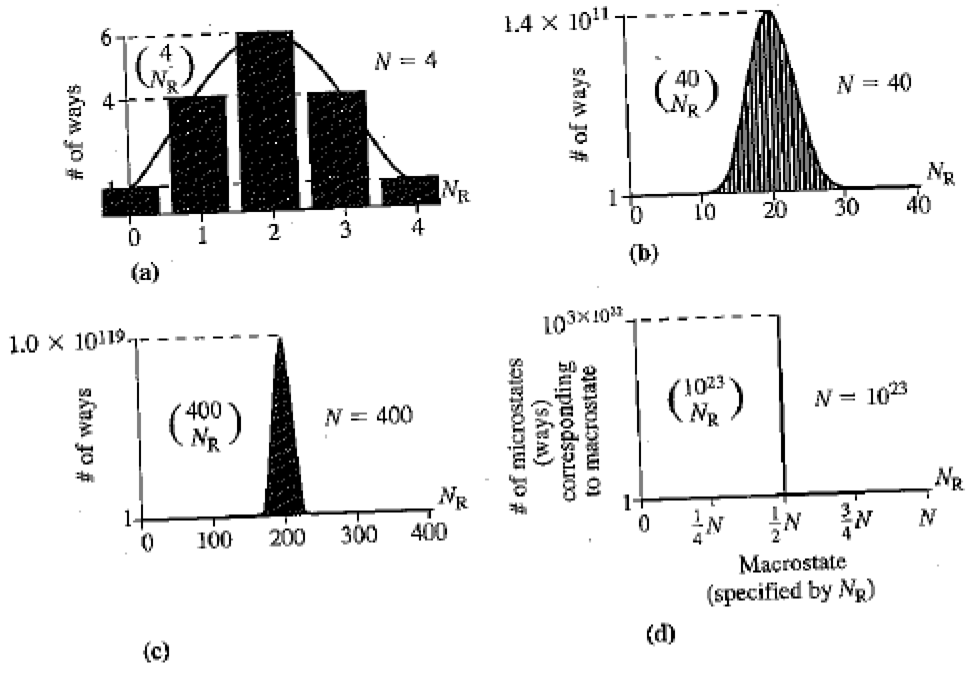
PH102, 2014W, Lecture Notes: January 30, Thurs, Lecture 8

Statistical Mechanics

Statistical mechanics:

- concerns making predictions about properties and behaviors in systems where the number of particles is huge, at the order of Avogadro's number (= 10^{23}).
- is necessary because we cannot possibly be sure about how individual particles work
- uses averages to predict system properties and behaviors
- averages can precisely represent a macroscopic thermodynamic system as the number of particles in the system increase. The graphs below illustrate that the most probable value can be very precise to describe the property of the system as n increases.

Figure 9.3 Number of ways of distributing particles on two sides of a room variation as total number of particles increases from 4 to 10^{23}.



- micro vs. macro states: micro states refer to all possible different arrangements of states that can produce a macroscopic state property that is independent of how microstates are arranged. Examples of such properties are the overall properties of number, energy, and volume and the local properties of pressure, temperature, and particle concentration.
- The most probable state is when N is large is called equilibrium state.

Boltzman Distribution

- Boltzman probability: The probability of an individual particle will be in state *n* associated with E_n
  $$P(E_n) = A\, e^{-\frac{E_n}{k_B T}}$$
  Where *n* stands for the set of quantum numbers necessary to specify the individual-particle state
- Particles in the large systems of distinguishable particles obey the Boltzman probability.
- Probability drops exponentially with energy. The higher energy associated with the state, the less likely the probability of particle being in that state.
- The probability summed over all individual particle states n is 1:
  $$\sum \ P(E_n) = \sum_n A\, e^{-\frac{E_n}{k_B T}} = 1 \rightarrow A = \frac{1}{\sum_n e^{-\frac{E_n}{k_B T}}}$$
  $$P(E_n) = \frac{e^{-\frac{E_n}{k_B T}}}{\sum_n e^{-\frac{E_n}{k_B T}}}$$
- Average Energy $\bar{E}$
  $$\bar{E} = \sum E_n\, P(E_n) = \frac{\sum_n E_n\, e^{-\frac{E_n}{k_B T}}}{\sum_n e^{-\frac{E_n}{k_B T}}}$$
- Occupation Number $\mathcal{N}$: the number of particles expected in a given state of E_n
  $$\mathcal{N}(E_n)_{Boltman} = N\, P(E_n) = N \frac{e^{-\frac{E_n}{k_B T}}}{\sum_n e^{-\frac{E_n}{k_B T}}}$$
- (Number of particles of E_n) = $\mathcal{N}(E_n)$ (number of states associated with energy E_n)
- Using the occupation number, average energy can be rewritten as:
  $$\bar{E} = \sum E_n\, P(E_n) = \frac{\sum_n E_n\, e^{-\frac{E_n}{k_B T}}}{\sum_n e^{-\frac{E_n}{k_B T}}} = \frac{\sum_n E_n \mathcal{N}(E_n)}{\sum_n \mathcal{N}(E_n)}$$
  Average energy is the energy of a given state times the number of particles in that state, summed over all states and then divided by the total number of particles in all states.

