \quad (E = \text{total energy})$$

  + But then

$$\ln \Omega \propto N \ln E \Rightarrow \frac{d\ln\Omega}{dE} \propto \frac{N}{E}.$$

  E/N is the average energy per particle, which is how we think of temperature.

  + We define

$$\frac{1}{kT} = \frac{d\ln\Omega}{dE}, \text{ where } k = \text{Boltzmann's constant}$$

- Boltzmann Factor
  - The probability that any randomly selected particle is in a given state of energy E is proportional to the <u>Boltzmann factor</u>

$$P \propto e^{-E/kT} \quad \text{in equilibrium}$$

  - Heuristic Derivation:

    Assume the probability is proportional to the number of possible states of the other $N-1$ particles with total energy E_N conserved.

    Then

$$P(E) \propto \Omega_{N-1}(E_N - E) \approx \exp\left[\ln \Omega(E_N) - E\left(\frac{d\ln\Omega}{dE}(E_N)\right)\right]$$

$$\propto e^{-E/kT}$$

    In other words, this is the # of ways of arranging <u>the</u> <u>other</u> <u>stuff</u>.

- Examples + Calculations
  - Maxwell-Boltzmann Distribution for velocity

    Consider a free particle in a gas of N particles
    - Probability of having energy E is

$$P(E) = \mathcal{N}\,\Omega(E)\,e^{-E/kT} \quad (\mathcal{N} = \text{normalization factor})$$

$$= \#\text{states} \times \text{probability/state}$$

    - This is $P(E)\,dE = \mathcal{N}\,V\sqrt{E}\,e^{-E/kT}\,dE$.

      With $E = \frac{1}{2}mv^2$, $\quad P(v)\,dv = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{-mv^2/2kT}$

    - We can now calculate things like average speed

$$\langle v\rangle = \int dv\, v P(v) \quad \text{or} \quad \langle v^2\rangle = \int dv\, v^2 P(v) \quad \text{etc.}$$

    - Carry these out, note $\langle v\rangle^2 \neq \langle v^2\rangle$.
    - Next, we see that $4\pi v^2 dv = \int_0^{\pi} d\theta \sin\theta \int_0^{2\pi} d\phi\, dv\, v^2 = \int d^3\vec{v}$

      so we have a probability for a particle to have velocity $\vec{v}$

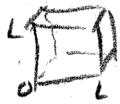
$$P(\vec{v})\,d^3\vec{v} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT}\, d^3\vec{v}.$$

      Calculate an avg. or two.

- Energy in waves

+ Consider a classical wave in a volume V.
+ States are given by the allowed wave vectors $\vec{k}$, which depend on the boundary conditions. Let's assume the wave is confined to the box, so it vanishes at box walls (Dirichlet b.c.)
+ This could be the motion of a held string or EM wave in a conductor

The standing wave if box has sides of length L $(V=L^3)$



$$\Phi = A\cos(\omega t)\sin\left(\frac{\pi n_x x}{L}\right)\sin\left(\frac{\pi n_y y}{L}\right)\sin\left(\frac{\pi n_z z}{L}\right)$$

$$n_{x,y,z} \in \mathbb{Z}_+$$

+ This corresponds to a sum of waves w/ wavenumbers

$$\vec{k} = \frac{\pi}{L}(\pm n_x, \pm n_y, \pm n_z) \quad \text{and} \quad \omega = 2\pi\nu = |E|/c \quad \text{(for light)}$$

Note that we don't get to choose negative values for $n_{x,y,z}$.

+ With $\nu^2 = \left(\frac{\omega}{2\pi}\right)^2 = \frac{c^2}{4L^2}(n_x^2+n_y^2+n_z^2)$, we can make a density of states (wave modes) in terms of ν: just # of lattice points from $\nu \to \nu + d\nu$. At large n, this is the same spherical shell volume

$$\Omega(\nu)\,d\nu = 2\cdot\frac{4\pi}{8}n^2\,dn = \left(\frac{8\pi V}{c^3}\right)\nu^2\,d\nu \quad \begin{cases} \frac{1}{8} \text{ b/c } n_{x,y,z}>0 \\ 2 \text{ for polarizations} \end{cases}$$

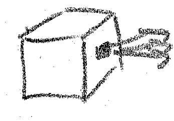
+ Meanwhile, the energy in a mode is determined by the amplitude (indep. variable). The average energy in one mode is

$$\langle E\rangle = \int E\,\underbrace{P(E)}_{\text{Prob. of } E \text{ in the mode}}\,dE = \frac{\int_0^\infty E e^{-E/kT}\,dE}{\int_0^\infty e^{-E/kT}\,dE} = kT$$

