Chapter 4

The Semiconductor in Equilibrium

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Topics

- Thermal-equilibrium concentration of electron and holes
- Intrinsic carrier concentration
- Intrinsic Fermi-level position
- Dopant atoms and energy levels
- Extrinsic carrier concentration and temperature dependence
- Ionization energy of dopant atoms in silicon
- Fermi level in extrinsic semiconductor
- Degenerate semiconductors
- Fermi level in two systems in contact with each other and at thermal equilibrium.

Why?

- Current is determined by flow rate and density of charge carriers.
- The density of electron and holes are related to the density of states function and the Fermi distribution (or probability) function.







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Density of quantum states per unit volume at energy E





Fermi-Dirac distribution (or probability) function

$$\frac{N(E)}{g(E)} = f(E) = \frac{1}{1 + exp\left\{\frac{(E-E_F)}{kT}\right\}}$$

The probability that a quantum state at an energy E will be occupied by an electron

The ratio between filled and total quantum states at any energy E

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Fermi-Dirac distribution (or probability) function



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Distribution of electron and holes

Number of electrons at E (in conduction band)

$$n(E) = g_{c}(E) f_{F}(E)$$

The probability function

$$n(E) = g_{c}(E) f_{F}(E)$$

Fermi-Dirac
probability function

Number of holes at E (in valence band)

$$p(E) = g_{\nu}(E) \left[1 - f_{F}(E)\right]$$

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Electron concentration

 $n_0 = \int_{B \text{ ottom of conduction band}}^{T \text{ op of conduction band}} D \text{ ensity of states } * Probability function d E$

$$n_0 = \int_{E_c}^{\infty} g_c(E) f_F(E) dE$$

The equation is valid for both intrinsic and extrinsic semiconductors



$$n_0 = \int g_c(E) f_F(E) \, dE$$

$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$
Condition:
E - E_F >> kT

 $f_F(E) \approx \exp\left[\frac{-(E-E_F)}{kT}\right]$ Boltzman approximation

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Comparison of Fermi-Dirac probability function and Maxwell-Boltzmann approximation



are within 5% of each other when $E-E_F \ge 3KT$



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$$n_{0} = \int_{E_{c}}^{\infty} \frac{4\pi (2m_{n}^{*})^{3/2}}{h^{3}} \sqrt{E - E_{c}} \exp\left[\frac{-(E - E_{F})}{kT}\right] dE$$

$$\eta = \frac{E - E_{c}}{kT}$$

$$n_{0} = \frac{4\pi (2m_{n}^{*}kT)^{3/2}}{h^{3}} \exp\left[\frac{-(E_{c} - E_{F})}{kT}\right] \int_{0}^{\infty} \eta^{1/2} \exp\left(-\eta\right) d\eta$$
Gamma function:
$$\frac{1}{2} \sqrt{\pi}$$



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$$n_0 = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2} \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

$$N_c = 2\left(\frac{2\pi m_n^* kT}{h^2}\right)^{3/2}$$

 N_{c} = <u>effective</u> density of states function in the conduction band

$$n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

The equation is valid for both intrinsic and extrinsic semiconductors

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Hole concentration $p_0 =$

$$p_0 = \int g_v(E) [1 - f_F(E)] \, dE$$

$$1 - f_F(E) = \frac{1}{1 + \exp\left(\frac{E_F - E}{kT}\right)}$$

$$1 - f_F(E) = \frac{1}{1 + \exp\left(\frac{E_F - E}{kT}\right)} \approx \exp\left[\frac{-(E_F - E)}{kT}\right]$$

$$p_0 = \int_{-\infty}^{E_v} \frac{4\pi (2m_p^*)^{3/2}}{h^3} \sqrt{E_v - E} \exp\left[\frac{-(E_F - E)}{kT}\right] dE$$

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$$p_0 = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2} \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

$$N_v = 2\left(\frac{2\pi m_p^* kT}{h^2}\right)^{3/2}$$

 N_{v} = effective density of states function in the valence band

$$p_0 = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

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Effective density of states function and effective mass values

	N _c (cm ⁻³)	N _v (cm ⁻³)	m _n */m _o	m _p */m _o
Si	2.8 x 10 ¹⁹	1.04 x 10 ¹⁹	1.08	0.56
Gallium Arsenide	4.7 x 10 ¹⁷	7.0 x 10 ¹⁸	0.067	0.48
Germanium	1.04 x 10 ¹⁹	6.0 x 10 ¹⁸	0.55	0.37

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Intrinsic semiconductor

• Intrinsic electron concentration = Intrinsic hole concentration



Why?

- charge carriers due to thermal excitation
- thermally generated electrons and holes always created in pairs.



