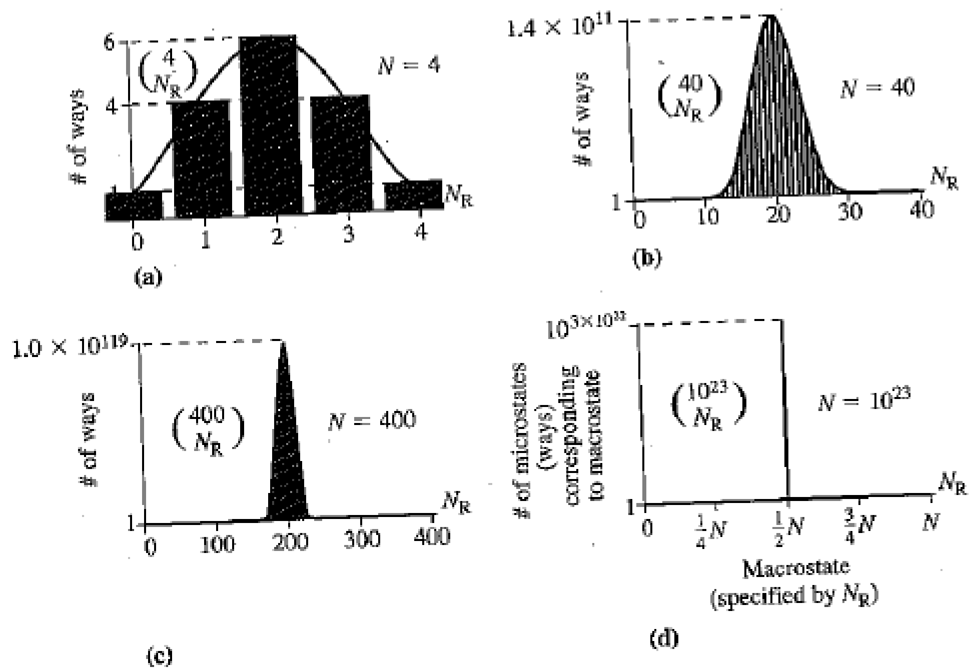
PH102, 2012W, Lecture Notes: February 3, Fri, Class 11

Statistical Mechanics: Classical-Boltzman Distribution

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.

Three different types of distributions

Distribution	Occupation index	Particles	Identical particles?	Spin	Distingui-shable?	Exclusion principle?	Examples
Boltzman	$\frac{1}{Be^{E/k_BT}}$	Classical	Yes	Any spin	Yes	No	Gas molecules that are sufficiently widely separated not to share the same space
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

Boltzman Distribution

- Boltzman probability: The probability of an individual particle will be in state *n* associated with E_n

$$P(E_n) = A\, e^{-\frac{E_n}{k_BT}}$$

Where *n* stands for the set of quantum numbers necessary to specify the individual-particle state.

- $k_BT(when\ T = 300K, room\ temperature) = \left(\frac{1.38x10^{-23}J}{K}\right)(300K) - 4.14 \text{ x } 10^{-21}J = 0.026\ eV$
- 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:

$$\sum\ P(E_n) = \sum_n A\, e^{-\frac{E_n}{k_BT}} = 1 \rightarrow A = \frac{1}{\sum_n e^{-\frac{E_n}{k_BT}}}$$

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

- Average Energy $\bar{E}$

$$\bar{E} = \sum E_n\, P(E_n) = \frac{\sum_n E_n\, e^{-\frac{E_n}{k_BT}}}{\sum_n e^{-\frac{E_n}{k_BT}}}$$

- 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 $D(E) \equiv \frac{Differential\ number\ of\ states\ within\ range\ of\ dE\ of\ E}{dE}$

$$\bar{E} = \frac{\int E\, \mathcal{N}(E) D(E) dE}{\int \mathcal{N}(E) D(E) dE}$$

One dimensional Harmonic Oscillator Example

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

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega_0$$

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

Let's shift the Energy by -1/2 $\hbar\omega_0$ so that

$$E_n = n\hbar\omega_0$$

Describe the energy of ith 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:

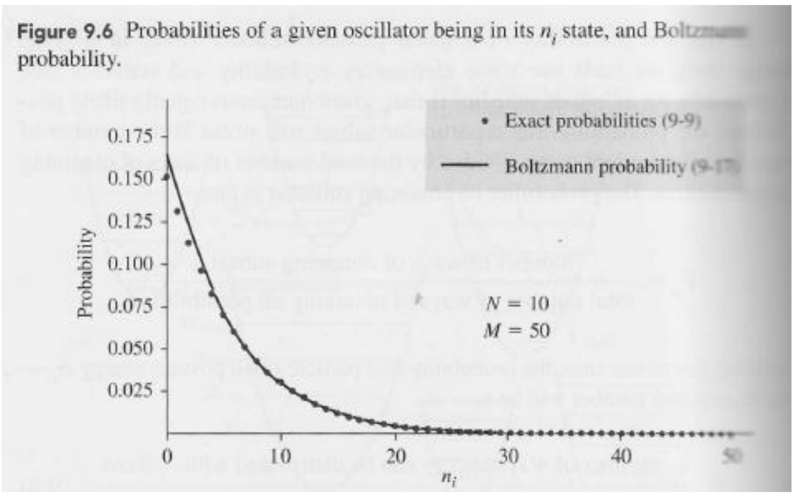


Figure 9.6 Probabilities of a given oscillator being in its n_i state, and Boltzmann probability.

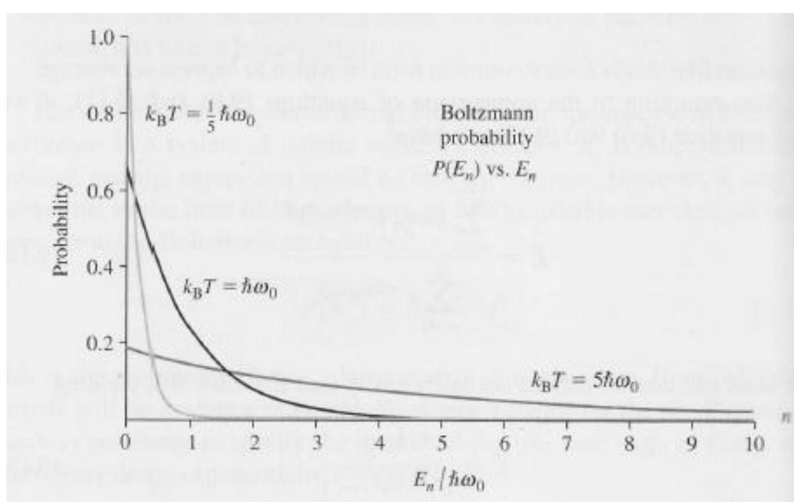
Note that the probability of getting higher energy ($E_{n_i} = n_i \hbar\omega_0$) becomes very small.

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

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

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

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 this from the summation notation when energy level gets very close $\hbar\omega_0 \rightarrow 0$

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