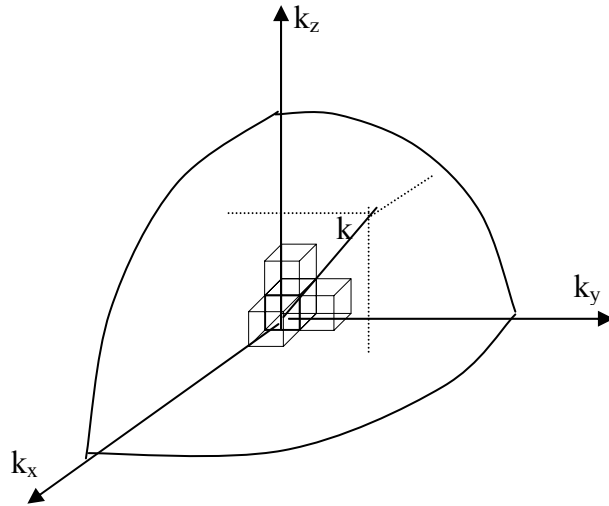


2.57 Nano-to-Macro Transport Processes
Fall 2004
Lecture 10

Review on previous lectures



In above figure, we can find the volume of one state is $V_1 = (2\pi/L)^3$. In the sphere, the number of states within k and $k+dk$ is

$$\Delta N = \frac{4\pi k^2 \Delta k}{V_1} = \frac{V k^2 \Delta k}{(2\pi)^3},$$

in which $V=L^3$ is the crystal volume.

The density of states is defined as the number of quantum states per unit interval of energy and per unit volume

$$D(E) = \frac{1}{V} \frac{\Delta N}{\Delta E} = \frac{k^2}{2\pi^2} \frac{\Delta k}{\Delta E} = \frac{k^2}{2\pi^2} \frac{dk}{dE}.$$

A factor that considers polarization of waves may be added (electron, spin up and down, thus a factor of 2, photon, two polarizations, phonons, 3 polarizations)

For an energy level E_i , the Boltzmann factor for its occupying probability is

$$P(E_i) = A \exp(-E_i / k_B T),$$

in which the constant A can be determined by normalization over all quantum states

$$\sum_{\text{All QS}} P(E_i) = 1.$$

For an open system exchanging energy with the outside, the probability becomes

$$P(E_i, N_i) = A \exp[-(E_i - \mu N_i) / k_B T],$$

where N_i is the particle number, chemical potential μ is the criteria for the equilibrium state of mass exchanging process with the outside, just as pressure for mechanical equilibrium and temperature for thermal equilibrium.

For electrons at a quantum state with energy E , the Fermi-Dirac distribution gives the average number of electrons as

$$\langle n \rangle = f(E) = \frac{1}{1 + e^{(E_i - \mu)/k_B T}}.$$

For phonons, the Pauli exclusion principle is no longer applicable. And the occupancy of the quantum state is changed into

$$\langle n \rangle = f(\nu) = \frac{1}{e^{h\nu/k_B T} - 1},$$

which is called Bose-Einstein distribution.

For molecules, similar results exist

$$\langle n \rangle = f(E) = \frac{1}{e^{(E_i - \mu)/k_B T} - 1},$$

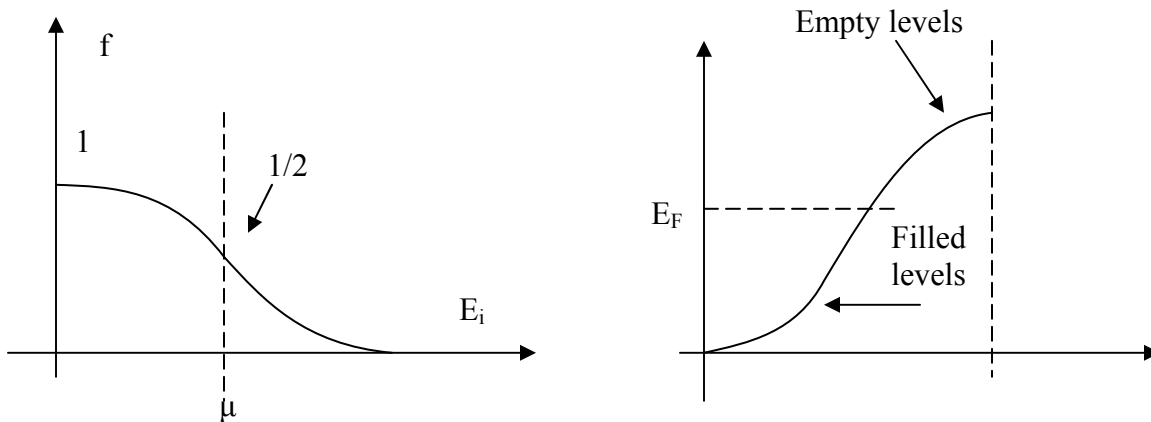
where μ is again the chemical potential of the boson gas.