INTRINSIC Semiconductor

Intrinsic Fermi level

$$n_0 = n_i = N_c \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right]$$

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$$p_0 = p_i = n_i = N_v \exp\left[\frac{-(E_{Fi} - E_v)}{kT}\right]$$

Intrinsic carrier concentration

$$n_i^2 = N_c N_v \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right] \cdot \exp\left[\frac{-(E_{Fi} - E_v)}{kT}\right]$$

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$$n_i^2 = N_c N_v \exp\left[\frac{-(E_c - E_v)}{kT}\right] = N_c N_v \exp\left[\frac{-E_g}{kT}\right]$$

Commonly accepted values of n_i at T=300K

Semiconductor	N _i		
Silicon	1.5 x 10 ¹⁰ cm ⁻³		
Gallium Arsenide	1.8 x 10 ⁶ cm ⁻³		
Germanium	2.4 x 10 ¹³ cm ⁻³		

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$$\log_{10}(n_i) = \frac{1}{2} \log_{10}(N_c N_v) - \frac{E_g}{2kT} \log_{10} e$$

Plot of $\log_{10}(n_i)$ vs. 1/T is straight line.

Slope is negative. From the slope E_g can be calculated

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Application of the intrinsic semiconductors

- High Electron Mobility
 Transistor
- High resistivity
 substrate for RF circuits
- amorphous-Si Solar Cells



Structure of solar cell



Where is the intrinsic Fermi level?



 E_{F_i} (Intrinsic Fermi level): E_F at which electron and hole concentration becomes equal



Even in intrinsic semiconductor, Fermi level is not exactly at centre between conduction and valence bands.

 $\frac{1}{2}$

The Extrinsic Semiconductor

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Intrinsic silicon lattice

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Acceptor and Donor Impurities:

- In Si four electrons in the valence shell participate in bonding.
- atom with more than 4 valence electrons \rightarrow donor impurity
- less than 4 \rightarrow acceptor impurity.

Antimony Arsenic Phosphorous



Boron Aluminum Gallium







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Donor Impurity:



• At very low temperature, the donor (excess) electron is still bound to the impurity atom.

• However, the donor electron is loosely bound to the impurity atom and can become free with small amount of thermal energy. Impurity atom is then ionized and positively charged.



Donor electron energy level:



- little energy required to move donor electrons from donor states to conduction band.
- positively charged donor ions are fixed but donor electrons in the conduction band can move through the crystal.

Acceptor Impurity:

• One covalent bond is incomplete for Si.

• With little thermal energy, a valence electron can break from another covalent bond and can occupy this position, thus creating a hole at the location of the broken covalent bond.

• The acceptor impurity is then ionized and negatively charged.

Acceptor Energy Level:

- little energy required to move valence electrons to acceptor levels.
- negatively charged acceptor ions are fixed but holes in the valence band can move through the crystal.

Electron concentration vs. temperature in n-type semiconductor

Electron concentration vs. temperature showing partial ionization, extrinsic and intrinsic regions.

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Electron concentration vs. temperature in extrinsic semiconductor

- At low temperatures, donor impurities are partially ionized. As temperature increases the percentage of ionized donor impurities also increases
- Once all donor impurities are ionized, there is no increase in carrier concentration. Even though intrinsic carrier concentration continues to increase, it is still small compared to extrinsic concentration.
- •At high temperatures, intrinsic carrier concentration dominates and electron concentration continues to increase again.

The ionization energy is the energy necessary to remove an electron from the neutral atom.

In case of donor atoms, the ionization energy is the energy necessary to elevate an electron from the donor level to conduction band.

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• In the next few slides, we will calculate the approximate ionization energy for donor atoms.

•We use Bohr atomic model for these calculations. For hydrogen atom, Bohr model and quantum mechanics give similar results.

•Donor impurity atom can be visualized as one donor electron orbiting the positively charged donor ion. This condition is similar to that in a hydrogen atom.

•However we have to consider permittivity of silicon instead of permittivity of free space.

Angular Momentum Quantization

• Bohr proposed that circumference of electron orbit = integer number of wavelengths $\rightarrow 2\pi r = n\lambda_n$

Then angular momentum,
$$L = mvr = \frac{hr}{\lambda} = \frac{hr}{\left[\frac{2\pi r}{n}\right]} = \frac{nh}{2\pi}$$

angular momentum of electron is quantized.

Ionization energy calculation:



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As defined in Chapter 2,
Bohr radius =
$$a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_0e^2} = 0.53$$
 Å

 $\frac{\text{orbiting electron radius}}{\text{Bohr radius}} = \frac{r_n}{a_0}$

$$\frac{r_n}{a_0} = n^2 \epsilon_r \left(\frac{m_0}{m^*}\right)$$

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For silicon,

$$\varepsilon_r = 11.7 \text{ and } \frac{\text{m}^*}{\text{m}_0} = 0.26$$

For n=1,
$$\frac{r_1}{a_0} = 45$$

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•
$$r_1/a_0 = 45$$
 or $r_1 = 23.9 A^0$

• This radius ~ 4 lattice constants of Si.

