# 6.730 Physics for Solid State Applications

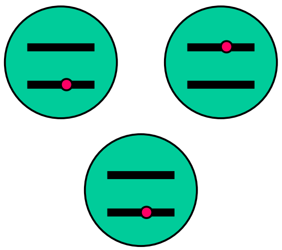
## Lecture 24: Chemical Potential and Equilibrium

### Outline

- Microstates and Counting
- System and Reservoir Microstates
- Constants in Equilibrium
  - Temperature & Chemical Potential
- Fermi Integrals and Approximations

# Microstates and Counting

## Ensemble of 3 '2-level' Systems



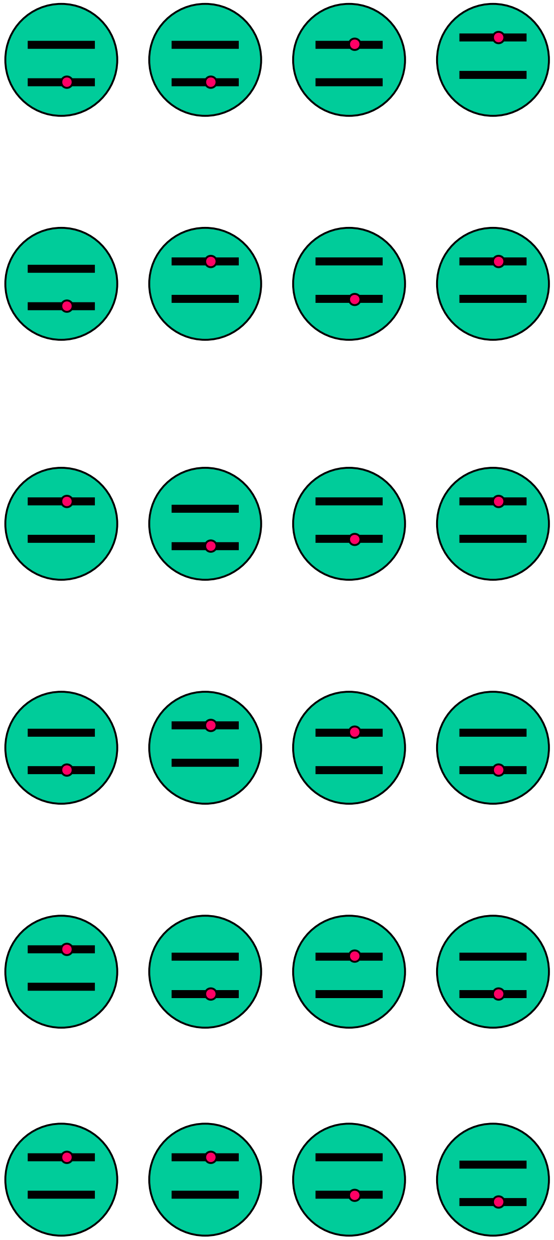
| Total Energy | # of Microstates |
|---|---|
| $E$=0 | $g$=1 |
| $E$=1 | $g$=3 |
| $E$=2 | $g$=3 |
| $E$=3 | $g$=1 |

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

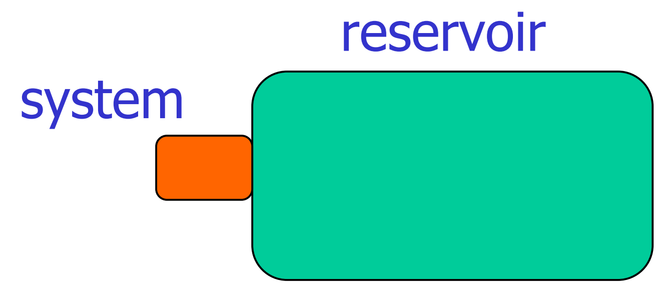
The larger the systems, the stronger the dependence on $E$

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

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




<u>Example</u>

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

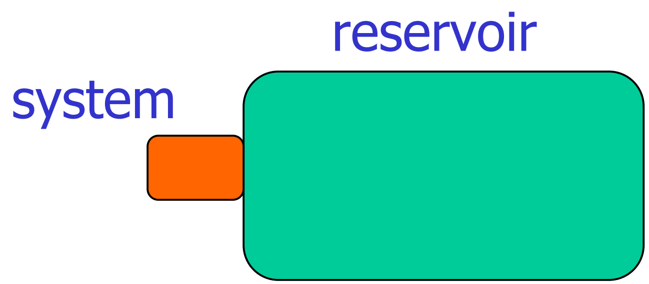
Consider a system of **3** '2-levels' + a reservoir of **10** '2-levels'

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

| | | |
|---|---|---|
| Probability of finding: | $E_s = 0$ | 45/78 |
| | $E_s = 1$ | 30/78 |
| | $E_s = 2$ | 3/78 |

Most electrons are in the ground state so <u>reservoir entropy is maximized</u> !

# System + Reservoir Microstates




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

For sufficiently large reservoirs….