The Bose-Einstein distribution changes the “plus one” in the denominator of the Fermi-Dirac distribution into minus one. When $E - \mu \gg k_B T$, we can ignore the ± 1 term in the denominator. Both distributions reduce to the Boltzmann distribution function,

$$f(E, T, \mu) = \exp\left(-\frac{E - \mu}{k_B T}\right) \text{ or } f(E, T) = \exp\left(-\frac{E}{k_B T}\right).$$

For high temperatures, the energy separation is so small that we should still use the “classic” Boltzmann distribution function.

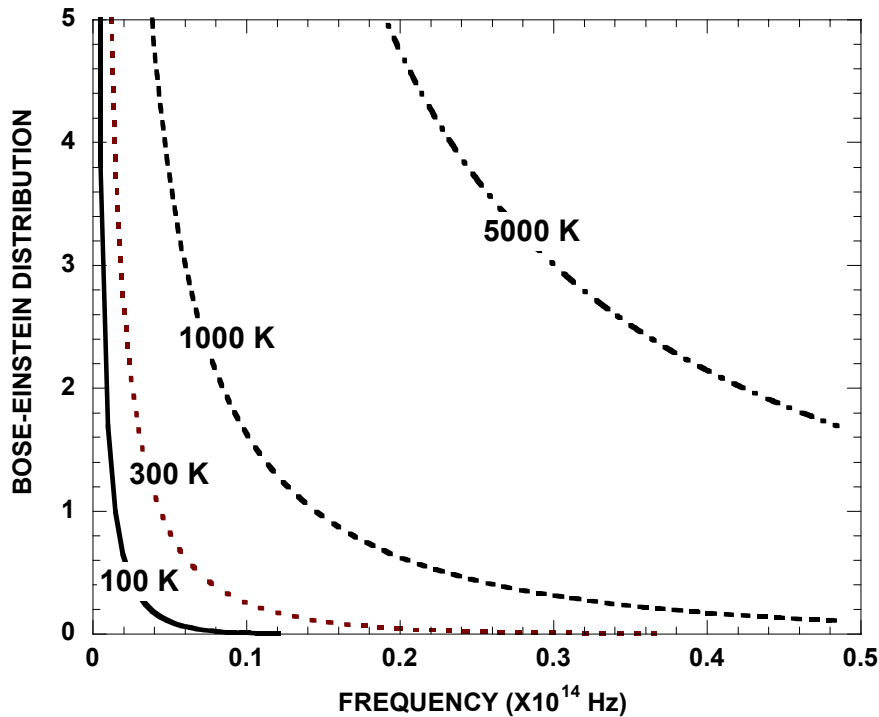
In the following figure, the Fermi-Dirac distribution is drawn. At $T=0$ K, we have $E_F = \mu$. From the right figure, we can see that electrons close to the Fermi level can be affected by the increased temperature. Only these electrons contribute to the electricity conduction.



For electrons in a box (with constraints in three dimensions), the quantized energy levels are

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2); k_x, k_y, k_z = 2\pi n / L.$$

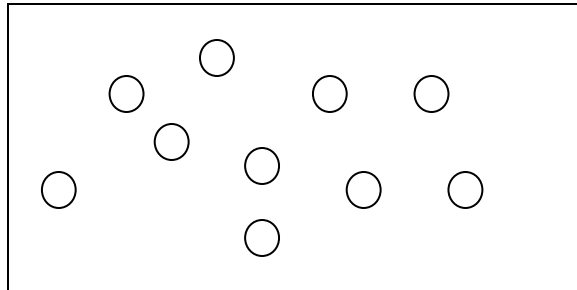
The Bose-Einstein distribution is presented in the following figure according to the temperature. For constrained electrons, we can find that the ground state (quantum numbers $n=l=i=1$) has much larger occupancy than any other energy level. This is more apparent at lower temperatures. Therefore, most molecules will go to the ground state when the temperature approaches 0 K. The phenomenon is called the Bose-Einstein condensation. The experimental work in dilute gases of alkali atoms earned Professor Ketterle a Nobel Prize in 2001.