• Each unit cell contains 8 silicon atoms.

• Donor electron thus loosely bound to the donor atom.

• We will next find the approximate ionization energy.

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Total energy
$$E = T + V$$

Kinetic energy Potential energy
 $T = \frac{1}{2}m^*v^2 \longrightarrow T = \frac{m^*e^4}{2(n\hbar)^2(4\pi\epsilon)^2}$ (refer slide 37)

$$V = \frac{-e^2}{4\pi\epsilon r_n} = \frac{-m^*e^4}{(n\hbar)^2(4\pi\epsilon)^2}$$

$$E = T + V = \frac{-m^* e^4}{2(n\hbar)^2 (4\pi\epsilon)^2}$$

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- Ionisation energy of Hydrogen in lowest energy state = -13.6eV
- For Si, it is -25.8meV << band gap.
- Calculations using Bohr model give only the order of magnitude of the

ionisation energy. Actual values differ.

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			Impurity	Ionization energy (eV)
			Donors	
Impurity ionization energies in Silicon and Germanium				
			Selenium	0.0059
Impurity	Ionization energy (eV)		Tellurium	0.0058
	Si	Ge	Silicon	0.0058
Donors			Germanium	0.0061
Phosphorus	0.045	0.012		
Arsenic	0.05	0.0127	Acceptors	
			Beryllium	0.028
Acceptors			Zinc	0.0307
			Cadmium	0.0347
Boron	0.045	0.0104	Silicon	0.0345
Aluminum	0.06	0.0102	Germanium	0.0404
				AL.

Impurity ionization energies in gallium arsenide

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EXTRINSIC Semiconductor



$$n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

$$p_0 = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

The equation is valid for both intrinsic and extrinsic semiconductors

Another form (relation between E_F and E_{Fi})



$$n_0 p_0 = n_i^2$$

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If the impurity concentration is very high....

Fermi level will be very close to conduction band or valence band.

No Boltzmann approximation

Use The Fermi-Dirac Integral

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$$f_F(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{kT}\right)}$$

Boltzman approximation
$$\int f_F(E) \approx \exp\left[\frac{-(E - E_F)}{kT}\right]$$

$$n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

Only if $E_{c}-E_{F} > 3KT$

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Fermi-Dirac Integral



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Degenerate Semiconductors

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If the impurity atoms are very close each other...

- Donor electrons interact with each other
- The single discrete donor energy will split into a band
- The band may overlap the conduction band
- If the concentration exceed $N_{\rm c},~E_{\rm F}$ lies within the conduction band



Fermi level in the conduction band: Metallic conduction

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Statistics of donors and acceptors

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How many electrons still in the donor levels compared to the total number of electrons?

depends on the temperature and the Fermi level....

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Probability function for donor & acceptor levels



This same as the Fermi-Dirac probability function except the pre-exponential coefficient of $\frac{1}{2}$.

$$n_d = N_d - N_d^+$$
 Concentration of ionized donors

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similar for holes:

$$p_a = \frac{N_a}{1 + \frac{1}{g} \exp\left(\frac{E_F - E_a}{kT}\right)} = N_a - N_a^-$$

g=degeneration factor; 4 for GaAs and Si acceptor levels



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Low temperature



Moderate temperature



High temperature





Moderate temperature



$$n_d \approx \frac{N_d}{\frac{1}{2} \exp\left(\frac{E_d - E_F}{kT}\right)} = 2N_d \exp\left[\frac{-(E_d - E_F)}{kT}\right]$$

If E_d - E_F >> kT, then even E_c - E_F >> KT

Then,
$$n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

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Fraction of electrons still in the donor states

$$\frac{n_d}{n_d + n_0} = \frac{2N_d \exp\left[\frac{-(E_d - E_F)}{kT}\right]}{2N_d \exp\left[\frac{-(E_d - E_F)}{kT}\right] + N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]}$$

$$\frac{n_d}{n_d + n_0} = \frac{1}{1 + \frac{N_c}{2N_d} \exp\left[\frac{-(E_c - E_d)}{kT}\right]}$$

$$n = N_D$$

$$N_D^+ = N_D$$

With Phosphorus doping of $N_d=10^{16}$ cm⁻³, at T=300K, $n_d/(n_d+n_0)=0.41\%$

Almost complete ionization at Room Temp!

