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

<table>
<thead>
<tr>
<th>Total Energy</th>
<th># of Microstates</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E=0$</td>
<td>$g=1$</td>
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<tr>
<td>$E=1$</td>
<td>$g=3$</td>
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<tr>
<td>$E=2$</td>
<td>$g=3$</td>
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<td>$g=1$</td>
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As we shall see, $g$ is related to the entropy of the system...
Microstates and Counting

Ensemble of 4 ‘2-level’ Systems

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</tr>
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<td>E=2</td>
<td>g=6</td>
</tr>
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<td>g=4</td>
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</table>

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

\[ g(E_T) = \sum_{E_s} g_S(E_s) g_R(E_T - E_s) \]

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:

- \( E_s = 0 \) : \( \frac{45}{78} \)
- \( E_s = 1 \) : \( \frac{30}{78} \)
- \( E_s = 2 \) : \( \frac{3}{78} \)

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...

\[ g(E_T) = \sum_{E_s} g_S(E_s) g_R(E_T - E_s) \approx g_S(E_s) g_R(E_T - E_s) \mid_{\text{max}} \]

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

Now we have a tool to look at equilibrium...
System + Reservoir in Equilibrium

\[ g(E_T) \approx g_S(E_s) g_R(E_T - E_s) \mid_{\max} \]

Equilibrium is when we are sitting in this max entropy \((g)\) state...

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

\[ E_T = E_S + E_R \]

\[ dE_T = dE_S + dE_R = 0 \quad \Rightarrow \quad dE_S = -dE_R \]

\[
\frac{\partial \ln g_R}{\partial E_R} = \frac{\partial \ln g_S}{\partial E_S}
\]

is the same for two systems in equilibrium
We observe that two systems in equilibrium have the same temperature, so we hypothesize that...

\[ g(E_T) \approx g_S(E_s) g_R(E_T - E_s) \mid_{\text{max}} \]

\[ \frac{\partial \ln g_R}{\partial E_R} = \frac{\partial \ln g_S}{\partial E_S} \]

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

\[ S = k_B \ln g \quad \Rightarrow \quad \frac{1}{T} \equiv \frac{1}{k_B} \frac{\partial S_R}{\partial E_R} = \frac{1}{k_B} \frac{\partial S_S}{\partial E_S} \]
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

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

\[
= \exp \left( \frac{-(E_j - E_k)}{k_B T} \right)
\]
System + Reservoir in Equilibrium

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

\[ E_T = E_S + E_R \]

\[ N_T = N_S + N_R \]

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

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

\[
\Delta S_R = -(N_j - N_k) \left( \frac{\partial S}{\partial N} \right)_{N_T} - (E_j - E_k) \left( \frac{\partial S}{\partial E} \right)_{E_T}
\]

..where \( \mu \) is the electrochemical potential
System + Reservoir in Equilibrium

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

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

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

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

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

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

system 1 \hspace{1cm} \text{reservoir} \hspace{1cm} \text{system 2}

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

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

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

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

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

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

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

\[ = \frac{2}{\sqrt{\pi}} N_c F_{1/2} \]
Counting and Fermi Integrals

3-D Hole Density

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

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

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

\[ m_{hh}^*|_{\text{GaAs}} = 0.51 \, m \quad m_{lh}^*|_{\text{GaAs}} = 0.087 \, m \]

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

\[ (m_{\text{eff}}^*)^{3/2} = (m_{hh}^*)^{3/2} + (m_{lh}^*)^{3/2} \]
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!