3-15-11

Welcome back from spring break

Read course announcements
- reading in Schroeder 6.1, 6.2
- Assignment 7 posted
- midterms returned on Thursday
- solutions to midterm posted

Chapter 6: Boltzmann Statistics

We jump from Chapter 3 to Chapters 6 and 7, and finish course in Chapter 5, on phase transitions

Discuss new way to study macroscopic equilibrium, relating energy of microscopic components to macroscopic properties. We will no longer need to calculate multiplicity Ω and entropy S although our knowledge of these crucial for developing the new ideas.

Can illustrate some of the problems we will think about, calculate from supercomputer simulation "Inner Life of a cell"

- self-assembly of microtubules
- liquid lipid bilayers
- changes in # of particles
-

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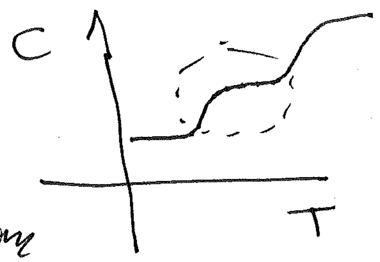
Will apply Boltzmann statistics to:



- ideal gas of molecules
  - understand freezing of rotational degrees of freedom
  - speed distribution of molecules (Maxwell-Boltzmann
  - extend Sackur-Tetrode to molecules

- biophysics:
  - binding of O_2 to hemoglobin, ~~while~~ why CO causes suffocation
  - self-assembly, disassembly of large molecules
  - nervous systems, why neurons have $\Delta V_{membrane} \simeq 50 mV$

- electrons: metals, white dwarfs

- photons: blackbody radiation
  cosmology
  global warming

- phonons: Fix Einstein's theory to allow coupled oscillators
  with different frequencies

- Bose-Einstein condensates: hot frontier in physics
  and engineering

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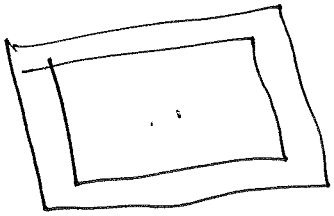
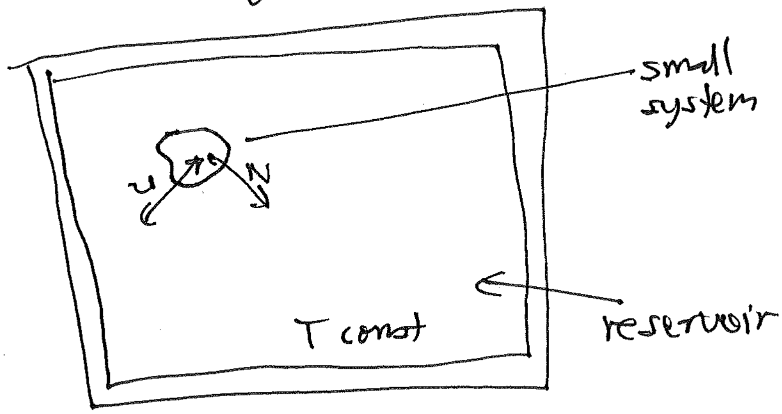
Will develop and apply powerful formalism called Boltzmann statistics that avoids calculating multiplicities Ω

Insight is to consider subsystem that is in equilibrium with a large unchanging reservoir of temperature T



Chapter 3:
system isolated
U, V, N conserved



Chapters 6 and 7
U, N, V can vary while in equilibrium with reservoir

A new insight will be that small system will be in equilibrium not when entropy is a maximum but when new quantities called <u>thermodynamic potentials</u> for system reach minimum value

enthalpy $H = U + PV$ constant pressure, constant S

Helmholtz free energy $F = U - TS$ constant V, constant T

Gibbs free energy $G = U - TS + PV$ constant T, constant P

← familiar to you from chem, biology courses

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Do not need to memorize these and other thermodynamic potentials, can all be derived quickly from the thermodynamic identity

$$dU = TdS - PdV + \mu dN \qquad U = U(S,V,N)$$

by integration by parts. For example:

$$dU = TdS - PdV + \mu dN$$

$$= d(TS) - SdT - d(PV) + VdP + \mu dN$$

$$\Rightarrow \quad d(\underbrace{U - TS + PV}_{G = G(T,P,N)}) = -SdT + VdP + \mu dN$$

can quickly further discover that

$$S = -\left(\frac{\partial G}{\partial T}\right)_{P,N} \qquad V = \left(\frac{\partial G}{\partial P}\right)_{T,N}$$