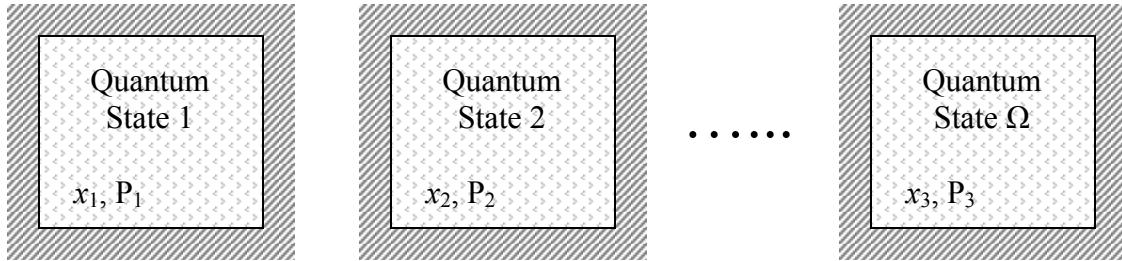
Consider particles in an isolated system. For statistics, we normally calculate the time average value

$$\bar{x} = \frac{1}{T} \int_0^T x(t) dt.$$

However, this is impractical when the particle number is very big. To simplify, we focus on the probability of a system to be at a specific accessible quantum state.



Suppose we have Ω quantum states. We can treat each accessible quantum state as a system. The collection of these Ω systems is called an ensemble. Three ensembles are analyzed in the table.



Microcanonical ensemble	Canonical ensemble	Grand canonical
<p>U, V, N fixed Isolated systems</p> <p>Principle of equal probability: $P_i = 1/\Omega$ Boltzmann principle gives $S = k_B \ln \Omega = S(U, V, N)$ The entropy S is additive.</p> <p>$dU = TdS - pdV + \mu dN$ $dS = \left(\frac{\partial S}{\partial U}\right)_{V,N} dU + \left(\frac{\partial S}{\partial V}\right)_{U,N} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$</p> <p>If we know the function S(U,V,N) [or U(S,V,N)], we can determine all other thermodynamic state variables. The function S(U,V,N) is called a thermodynamic potential.</p>	<p>V, N, T fixed In contact with a thermal reservoir; isothermal.</p> <p>Since the reservoir also has many quantum states, a quantum state of one system can correspond to different number of real quantum states. The principle of equal probability is no longer valid. The probability becomes</p> <p>$P(E_i) = \frac{e^{-E_i/k_B T}}{Z}$ $Z = \sum_i e^{-E_i/k_B T}$</p> <p>The Helmholtz free energy $F = U - TS$ $= F(T, V, N)$ $= -k_B T \ln Z$ becomes the thermal potential in this case.</p>	<p>V, μ, T fixed Open, isothermal system. Exchanging both energy and particles with the reservoir.</p> <p>$P(E_i, N_i) = \frac{e^{-(E_i - \mu N_i)/k_B T}}{Z}$ The numerator is the Gibbs factor and $Z = \sum_{E_i} \sum_{N_i} e^{-(E_i - \mu N_i)/k_B T}$.</p> <p>The grand canonical potential is $G(T, V, \mu)$ $= U - TS - \mu N$ $= -k_B T \ln Z$</p> <p>Note: G is not Gibbs energy.</p>

Denote P as the probability of a quantum state. A fundamental assumption made in statistical mechanics is that the ensemble average of an observed quantity is equal to the time average of the same quantity, i.e.

$$\bar{x} = \langle x \rangle = \sum_{i=1}^{\Omega} P_i x_i,$$

which is called the **ergodic hypothesis**.

Internal energy and specific heat

For a constrained particle, its energy is expressed as

$$E = \frac{\hbar^2}{2m} (k_x^2 + k_y^2 + k_z^2),$$

where $k_x = \pm 2\pi i / L, k_y = \pm 2\pi j / L, k_z = \pm 2\pi n / L$ ($n, j, l=1,2,\dots$). The internal energy is

$$\begin{aligned} u_1 &= \langle E_1 \rangle \\ &= \frac{\sum_{k_x} \sum_{k_y} \sum_{k_z} E(k_x, k_y, k_z) \exp\left(-\frac{E - \mu}{k_B T}\right)}{\sum_{k_x} \sum_{k_y} \sum_{k_z} \exp\left(-\frac{E}{k_B T}\right)}, \end{aligned}$$

If the energy separation is very small (quasi-continuous), we can evaluate Z by integration instead of discrete summation, i.e.

$$\begin{aligned} Z &= \sum_{k_x} \sum_{k_y} \sum_{k_z} \exp\left(-\frac{E}{k_B T}\right) \\ &= \int_0^{\infty} e^{-E/k_B T} D(E) dE \\ &= \int_0^{\infty} e^{-E/k_B T} \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \sqrt{E} dE \\ &= \frac{V}{\lambda^3}, \end{aligned}$$

where the thermal de Broglie wavelength is $\lambda = \sqrt{\frac{\hbar^2}{2\pi m k_B T}}$.

