6.730 Physics for Solid State Applications

Lecture 25: Chemical Potential and Equilibrium

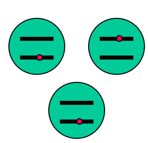
Outline

- Microstates and Counting
- System and Reservoir Microstates
- Constants in Equilibrium
  - Temperature & Chemical Potential
- Fermions and Bosons

April 7, 2004

Microstates and Counting

Ensemble of 3 ‘2-level’ Systems



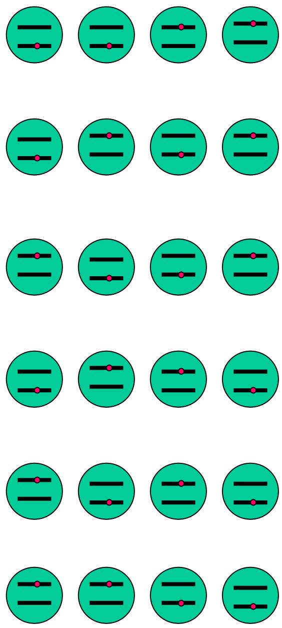
Total Energy	# of Microstates
E=0	g=1
E=1	g=3
E=2	g=3
E=3	g=1

As we shall see, g is related to the entropy of the system…

Microstates and Counting

Ensemble of 4 '2-level' Systems

E=2



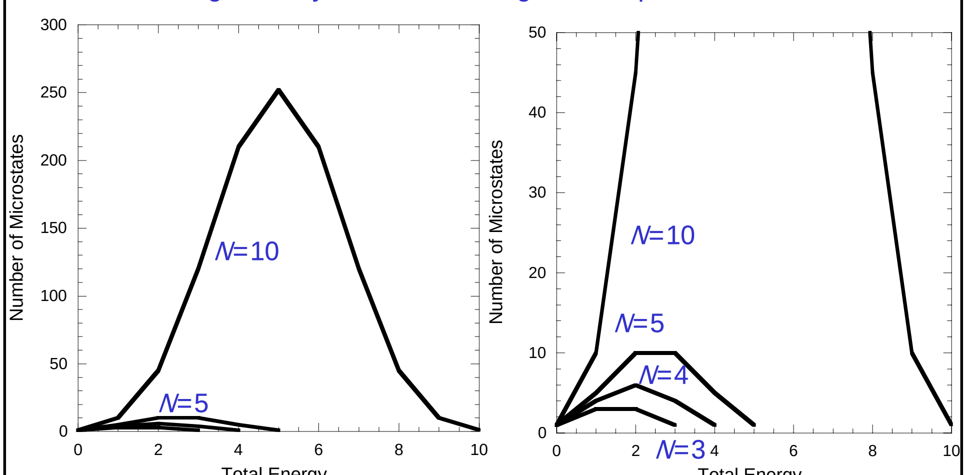
Total Energy	# of Microstates
E=0	g=1
E=1	g=4
E=2	g=6
E=3	g=4
E=4	g=1

E=2

$$g = \frac{4!}{2!(4-2)!} = \frac{24}{2 \cdot 2} = 6$$

Microstates and Counting

The larger the systems, the stronger the dependence on *E*

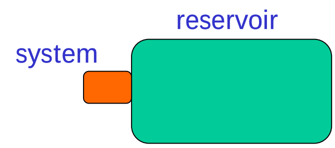


For most mesoscopic and macroscopic systems, *g* is a monotonically increasing function of *E*

System + Reservoir Microstates

Gibb's Postulate = all microstates are equally likely

$$\boxed{g(E_T) = \sum_{E_s} g_S(E_s)\, g_R(E_T - E_s)}$$



Example

$$g(E_T = 2) = g_S(2)\, g_R(0) + g_S(1)\, g_R(1) + g_S(0)\, g_R(2)$$

Consider a system of **3** '2-levels' + a reservoir of **10** '2-levels'

$$g(E_T = 2) = 3 \cdot 1 + 3 \cdot 10 + 1 \cdot 45 = 78$$

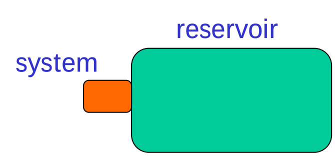
Probability of finding: $E_s = 0$ 45/78 ← Most likely mircostate of S&R

$E_s = 1$ 30/78

$E_s = 2$ 3/78

Most electrons are in the ground state so reservoir entropy is maximized !

System + Reservoir Microstates



$$g(E_T) = \sum_{E_s} g_S(E_s)\, g_R(E_T - E_s)$$

For sufficiently large reservoirs….