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

from $dG = -SdT + VdP + \mu dN$

<u>Class project:</u> what thermodynamic potential to use if T, V, μ are experimental variables?

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Compare Chapters 2, 3 with Chapters 6, 7

For isolated systems, strategy was:

$$\Omega(N,V,U) \to S(N,V,U) = k\ln\Omega$$

$$\to \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}$$

$$\to U = U(T)$$

$$\to C_V(T) = \left(\frac{\partial U}{\partial T}\right)_{N,V},\quad M(B,T),\ \text{etc.}$$

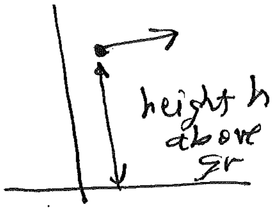
$$\Omega = \binom{N}{N_\uparrow}$$

$$= \binom{N+q-1}{q}$$

$$= V^N U^{3N/2} f(N)$$

For small systems in equil w/ reservoir with constant T, key input is not multiplicity but <u>energy levels $\{E_n\}$ of each microstate</u>. Levels can be classical

$$E(z,p) = \frac{p^2}{2m} + mgz$$



or quantum $\quad E_n = -\frac{R}{n^2}$ for H atom

or combination.

Key quantity to work with is the <u>partition function</u> $Z(T)$:

$$Z(T) = e^{-\frac{E_1}{kT}} + e^{-\frac{E_2}{kT}} + \cdots$$

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Comparison of formulas

Ω	Z
$S = k \ln \Omega$	$S = \frac{\partial}{\partial T}\left[kT \ln Z\right]$
$P = T\left(\frac{\partial S}{\partial V}\right)_{u,V}$	$P = kT\left(\frac{\partial \ln Z}{\partial V}\right)_{T,N}$
$\mu = -T\left(\frac{\partial S}{\partial N}\right)_{u,V}$	$\mu = -kT\left(\frac{\partial \ln Z}{\partial N}\right)_{T,V}$
$1/T = +\left(\frac{\partial S}{\partial U}\right)_{V,N}$	no analog since T is given as property of reservoir which system is in equilibrium ~~from~~ with

Knowledge of Z will allow us to calculate all statistical properties of macroscopic system

fluxes, electrical currents, max mass of star, etc.

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Derivation of the Boltzmann factor $e^{-E_n/kT}$

Following is one of the few derivations that I will ask you to memorize and master in all details, one of most important insights of the course

My discussion somewhat different from Schroeder, would recommend mastering my reasoning first.

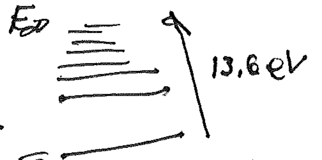
Assume we have a "small" system which has known ~~energy~~ states with energies given by (assumed known)

$$E_1 \leqslant E_2 \leqslant E_3 \leqslant \cdots$$

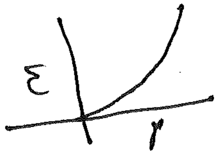
$\uparrow$ ground state

Examples:

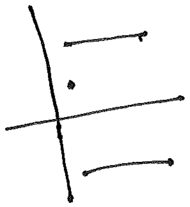
hydrogen atom H: $E_n = -\frac{13.6\,\text{eV}}{n^2}$



ideal gas ~~mole~~ atom $E = \frac{p^2}{2M}$

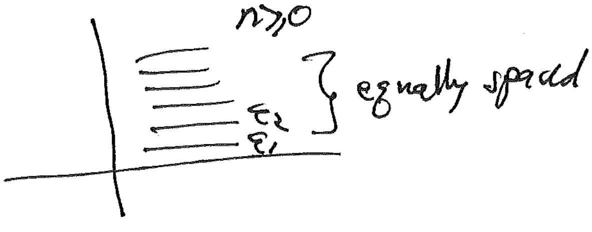


paramagnet dipole $E = -\mu B$ or $+\mu B$



Einstein oscillator $E_n = (n+\frac{1}{2})hf$

$n \geq 0$



Degenerate energy states

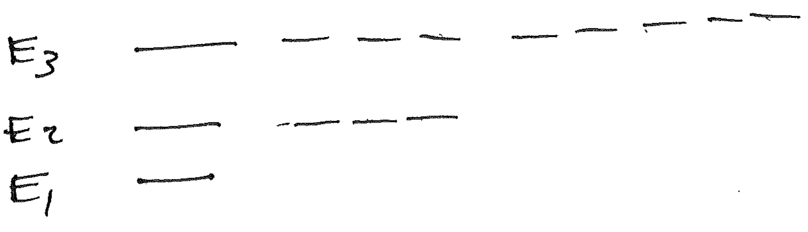
Especially for quantum systems, different state can have same energy. These are called "<u>degenerate states</u>"

Familiar example is H atom

$E_1 = -\frac{13.6\,\text{eV}}{1^2}$ only one state 1s

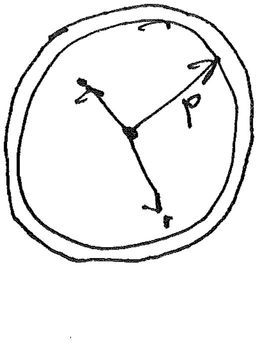
$E_2 = -\frac{13.6\,\text{eV}}{2^2}$ $1+3=\underline{\underline{4}}$ deg. stat 2s, $2p_x$, $2p_y$, $2p_z$

$E_3 = -\frac{13.6\,\text{eV}}{3^2}$ $1+3+5=3^2=9$ degenerate states
3s, 3p 3d



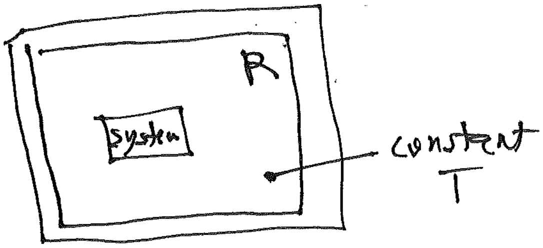
Even for classical molecule, there are degenerate states

for fixed $E = \frac{\vec{p}^2}{2m}$, $\vec{p}$ can be any vector on sphere of radius $\sqrt{2mE}$



degeneracy $\propto 4\pi p^2 dp$

Assumptions: our small system is in contact with a large constant-temperature reservoir, sometimes also called a heat bath



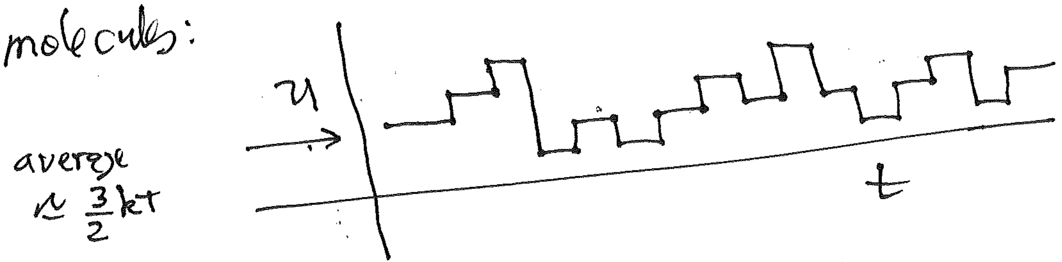
large means: $$\underset{\substack{\uparrow \\ \text{label for} \\ \text{reservoir}}}{U_R} \gg \underset{\substack{\uparrow \\ \text{label for system} \\ \text{(not entropy)}}}{U_S}$$

key question to ask: what is probability to observe system in particular state s, with energy E_s?