- When the energy levels are very closely spaced, then
  Density of states $D(E) \equiv \frac{Differential\ number\ of\ states\ within\ range\ of\ dE\ of\ E}{dE}$
  $$\bar{E} = \frac{\int E\, \mathcal{N}(E) D(E) dE}{\int \mathcal{N}(E) D(E) dE}$$
  $$N = \int \mathcal{N}(E) D(E) dE$$

One dimensional Harmonic Oscillator Example

$$\frac{-\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2}+\frac{1}{2}kx^2\ \psi(x) = \mathrm{E}\ \psi(x)$$

$$E_n = \left(n+\frac{1}{2}\right)\hbar\omega_0 \quad (\mathrm{n} = 0, 1, 2\ldots)$$

$$\psi_n(x) = \left(\frac{b}{2^n n!\sqrt{\pi}}\right)^{\frac{1}{2}} H_n(bx)e^{-\frac{1}{2}b^2x^2}$$

Let's shift the Energy by -1/2 $\hbar\omega_0$ and n starts from 1, instead of 0, so that

$$E_n = n\hbar\omega_0$$

Describe the energy of *i*th oscillator is in the n_ith energy level

$$E_{n_i} = n_i\hbar\omega_0$$

The total energy of the N oscillators in a system is

$$E = \sum_{i=1}^{N} n_i\hbar\omega_0 = M\hbar\omega_0 \ \ where\ M = \sum_{i=1}^{N} n_i$$

(=Sum of the quantum numbers of all N oscillators in the system)

Suppose that N=10 and M=50, average energy becomes:

$$\bar{E} = \frac{E}{N} = \frac{50\hbar\omega_0}{10} = 5\hbar\omega_0$$

Using the exact mathematics,

Number of ways N integers can add to M $= \frac{(M+N-1)!}{M!(N-1)!} = \binom{M+N-1}{M}$

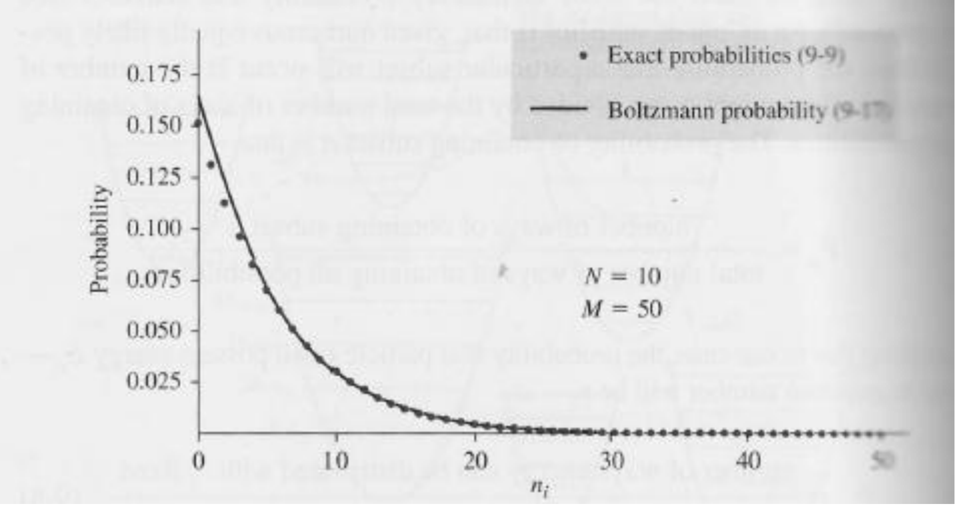
For the ith oscillator to have a fixed energy of E_{n_i}, is the same as N-1 oscillators to add to the (M-n_i),

$$P_{n_i} = \binom{(M-n_i)+N-1}{(M-n_i)} \Big/ \binom{M+N-1}{M}$$

If you draw $P_{n_i}$for N=10 and M=50, then you get the following graph:

$$\binom{N}{N_R} = \frac{N!}{N_R!\,(N-N_R)!}$$

Figure 9.6 Probabilities of a given oscillator being in its n_i state, and Bolt probability.