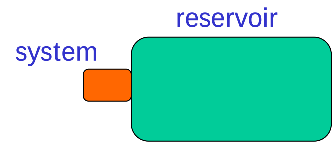
$$g(E_T) = \sum_{E_s} g_S(E_s)\, g_R(E_T - E_s) \approx g_S(E_s)\, g_R(E_T - E_s)\,|_{\max}$$

...we only care about the most likely microstate for S+R

Now we have a tool to look at equilibrium...

System + Reservoir in Equilibrium

$$g(E_T) \approx g_S(E_s)\, g_R(E_T - E_s)\,|_{\max}$$



Equilibrium is when we are sitting in this max entropy (*g*) state…

$$dg = g_S \frac{\partial g_R}{\partial E_R} dE_R + g_R \frac{\partial g_S}{\partial E_S} dE_S = 0$$

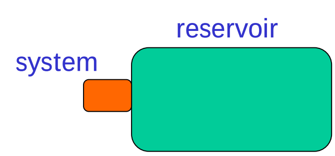
$$E_T = E_S + E_R$$

$$dE_T = dE_S + dE_R = 0 \implies dE_S = -dE_R$$

$$\boxed{\frac{\partial \ln g_R}{\partial E_R} = \frac{\partial \ln g_S}{\partial E_S}}$$ is the same for two systems in equilibrium

System + Reservoir in Equilibrium

$$g(E_T) \approx g_S(E_s)\, g_R(E_T - E_s)\,|_{\max}$$



$$\frac{\partial \ln g_R}{\partial E_R} = \frac{\partial \ln g_S}{\partial E_S}$$

We observe that two systems in equilibrium have the same temperature, so we hypothesize that…

$$\frac{1}{T} \equiv k_B \frac{\partial \ln g_R}{\partial E_R} = k_B \frac{\partial \ln g_S}{\partial E_S}$$

This microscopic definition of temperature is a central result of stat. mech.

Boltzmann Distributions

$$\frac{1}{T} \equiv \frac{\partial \ln g_R}{\partial E_R} = \frac{\partial \ln g_S}{\partial E_S}$$

S is the thermodynamic entropy of a system

Boltzmann observed that...

$$S_T = S_R + S_S \quad \text{and} \quad g_T = g_R g_S$$

...so he hypothesized that

$$S = k_B \ln g \implies \frac{1}{T} \equiv \frac{1}{k_B}\frac{\partial S_R}{\partial E_R} = \frac{1}{k_B}\frac{\partial S_S}{\partial E_S}$$

$$\implies g = e^{S/k_B}$$

Boltzmann Distributions

$$\frac{P(E_j)}{P(E_k)} \approx \frac{g_S(E_j)\, g_R(E_T - E_j)}{g_S(E_k)\, g_R(E_T - E_k)} \approx \frac{g_R(E_T - E_j)}{g_R(E_T - E_k)}$$

reservoir controls system distribution (to logarithmic accuracy)

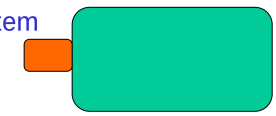
use $g = e^{S/k_B}$

$$= \exp\left(\frac{S(E_T - E_j) - S(E_T - E_k)}{k_B}\right) = \exp\left(\frac{-(E_j - E_k)}{k_B}\frac{\partial S}{\partial E}|_{E_T}\right)$$

$$= \exp\left(\frac{-(E_j - E_k)}{k_B T}\right)$$

System + Reservoir in Equilibrium

Now we allow system and reservoir to
exchange particles as well as energy...



$$E_T = E_S + E_R$$

$$N_T = N_S + N_R$$

$$\frac{P(N_j, E_j)}{P(N_k, E_k)} \approx \frac{g_R(N_T - Nj, E_T - E_j)}{g_R(N_T - N_k, E_T - E_k)}$$

$$= \exp\left(\frac{S_R(N_T - N_j, E_T - E_j) - S_R(N_T - N_k, E_T - E_k)}{k_B}\right)$$

System + Reservoir in Equilibrium

$$\frac{P(N_j, E_j)}{P(N_k, E_k)} = \exp\left(\frac{S_R(N_T - N_j, E_T - E_j) - S_R(N_T - N_k, E_T - E_k)}{k_B}\right)$$

$$= \exp\left(\frac{\Delta S_R}{k_B}\right)$$

Entropy of reservoir can be expanded for each case...

$$S_R(N_T - N_k, E_T - E_k) = S_R(N_T, E_T) - N_k \left(\frac{\partial S}{\partial N}\right)_{N_T} - E_k \left(\frac{\partial S}{\partial E}\right)_{E_T}$$

Difference in entropy of the two configurations is...