Let $y = \frac{1}{k_B T}$. The energy expression can be rewritten as

$$\langle E_1 \rangle = \frac{1}{Z} \frac{\partial Z}{\partial y} = -\frac{d}{dy} \ln Z = \frac{3}{2} k_B T,$$

which is just the familiar energy expression. It is also a special case of the **equipartition** theorem, which states that at high temperature every degree of freedom with a quadratic energy term contributes $k_B T/2$ to the average energy of the system.

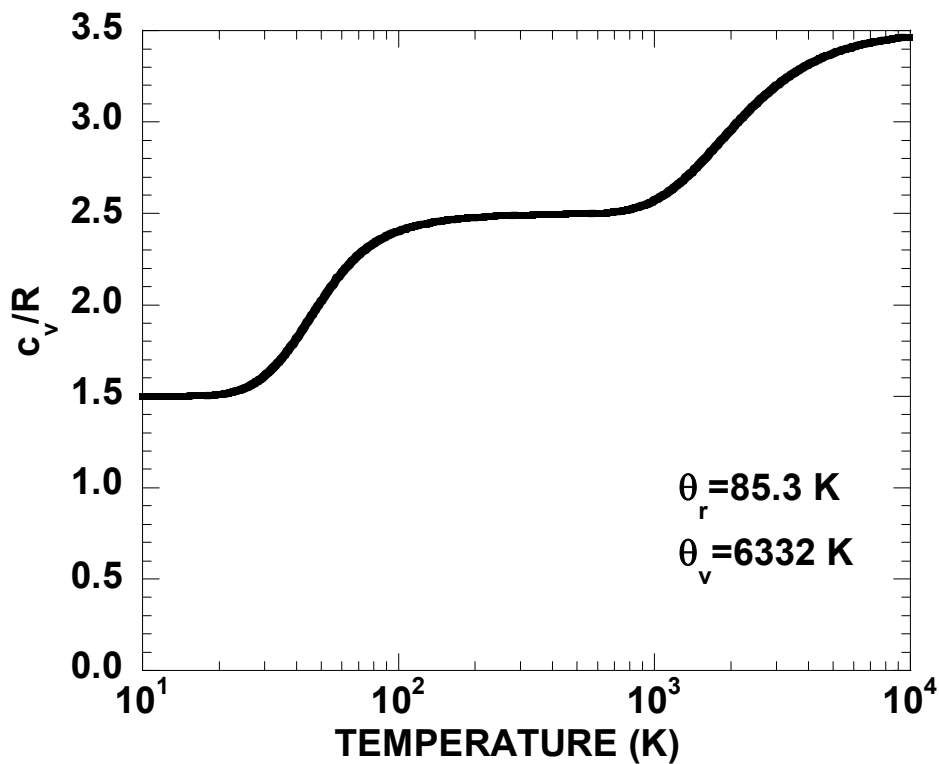
The internal energy is

$$u = \frac{3}{2} k_B N_A T = \frac{3}{2} R_u T,$$

in which R_u is the universal gas constant. The specific heat is

$$C_V = \frac{\partial u}{\partial T} = \frac{3}{2} R_u.$$

In the following figure we draw the specific heat of hydrogen gas. At low temperatures, only the translational energy levels are fully excited and the specific heat is $3R_u/2$. As the temperature increases, the rotational energy levels start to be excited and contribute to the specific heat to a maximum of R such that the total specific heat reaches $5R_u/2$. At even higher temperatures, the vibrational energy levels start contributing to the specific heat that approaches a final value of $7R_u/2$.



For photons, we have

$$\langle n \rangle = f(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1}.$$

The internal energy is

$$u = \sum_{k_x} \sum_{k_y} \sum_{k_z} \hbar\omega f(\omega) = \int_0^\infty \hbar\omega f(\omega) D(\omega) d\omega,$$

where the density of states (two transverse electromagnetic waves) is

$$D(\omega) = 2 \times \frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3 d\omega} = \frac{\omega^2}{\pi^2 c^3}; \omega = ck \text{ for light.}$$