+ The total energy/volume with freq. from $\nu \to \nu + d\nu$ in an EM wave

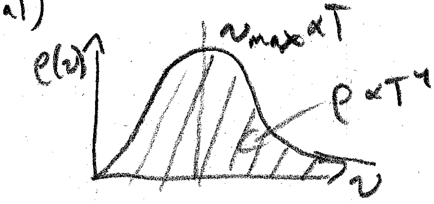
$$\rho(\nu)\,d\nu = \left(\frac{8\pi}{c^3}\right)kT\,\nu^2\,d\nu \qquad \text{\underline{Rayleigh-Jeans Law}}$$

This is related to the spectrum of light from a small hole cut in our box



Unfortunately, it is completely wrong! See ultraviolet catastrophe – more + more energy at higher frequency.

- Historical Intro to Quantum
  - Blackbody Radiation + Planck's Law
    - Perfectly thermal radiation from an object that absorbs + emits light perfectly (no reflection)
      - To maintain equilibrium absorption + emission must be the same in each frequency range
      - Real life approximate "blackbodies": incandescent lightbulb filament, the sun (or star); the most perfect is the cosmic microwave background from the early universe
    - We'll consider the energy density spectrum $\rho(\nu)$, like Rayleigh-Jeans law (energy per frequency interval)



      - The total energy density is

$$\rho = \int_0^\infty d\nu\, \rho(\nu) = \frac{4\sigma}{c} T^4$$

This is (a version of) the Stefan-Boltzmann law

$$\sigma = 5.7 \times 10^{-8}\, J/m^2 s K^4 = \text{Stefan-Boltzmann constant}$$

      - There is a ν_{max} where $\rho(\nu)$ is biggest, and $\nu_{max} \propto T$

This is the Wien Displacement law. This is usually written as $\lambda_{max} T = w$, $w = 2.9 \times 10^{-3}\, mK$.

Note: λ_{max} is defined by taking $\frac{d\tilde{\rho}}{d\lambda} = 0$, $\tilde{\rho} = \rho \frac{d\nu}{d\lambda}$

so $\lambda_{max} \neq c/\nu_{max}$

      - Clearly, the Rayleigh-Jeans law fails miserably at matching these experimental results (plus UV catastrophe). Classical physics is breaking.

- We've talked about light as made of photon particles. What if we postulate that (a) the energy of a photon is $\propto \nu$ and (b) the energy in a mode = total energy of the photons?
  - Then the energy is discrete: $h\nu, 2h\nu, \ldots$ h = Planck's constant
  - And the average energy per mode is

$$\langle E \rangle = \sum_{n=0}^{\infty} nh\nu \, e^{-nh\nu/kT} \Big/ \sum_{n=0}^{\infty} e^{-nh\nu/kT}$$

To calculate,

$$\sum_n e^{-nx} = \frac{1}{1-e^{-x}} \quad \text{and} \quad \sum_n n e^{-nx} = \frac{-d}{dx} \sum_n e^{-nx} = \frac{e^{-x}}{(1-e^{-x})^2}$$

so $\langle E \rangle = h\nu \big/ (e^{h\nu/kT} - 1) \leftarrow$ Decreases when $h\nu >$ classical avg.

  - Then we have Planck's Law

$$\rho(\nu)d\nu = \frac{8\pi h}{c^3} \frac{\nu^3}{e^{h\nu/kT}-1} d\nu$$

  - Wien's law comes from $d\rho/d\nu = 0$

$$\Rightarrow 3\left(e^{h\nu/kT}-1\right) - \nu\left(\frac{h}{kT} e^{h\nu/kT}\right) = 0$$

This is a function only of $h\nu/kT \Rightarrow \nu_{max} \simeq \left(\frac{2.8k}{h}\right)T$

  - The Stefan-Boltzmann law comes from the integral

$$\rho = \frac{8\pi h}{c^3} \int_0^{\infty} \frac{\nu^3}{e^{h\nu/kT}-1} d\nu = \frac{8\pi k^4 T^4}{c^3 h^3} \int_0^{\infty} dx \frac{x^3}{e^x - 1} = \left(\frac{8\pi^5}{15} \frac{k^4}{h^3 c^3}\right) T^4$$

  - Matching to w and σ gives

$$h = 6.626 \times 10^{-34}\ \text{Js}, \quad k = 1.381 \times 10^{-23}\ \text{J/K}.$$