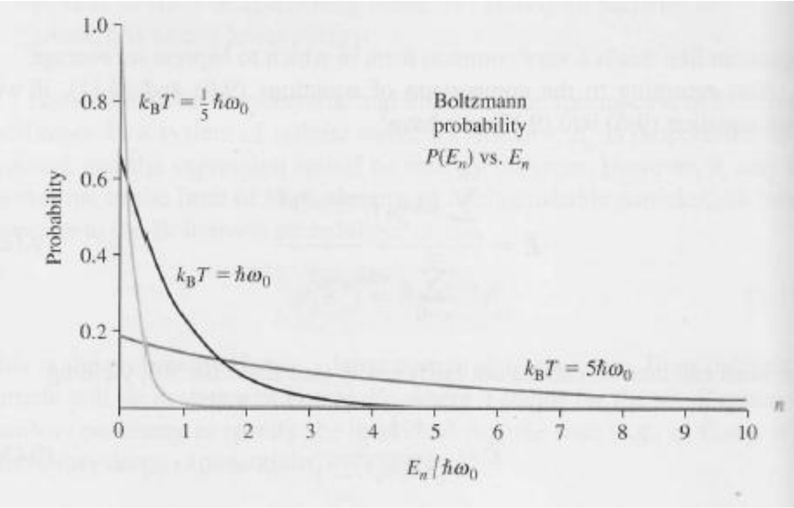
Note that the probability of getting higher energy ($E_{n_i} = n_i\hbar\omega_0$) becomes very small.

Using the Bolzman probability for harmonic oscillators: $E_n = n\hbar\omega_0$

$$P(E_n) = \frac{e^{-\frac{n\hbar\omega_0}{k_BT}}}{\sum_n e^{-\frac{n\hbar\omega_0}{k_BT}}}$$

$\bar{E} = \sum E_n P(E_n) = \frac{\sum_n n\hbar\omega_0 e^{-\frac{n\hbar\omega_0}{k_BT}}}{\sum_n e^{-\frac{n\hbar\omega_0}{k_BT}}} = \frac{\hbar\omega_0}{e^{\frac{n\hbar\omega_0}{k_BT}}-1}$ Since $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$; $\sum_{n=0}^{\infty} nx^n = \frac{x}{(1-x)^2}$

Note that the Boltzman probability decreases as En gets higher. As temperature decreases, the probability of oscillators to have lower energy levels increases.



Density of states when energy is closely spaced:

$$E = n\hbar\omega_0$$

$$n = \frac{E}{\hbar\omega_0}$$
$$dn = \frac{dE}{\hbar\omega_0}$$

Density of states becomes $\frac{dn}{dE} = D(E) = \frac{1}{\hbar\omega_0}$

$$\bar{E} = \frac{\int E\,\mathcal{N}(E)D(E)dE}{\int \mathcal{N}(E)D(E)dE} = \frac{\int E\;NAe^{-E/k_BT}1/\hbar\omega_0 dE}{\int NAe^{-E/k_BT}1/\hbar\omega_0 dE} = k_BT$$

Since $\int_0^\infty x^m e^{-bx}dx = \frac{m!}{b^{m+1}}$

We can obtain the same result from the summation notation on the previous page when energy level gets very close $\hbar\omega_0 \to 0$

Then, $\bar{E} = \frac{\hbar\omega_0}{e^{\frac{\hbar\omega_0}{k_BT}}-1} = \frac{\hbar\omega_0}{1+\frac{\hbar\omega_0}{k_BT}-1} = k_BT$

Since $e^x = 1 + x + x^2 + \cdots \qquad when\ x\ is\ small$

Probability Distributions: Maxwell-Boltzman, Fermi-Dirac, Bose-Einstein

Three different types of distributions

Consider that *k* energy states in an increasing order are available for the particles to occupy and $\mathcal{N}(E_i)$ represents the number of particles occupying the *i*th energy state. All systems should satisfy two conditions:

- Conservation of particles: $\sum \mathcal{N}(E_i) = \mathcal{N}(E_1) + \mathcal{N}(E_2) + \cdots + \mathcal{N}(E_k) = N$
- Conservation of energy: $\sum \mathcal{N}(E_i)E_i = \mathcal{N}(E_1)E_1 + \mathcal{N}(E_2)E_2 + \cdots + \mathcal{N}(E_k)E_k = E$

In order to compare differences among three types of probability distributions, consider systems of four harmonic oscillators where $E_i = n_i\hbar\omega_0$ and n_i represents a quantum number associated with the energy state of the *i*th particle, which starts from 0, 1,…).