$$\Delta S_R = -(N_j - N_k) \underbrace{\left(\frac{\partial S}{\partial N}\right)_{N_T}}_{-\frac{\mu}{T}} - (E_j - E_k) \underbrace{\left(\frac{\partial S}{\partial E}\right)_{E_T}}_{\frac{1}{T}}$$

..where μ is the electrochemical potential

System + Reservoir in Equilibrium

$$dS = \left(\frac{\partial S}{\partial N}\right)_E dN + \left(\frac{\partial S}{\partial E}\right)_N dE$$

If dS = 0, that is S is held constant, then

$$0 = \left(\frac{\partial S}{\partial N}\right)_E dN + \left(\frac{\partial S}{\partial E}\right)_N dE$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{E_T}$$

$$\frac{-\mu}{T} \equiv \left(\frac{\partial S}{\partial N}\right)_{N_T}$$

So that

$$\left(\frac{\partial E}{\partial N}\right)_S = -\left(\frac{\partial S}{\partial N}\right)_E \Big/ \left(\frac{\partial S}{\partial E}\right)_N$$

$$\Rightarrow \quad \mu = \left(\frac{\partial E}{\partial N}\right)_S$$

Chemical potential is change in energy of system if one particle is added without changing entropy

Electrochemical potential

The electrochemical potential, a.k.a, the fermi level is $\mu = \left(\frac{\partial E}{\partial N}\right)_S$

The energy can be divided into two parts if the particle has charge

$$E = E_{\text{orbital,nocharge}} + E_{\text{electrostatic,withcharge}}$$

$$\Rightarrow \quad \mu = \left(\frac{\partial E_{\text{orbital}}}{\partial N}\right)_S + \left(\frac{\partial E_{\text{electrostatic}}}{\partial N}\right)_S$$

If the electric field is $\mathbf{E}(r) = -\nabla\phi$

then the change in electrostatic energyis $dE = -e\,\phi\, dN$

$$\Rightarrow \quad \mu = \mu' - e\,\phi(x)$$

Fermi level or the electrochemical potential

the electrochemical potential for an electrically neutral particle

System + Reservoir in Equilibrium

$$dS = \left(\frac{\partial S}{\partial N}\right)_E dN + \left(\frac{\partial S}{\partial E}\right)_N dE$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{E_T} \qquad \frac{-\mu}{T} \equiv \left(\frac{\partial S}{\partial N}\right)_{N_T}$$

$$dS = -\frac{\mu}{T}dN + \frac{1}{T}dE$$

$$\Rightarrow \quad dE = T\,dS + \mu\,dN$$

System + Reservoir in Equilibrium

Example: Fermi-Dirac Statistics

$$\frac{P(N_j, E_j)}{P(N_k, E_k)} = \exp\left((N_j - N_k)\frac{\mu}{k_B T} - (E_j - E_k)\frac{1}{k_B T}\right)$$

Consider that the system is a single energy level which can either be...

occupied: $E_S = E \qquad N_S = 1$

unoccupied: $E_S = 0 \qquad N_S = 0$

$$\frac{P(1,E)}{P(0,0)} = \exp\left(\frac{\mu}{k_B T} - E\frac{1}{k_B T}\right) = \exp\left(\frac{\mu - E}{k_B T}\right)$$

Normalized probability...(for fermions)

$$f(E) = \frac{P(1,E)}{P(0,0) + P(1,E)} = \frac{\exp\left(\frac{\mu - E}{k_B T}\right)}{1 + \exp\left(\frac{\mu - E}{k_B T}\right)} = \frac{1}{1 + \exp\left(\frac{E-\mu}{k_B T}\right)}$$

System + Reservoir in Equilibrium

Example: Bose-Einstein Statistics

$$\frac{P(N_j, E_j)}{P(N_k, E_k)} = \exp\left((N_j - N_k)\frac{\mu}{k_B T} - (E_j - E_k)\frac{1}{k_B T} \right)$$

Consider that the system is a single energy level which can either be...

occupied with n particles: $E_S = NE + \epsilon \qquad N_S = N$

unoccupied: $E_S = 0 \qquad N_S = 0$

$$\frac{P(N, NE)}{P(0,0)} = \exp\left(\frac{N\mu}{k_B T} - NE\frac{1}{k_B T}\right) = \left(\exp\left(\frac{\mu - E}{k_B T}\right)\right)^N$$

