Welcome back from spring break

Read course announcements
- reading in Schneider 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 $\Omega$ 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 "Life of a cell":

- self-assembly of microtubules
- liquid lipid bilayers
- change in # of particles
Will apply Boltzmann statistics to:

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

- biophysics:
  - binding of O₂ to haemoglobin, why CO causes suffocation
  - self-assembly, disassembly of large molecules
  - nervous system, why neurons have AV membrane ≈ 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
Will develop and apply powerful formalism called Bolzmann statistics that avoids calculating multiplied $S^2$
Insight is to consider subsystem that is in equilibrium with a large unchanging reservoir of temperature $T$

\[ H = U + PV \]

\[ F = U - TS \]

\[ G = U - TS + PV \]

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

Chapter 3:
- system isolated
- $U, V, N$ conserve

Chapter 6 and 7:
- $U, N, V$ can vary while in equilibrium with reservoir

\* Familiar to you from chem, biology courses
Do not need to memorize these and other thermodynamic potentials, can all be derived quickly from the thermodynamic identity

\[ dU = TdS - PdV + \mu dN \quad U = U(S, V, N) \]

by integration by parts. For example:

\[ dU = TdS - PdV + \mu dN \]

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

\[ \Rightarrow \quad d(U - TS + PV) = -SdT + VdP + \mu dN \]

\[ G = G(T, P, N) \]

can quickly further discover that

\[ S = -\left( \frac{\partial G}{\partial T} \right)_P, N \]

\[ V = \left( \frac{\partial G}{\partial P} \right)_T, N \]

\[ \mu = \left( \frac{\partial G}{\partial N} \right)_T, P \]

from \[ dG = -SdT + VdP + \mu dN \]

Class project: what thermodynamic potential to use if \( T, V, \mu \) are experimental variables?
Compare Chapters 2, 3 with Chapter 6.7

For isolated system, strategy was:

\[ S_z (N, V, u) \rightarrow S (N, V, u) = k \ln S_2 \]

\[ \frac{1}{T} = \left( \frac{g}{\mu} \right)_V \]

\[ U = U(T) \]

\[ C_V(T) = \left( \frac{\partial U}{\partial T} \right)_{N, V} \]

For small system in equal w/ reservoir with constant T, key input is not multiplicity but energy levels \( \Sigma E_n \) of each microstate. Levels can be classical

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

or quantum

\[ E_n = -\frac{R}{n^2} \quad \text{for H atom} \]

or combination.

Key quantity to work with is the partition function \( Z(T) \):

\[ Z(T) = e^{\frac{-E_1}{kT}} + e^{\frac{-E_2}{kT}} + \ldots \]
Comparison of Formulas

\[ S_z \]
\[ S = k \ln S_z \]
\[ P = T \left( \frac{\partial S}{\partial V} \right)_{T,N} \]
\[ \mu = -T \left( \frac{\partial S}{\partial N} \right)_{T,V} \]
\[ \frac{1}{T} = \frac{\partial S}{\partial U} \]

\[ Z \]
\[ S = \frac{1}{2T} \left[ kT \ln Z \right] \]
\[ P = kT \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N} \]
\[ \mu = -kT \left( \frac{\partial \ln Z}{\partial N} \right)_{T,V} \]

no analog since \( T \) is given as property of reservoir which system is in equilibrium with.

Knowledge of \( Z \) will allow us to calculate all statistical properties of macroscopic system.

Fluxes, electrical currents, max max of stars, etc.
Derivation of the Boltzmann Factor $e^{-\frac{E}{kT}}$

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 Schrödery, would recommend mastering my reasoning first.

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

$$E_1 \leq E_2 \leq E_3 \leq \ldots$$

↑

ground state

Examples:
- hydrogen atom $H$:
- ideal gas mole atom
- paramagnet dipole
- Einstein oscillator

\[
E_n = -\frac{13.6\text{eV}}{n^2} \quad E = \frac{p^2}{2m} \quad E = -\mu B \text{ or } +\mu B \quad E_n = (n + \frac{1}{2}) \hbar \omega
\]

\begin{itemize}
  \item equally spaced
\end{itemize}
Degenerate energy states

Especially for quantum systems, different states can have same energy, these are called "degenerate states"

Familiar example is H atom

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

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

\[ E_3 = -\frac{13.6\text{ eV}}{3^2}, \quad 1+3+5 = 9 = 3 \text{ deg. stat} \quad 3s, 3p, 3d \]

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 \( \sqrt{2mE} \)

\[ \text{degeneracy } \propto 4\pi r^2 \text{dp} \]
Assumptions: our small system is in contact with a large constant-temperature reservoir, sometimes also called a heat bath.

Large means: \( U_R \gg U_s \)

\( U_R \) for reservoir
\( U_s \) for system (not entropy)

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:

\[
\text{average } \frac{1}{2} kT
\]

\( \langle E_{\text{kin}} \rangle \approx \frac{3}{2} kT \) by equipartition
Can't apply SC or S or 2nd law $\frac{dS}{dt} > 0$, equal $\Rightarrow$ Maxw to system or reservoir but can apply SC and 2nd law to system and reservoir, which we assume are isolated

$E = \text{total energy conserved}$

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, $SC(U)$ is rapid increasing $F$ of $U$

e.g. $S_2 \propto U^{3/2}$ for ideal gas of $N$ atoms, $S_2 \propto \left(\frac{e^2}{W}\right)^N \Rightarrow N$ 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

$P_s = \text{prob to observe system } S \text{ to be in state } s$

with energy $E_j$

$\propto S_{\text{total}}(E_s) = \sum_R SC_R(E-E_j)$

$P_s \propto SC_R(E-E_j)$

Since $E_s \ll E \Rightarrow SC(E_s)$ big # multiplying very big #
Let \( c \) be constant of proportionality.

\[
P_s = c \, S_R(E-E_s)
\]

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 \( S_R \) is a very large number, usually easier to work with \( \ln S_R = S/k \), which is just a large \( s \). We can write

\[
P_s = c \, S_R(E-E_s) \exp \left[ \ln(S_R(E-E_s)) \right]
\]

But:

\[
S_R(E-E_s) \approx S_R(E) - \left( \frac{\partial S_R}{\partial E} \right)_{E=E_s} E_s + \text{higher order terms in } E_s
\]

so

\[
P_s = c \, e^{S_R(E) - E_s / kT} = c \, e^{-E_s / kT}
\]
What is the constant \( \mathcal{Z} \)? Can be found by using the fact that system has to be in some state \( s \), i.e., probabilities \( P_s \) must add to one over all states:

\[
1 = \sum_s P_s = \sum_s \left[ e^{-\beta E_s / (kT)} \right] = \mathcal{Z} \sum_s e^{-\beta E_s / (kT)}
\]

or

\[
\mathcal{Z} = \frac{1}{\sum_s e^{-\beta E_s / (kT)}}
\]

Let's define the

\[
\beta = \frac{1}{kT}
\]

gets tiring to write \( \frac{1}{kT} \) all the time

Define "partition function" \( \mathcal{Z} \):

\[
\mathcal{Z} = \sum_s e^{-\beta E_s}
\]

\( \mathcal{Z} \) from German "zuständsumme" "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

\[
P_s = \frac{e^{-\beta E_s}}{\mathcal{Z}} = \frac{e^{-\beta E_s}}{\sum_s e^{-\beta E_s}}
\]