Consider the total energy of the system is $2\hbar\omega_0$. Where $\omega_0 \equiv \sqrt{\frac{k}{m}}$

First, when the particles (so we label particles a, b, c, d) are classical, which means they are distinguishable.

- Conservation of particles: the total number of particles is 4.
  Conservation of energy can be rewritten in terms of quantum numbers associated with the four particles: $n_a + n_b + n_c + n_d = 2$

Ways of distributing $2\hbar\omega_0$over four distinguishable particles:

n	10 possible ways										No. of possibilities where a particle can have n quantum number (#)	Probability of a particle having the n quantum number (P=#/40)	Probable number of particles to have the n quantum number P x 4
2	*a*	*b*	*c*	*d*							4	0.1	0.4
1					*ab*	*ac*	*ad*	*bc*	*bd*	*cd*	12	0.3	1.2
0	*bcd*	*acd*	*abd*	*abc*	*cd*	*bd*	*bc*	*ad*	*ac*	*ab*	24	0.6	2.4
										Total	40	1.0	4.0

If the four particles are BOSONs that can occupy the same quantum energy state and are indistinguishable from each other, then there are only two possible ways since ways 1 to 4 are the same and ways 5 to 10 are the same:

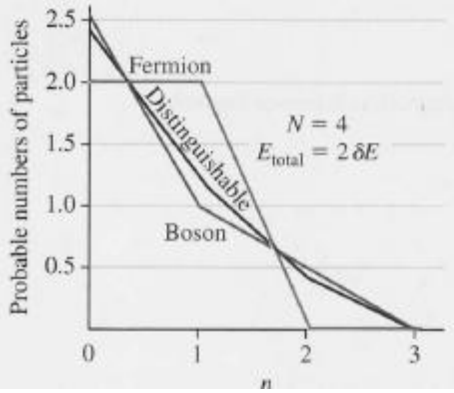
n	Two possible ways		(#)	(P=#/8)	P x 4
2	X		1	0.125	0.50
1		XX	2	0.250	1.00
0	XXX	XX	5	0.625	2.50
		Total	8	1.000	4.00

If the four particles are FERMIONs, then more than two particles cannot occupy the same quantum energy state. There is only one possible way:

n	1 possible way	(#)	(P=#/8)	P x 4
2		0	0.0	0.0
1	XX	2	0.5	2.0
0	XX	2	0.5	2.0
	Total	4	1.0	4.0

- In all three types of distributions, the probable number of particles in a given state decreases with increasing energy.
- Bosons like to be in the ground state more than the classical particles and Fermions less like to be in the ground state. Compare probable number for the ground state (Fermion,2.0) < (Classical, 2.4) < (Boson, 2.5)
- If we draw a graph for the probable number over *n*:

Figure 9.9 The probable number of particles at the allowed energies depends on whether the particles are bosons, fermions, or distinguishable.