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Extremely low temperature (T=0K)

n_d=N_d Freeze-out



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High temperature



 $n \gg N_D$ (because of thermally generated electrons)



$$n_0 = n_i = N_c \exp\left[\frac{-(E_c - E_{Fi})}{kT}\right]$$

 $p = n \gg N_D$ (because of thermally generated holes)

• At very high temperature behavior is just like the intrinsic semiconductor





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Compensated semiconductor

- Both donor and acceptor impurities in the same region
- If $N_d > N_a \rightarrow$ n-type compensated semiconductor
- If $N_d < N_a \rightarrow$ p-type compensated semiconductor
- If $N_d = N_a \rightarrow$ completely compensated (will behave like intrinsic material)
- Practical semiconductor is always compensated semiconductor.
 Eg. Substrate is predoped usually p-type. All other dopings are done on top of this.

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Charge neutrality :



Recall $n_0 + N_a = p_0 + N_d$

Using the relation $n_i^2 = n_0 p_0$

$$n_0 + N_a = \frac{n_i^2}{n_0} + N_d$$



 $n_{
m o}$ is not simply $N_{
m d}$



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Similarly in p-type semiconductor,

$$p_0 = \frac{N_a - N_d}{2} + \sqrt{\left(\frac{N_a - N_d}{2}\right)^2 + n_i^2}$$

Minority carrier concentration





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(n-type material)

(p-type material)

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IV. POSITION OF FERMI ENERGY LEVEL

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Where is the Fermi level of an extrinsic semiconductor?

$$n_0 = N_c \exp\left[\frac{-(E_c - E_F)}{kT}\right]$$

$$E_c - E_F = kT \ln\left(\frac{N_c}{n_0}\right)$$

N-type: $N_d >> n_i$ then $n_0 \approx N_d$

$$E_c - E_F = kT \ln\left(\frac{N_c}{N_d}\right)$$

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Where is the Fermi level of a p-type extrinsic semiconductor?

$$p_0 = N_v \exp\left[\frac{-(E_F - E_v)}{kT}\right]$$

$$E_F - E_v = kT \ln\left(\frac{N_v}{p_0}\right)$$

P-type: $N_a >> n_i$ then $p_0 \approx N_a$

$$E_F - E_v = kT \ln \left(\frac{N_v}{N_a}\right)$$

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Position of Fermi level for an (a) n-type and (b) p-type semicondcutor.

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Different expression for the n-type...

$$E_F - E_{Fi} = kT \ln\left(\frac{n_0}{n_i}\right)$$

Another expression for the p-type

$$E_{F_i} - E_F = kT \ln \left(\frac{p_0}{n_i}\right)$$

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Variation of E_F with doping concentration:





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Variation of E_F with temperature T

$$E_{F} - E_{Fi} = kT \ln\left(\frac{n_{0}}{n_{i}}\right)$$
$$E_{Fi} - E_{F} = kT \ln\left(\frac{p_{0}}{n_{i}}\right)$$

• At higher temperatures, the semiconductor becomes more intrinsic. n_i increases and Fermi level moves towards mid-gap

•At T=0, Fermi level is above E_d in ntype and below E_a in p-type semiconductor



Variation of Fermi level with temperature for different doping concentrations



EF must be equal when different systems are in contact and in thermodynamic equilibrium



Consider a material A, with Fermi level E_{FA} . Bands below E_{FA} are full and above are empty.

material B with Fermi level E_{FB} .



EF must be equal when different systems are in contact and in thermodynamic equilibrium



• When A and B are brought in contact, electrons will flow from A into lower energy states of B, until thermal equilibrium is reached.

• Thermal equilibrium $\rightarrow E_F$ same in A & B



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- Electron concentration $n_0 = N_c \exp \left[\frac{(E_c E_F)}{kT} \right]$ Holds for bound intrinsic as well or extrinsic
- Hole concentration $p_0 = N_v \exp\left[\frac{(E_F E_v)}{kT}\right]$ as extrinsic semiconductor

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Intrinsic carrier concentration :

$$n_i^2 = n_0 p_0 \quad N_c \neq N_v \exp\left[-\frac{(E_c - E_v)}{kT} - N_c N\right] \exp\left[-\frac{E_g}{kT}\right]$$

In intrinsic semiconductor, Fermi level is close to but not exactly in the centre between conduction and valence bands.

$$E_{Fi} - E_{midgap} = \frac{3}{4} k \mathcal{F} \ln \left(\frac{m_p^*}{m_n^*} \right)$$

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Summary

- In extrinsic semiconductor, Fermi level is close to conduction band (n-type) or valence band (p-type)
- Position of Fermi level in extrinsic semiconductor

$$E_F - E_{Fi} \quad k \mathcal{F} \ln \left(\frac{n_0}{n_1} \right)$$

• In compensated n-type semiconductor electron concentration is given by

$$n_{0} = \frac{N_{d} - N_{a}}{2} \quad \sqrt{\left(\frac{N_{d} - N_{a}}{2} - n_{i}^{2}\right)}$$

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• When two different systems are in contact and in thermal equilibrium, E_F must be the same in both systems.

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