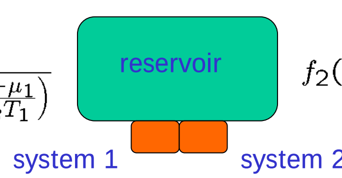
Average number of particles...(for bosons)

$$< N >= \sum_{n=o}^{\infty} n \left(\exp\left(\frac{\mu - E}{k_B T}\right)\right)^n / \sum_{m=o}^{\infty} \left(\exp\left(\frac{\mu - E}{k_B T}\right)\right)^m$$

$$= \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1}$$

Two Systems in Equilibrium

$$f_1(E) = \frac{1}{1 + \exp\left(\frac{E-\mu_1}{k_B T_1}\right)} \qquad f_2(E) = \frac{1}{1 + \exp\left(\frac{E-\mu_2}{k_B T_2}\right)}$$



Particles flow from 1 to 2... $R_{12} \sim \rho_1 f_1 \rho_2 (1 - f_2)$

Particles flow from 2 to 1... $R_{21} \sim \rho_2 f_2 \rho_1 (1 - f_1)$

In equilibrium... $R_{12} = R_{21}$

$$\rho_1 f_1 \rho_2 (1 - f_2) = \rho_2 f_2 \rho_1 (1 - f_1)$$

$$\frac{f_1}{1 - f_1} = \frac{f_2}{1 - f_2}$$

$$\exp\left(\frac{\mu_1 - E}{k_B T_1}\right) = \exp\left(\frac{\mu_2 - E}{k_B T_2}\right)$$

$$\boxed{\begin{array}{c} \mu_1 = \mu_2 \\ T_1 = T_2 \end{array}}$$

Summary

System which can exchange particles and energy with a reservoir

$$S = k_B \ln g \qquad dS = -\frac{\mu}{T} dN + \frac{1}{T} dE$$

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{E_T} \qquad \frac{-\mu}{T} \equiv \left(\frac{\partial S}{\partial N}\right)_{N_T}$$

General Probability Ratio

$$\frac{P(N_j, E_j)}{P(N_k, E_k)} = \exp\left((N_j - N_k)\frac{\mu}{k_B T} - (E_j - E_k)\frac{1}{k_B T}\right)$$

For Fermions $$f(E) = < N >= \frac{1}{1 + \exp\left(\frac{E-\mu}{k_B T}\right)}$$

For Bosons $$< N >= \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1}$$

Summary

System which can exchange only energy with a reservoir,

$$S = k_B \ln g \qquad dS = \frac{1}{T} dE \qquad \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{E_T}$$

General Probability Ratio $$\frac{P(E_j)}{P(E_k)} = \exp\left(-(E_j - E_k)\frac{1}{k_B T}\right)$$

For Fermions $$f(E) = < N >= \frac{1}{1 + \exp\left(\frac{E}{k_B T}\right)}$$

For Bosons $$< N >= \frac{1}{\exp\left(\frac{E}{k_B T}\right) - 1}$$

Looks as if μ=0, but in reality μ never entered the problem!
This is also true if the system can exchange particles, but there is no constraint on the total number of particles; for example, with photons and phonons.

Counting and Fermi Integrals

3-D Conduction Electron Density

$$n = \int_{E_c}^{\infty} 6 g_c(E) f(E) dE \qquad g_c(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\sqrt{E - E_c}$$

$$n = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{E}}{1+\exp\left(\frac{E-\mu}{k_BT}\right)}dE$$

$$= \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2}\int_{E_c}^{\infty}\frac{\sqrt{y}\sqrt{k_BT}}{1+e^{y-v}}\,k_BT dy \qquad y = \frac{E-\mu}{k_BT}$$

$$= \frac{2}{\sqrt{\pi}}2\left(\frac{m^*k_BT}{2\pi\hbar^2}\right)^{3/2}\int_{0}^{\infty}\frac{\sqrt{y}}{1+e^{y-v}}\,dy \qquad v = \frac{\mu - E_c}{k_BT}$$

$$\boxed{n = \frac{2}{\sqrt{\pi}}N_c F_{1/2}\left(\frac{\mu - E_c}{k_BT}\right)}$$

Note: the chemical potential

Specific Heat of Solid

$$C_v = \frac{d}{dT}\sum_{\sigma}\int_{-\infty}^{\infty}\left(\frac{1}{e^{\hbar\omega/k_BT}-1}\hbar\omega + 1/2\right)\, g_\sigma(\omega)\, d\omega$$

$$C_v = \frac{d}{dT}\sum_{\sigma}\int_{-\infty}^{\infty}\frac{\hbar\omega g_\sigma(\omega)d\omega}{e^{\hbar\omega/k_BT}-1}$$

$$C_v = \frac{1}{4k_BT^2}\sum_{\sigma}\int(\hbar\omega)^2 g_\sigma(\omega)\,\mathrm{cosech}^2(\hbar\omega/2k_BT)d\omega$$

Note: no chemical potential