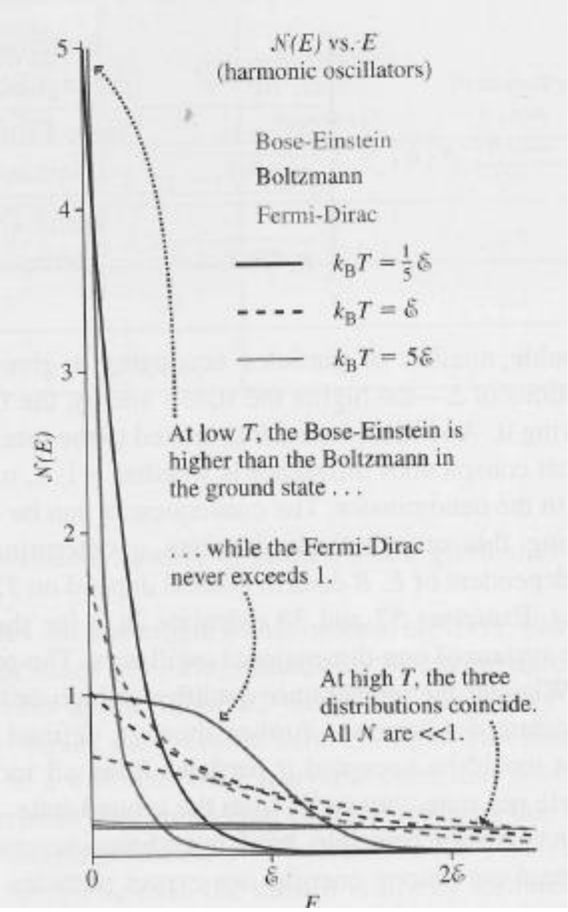


How do Boltzman, Bose-Einstein, and Fermi-Dirac distributions compare?

When N is large, the exact statistical probability calculations can be replaced with the three types of probability distributions depending upon the type of particles in a system.

Distribution	Occupation index	Particles	Identical particles?	Spin	Distinguishable?	Exclusion principle?	Examples
Boltzman	$\frac{1}{Be^{E/k_BT}}$	Classical	Yes	Any spin	Yes	No	Gas molecules
Bose-Einstein	$\frac{1}{Be^{E/k_BT}-1}$	Bosons	Yes	0 or integer spin	No	No	Photons in blackbody radiation
Fermi-Dirac	$\frac{1}{Be^{E/k_BT}+1}$	Fermions	Yes	1/2	No	Yes	Electrons in semiconductors

- In all three probability distributions, the probability of a particle occupying higher E state decreases.
- If k_BT is larger than an energy state, particles tend to diffuse and probability of particles occupying the same energy state decreases. See the graph when k_BT= 5E. There are almost no distinctions among the three types of distributions.
- If k_BT is smaller than an energy state, particles tend to pile up according to the rules allowed for the particular type of particles. See when $k_BT = \frac{1}{5}E$. Fermions the occupation number never exceeds 1. At low temperatures, bosons tend to congregate in the lowest-energy individual-particle state, while fermions tend to fill states, one particle per state, upto the some maximum energy.



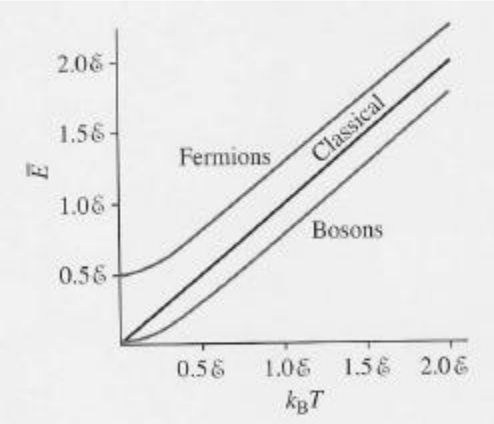
At low T, the Bose-Einstein is higher than the Boltzmann in the ground state . . .

. . . while the Fermi-Dirac never exceeds 1.

At high T, the three distributions coincide. All $\mathcal{N}$ are <<1.

(occupation number vs. E)

(Average energy vs. temperature)



- **At high temperatures (**$k_BT \gg E$**)**, both bosons and fermions follow the linear relationship of $\bar{E} = k_BT$, the same as the classical result. Still, energy is somewhat lower for bosons and higher for Fermions.

- **At low temperatures ($k_B T \ll E$)**, fermions’ energy falls to ½ E while bosons and classical particles fall to zero.

Fermi Energy

- At low temperatures, the Fermi-Dirac occupation number is nearly 1 to a certain energy, then drops zero suddenly. This energy is known as Fermi energy below which all the energy levels are filled up with fermions without vacancy at T=0. Mathematically, Fermi energy is defined as the energy of which occupation number becomes ½
  $\mathcal{N}(E_F) = \frac{1}{Be^{E/k_BT}+1} = \frac{1}{2}$ which makes $B = e^{-\frac{E_F}{k_BT}}$
  $$\mathcal{N}(E_F) = \frac{1}{e^{(E-E_F)/k_BT}+1}$$
- $k_B T(when\ T = 300K, room\ temperature)$
  $$= \left(1.38\text{x}10^{-23}\frac{J}{K}\right)(300K) = 4.14 \text{ x } 10^{-21} J = 0.026\ eV$$
- Occupation number vs. Energy: E_F can change according to temperature. However, E_F can be considered nearly constant in most daily applications.