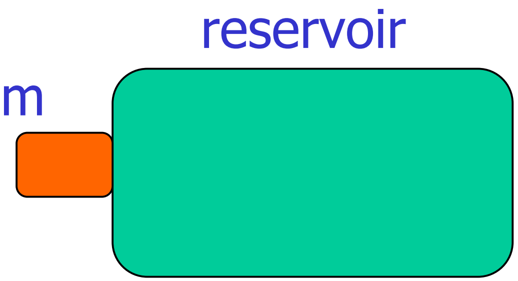
$$g(E_T) = \sum_{E_s} g_S(E_s)\, g_R(E_T - E_s) \approx g_S(E_s)\, g_R(E_T - E_s)\,|_{\text{max}}$$

…we only care about the <u>most</u> 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…

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

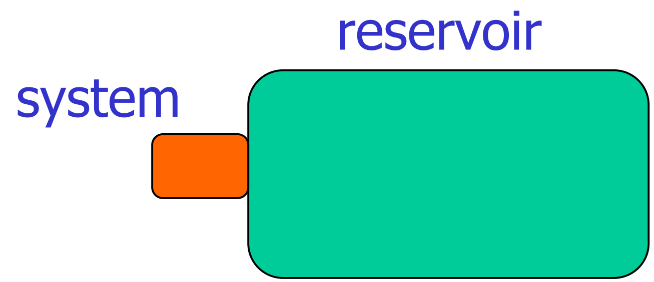
$$E_T = E_S + E_R$$

$$dE_T = dE_S + dE_R = 0 \;\Rightarrow\; dE_S = -dE_R$$

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

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…

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

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

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

# Boltzmann Distributions

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

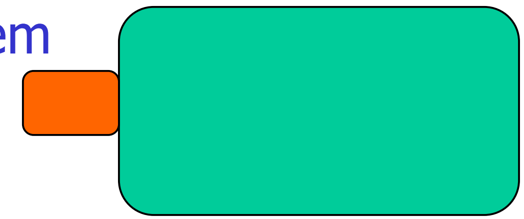
reservoir controls
system distribution

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

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

# System + Reservoir in Equilibrium

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




$$E_T = E_S + E_R$$

$$N_T = N_S + N_R$$

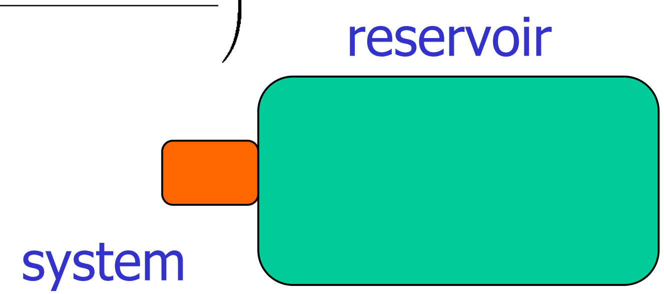
$$\frac{P(N_j, E_j)}{P(N_k, E_k)} \approx \frac{g_R(N_T - Nj, E_T - E_j)}{g_R(N_T - N_k, E_T - E_k)}$$

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

# 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 $\mu$ is the electrochemical potential

# System + Reservoir in Equilibrium

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

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

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

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

# 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: $E_S = E$ $N_S = 1$

unoccupied: $E_S = 0$ $N_S = 0$

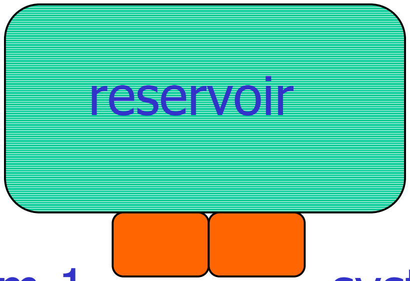
$$\frac{P(1, E)}{P(0, 0)} = \exp\left(\frac{\mu}{k_B T} - E\frac{1}{k_B T}\right) = \exp\left(\frac{\mu - E}{k_B T}\right)$$

Normalized probability…

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

# Two Systems in Equilibrium

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




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

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… $R_{12} = R_{21}$

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

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

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

$$\mu_1 = \mu_2$$

$$T_1 = T_2$$

# Counting and Fermi Integrals

## 3-D Conduction Electron Density

$$N = \int_{E_c}^{\infty} \rho_c(E) f(E) dE$$

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

$$\rho_c(E) = \frac{1}{2\pi^2}\left(\frac{2m^*}{\hbar^2}\right)^{3/2} \sqrt{E - E_c}$$

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

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

$$y = \frac{E - \mu}{k_B T}$$

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

$$v = \frac{\mu - E_c}{k_B T}$$

$$= \frac{2}{\sqrt{\pi}} N_c F_{1/2}$$

# Counting and Fermi Integrals

## 3-D Hole Density

$$P = \int_{-\infty}^{E_v} \rho_v(E)(1 - f(E))dE$$

$$P_{hh} = \frac{2}{\sqrt{\pi}} 2 \left( \frac{m_{hh}^* k_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2}\left( \frac{E_v - \mu}{k_B T} \right)$$

$$P_{lh} = \frac{2}{\sqrt{\pi}} 2 \left( \frac{m_{lh}^* k_B T}{2\pi\hbar^2} \right)^{3/2} F_{1/2}\left( \frac{E_v - \mu}{k_B T} \right)$$

$$m_{hh}^*|_{\mathsf{GaAs}} = 0.51\, m \qquad m_{lh}^*|_{\mathsf{GaAs}} = 0.087\, m$$

$$\frac{P_{lh}}{P_{hh}} = \left( \frac{m_{hh}^*}{m_{lh}^*} \right)^{3/2} \approx \left( \frac{0.51}{0.87} \right)^{3/2} = 13.7$$

$$(m_{\mathsf{eff}}^*)^{3/2} = (m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2}$$

# Counting and Fermi Integrals

## 2-D Conduction Electron Density

$$N = \int_{E_c}^{\infty} \rho_c(E) f(E) dE$$

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

$$\rho_c(E) = \frac{m^*}{\pi \hbar^2 d_x}$$

$$N = \frac{1}{d_x} \sum_{n_x} \frac{m^*}{\pi \hbar^2} \int_{E_{n_x}}^{\infty} \frac{1}{1 + e^{(E-\mu)/k_B T}} dE$$

$$= \frac{k_B T m^*}{\pi \hbar^2 d_x} \sum_{n_x} \ln\left(1 + e^{(\mu - E_{n_x})/k_B T}\right)$$

Exact solution !