for isolated system, we know answer: all states with same energy E_s are accessible microstates and so equally likely

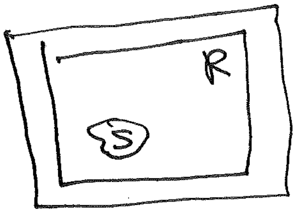
for non-isolated system, system can exchange energy with reservoir, sometimes gaining, sometimes losing energy

think of pollen grain in water, getting kicked by water molecules:



$\langle \frac{1}{2}mv^2 \rangle \simeq \frac{3}{2}kT$ by equipartition

Can't apply Ω or S or 2nd law $\frac{dS}{dt} > 0$, equil $\Leftrightarrow$ S_{max} to system or reservoir but can apply Ω and 2nd law to system and reservoir, which we assume are isolated



E = total energy conserved

you can see intuitively why some states s of system S are more or less probable: if energy of S increases, it removes energy from R which causes big reduction in # of microstates of R since, generally, $\Omega(U)$ is rapid increasing f^n of U, e.g. $\Omega \propto U^{3N/2}$ for ideal gas of N atoms, $\Omega \propto \left(\frac{eq}{N}\right)^N$ $q \gg N$ Einstein solid

If all microstates of isolated system are equally likely, situation in which system S has a lot of energy will be improbable since this corresponds to small fraction of accessible microstates

can guess

P_s = prob to observe system S to be in state s with energy E_s

$$\propto \Omega_{total}(E_s) = \Omega_R(E - E_s)$$

$$\boxed{P_s \propto \Omega_R(E - E_s)}$$

since $E_s \ll E \Rightarrow \Omega_S(E_s)$ big # multiplying very big #

Let c be constant of proportionality

$$P_s = c\,\Omega_R(\underset{\substack{\uparrow \\ \text{big energy} \\ \text{of reservoir}}}{E} - E_s)$$

$\uparrow$ tiny energy of small system (E_s)

This cries out for Taylor series around big number E, in small correction $-E_s$. But let's use wisdom obtained from Chapters 2 and 3, since Ω_R is a very large number, usually easier to work with $\ln \Omega_R = S/k$, which is "just" a large #.

We can write:

$$P_s = c\,\Omega_R(E-E_s)$$

write in terms of entropy $S = k\ln\Omega_R$

$$= c\,\exp\left[\ln\left(\Omega_R(E-E_s)\right)\right]$$

$$\boxed{P_s = c\,e^{S_R(E-E_s)/k}}$$

But:

$$S_R(E-E_s) \simeq S_R(E) - \left(\frac{\partial S_R}{\partial E}\right)_{V,N} E_s + \text{higher order terms in } E_s$$

$$\simeq S_R(E) - \frac{1}{T_R}E_s$$

so

$$P_s = c\,\underbrace{e^{S_R(E)}}_{\text{constant}}\,e^{-E_s/(kT)} = \underset{\substack{\uparrow \\ \text{new constant } c\,e^{S_R(E)}}}{\tilde{c}}\;\underbrace{e^{-E_s/(kT)}}_{\text{exponential is called the "Boltzmann factor"}}$$

What is the constant $\tilde{c}$? Can obtain by using fact that system has to be in some state s, i.e., probabilities P_s must add to one over all states

$$1 = \sum_s P_s = \sum_s \left[\tilde{c}\, e^{-E_s/(kT)}\right] = \tilde{c} \sum_s e^{-E_s/(kT)}$$

or $$\tilde{c} = \frac{1}{\sum_s e^{-\cancel{\beta}E_s/(kT)}}$$

Let's define the $\boxed{\beta = \frac{1}{kT}}$ gets tiring to write $\frac{1}{kT}$ all the time

define "partition function" Z

$$Z = \sum_s e^{-\beta E_s}$$

Z from German "Zustandssume" "sum over states"

Then probability to observe small system to be in state s with energy E_s when in equilibrium with large reservoir with fixed temperature T is

$$\boxed{P_s = \frac{e^{-\beta E_s}}{Z} = \frac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}}$$