

MSE 423 Fall 2024 – Week 13

In/homogeneous semiconductors



Russell Ohl



Shockley, Bardeen, and Brattain

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Last week

- Tight-binding (LCAO for a solid)
- Bloch sums for an atomic (“exploded”) crystal and for a real crystal
- From levels to bands
- How many bands are filled?
- Band structure of graphene, carbon nanotubes
- Semiconductors – basic electrical and optical properties
- Density of carriers at thermal equilibrium
- Density of available states
- Law of mass action

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Intrinsic case

$$n_c(T) = N_c(T)e^{-(\epsilon_c - \mu)/K_B T}$$

$$p_v(T) = P_v(T)e^{-(\mu - \epsilon_v)/K_B T}$$

$$1 = \frac{n_c(T)}{p_v(T)} = \frac{N_c(T)}{P_v(T)} e^{2\mu/K_B T} e^{(2\epsilon_v + E_g)/K_B T}$$

$$\mu = \mu_i = \epsilon_v + \frac{E_g}{2} + \frac{k_B T}{2} \ln \frac{P_v(T)}{N_c(T)}$$

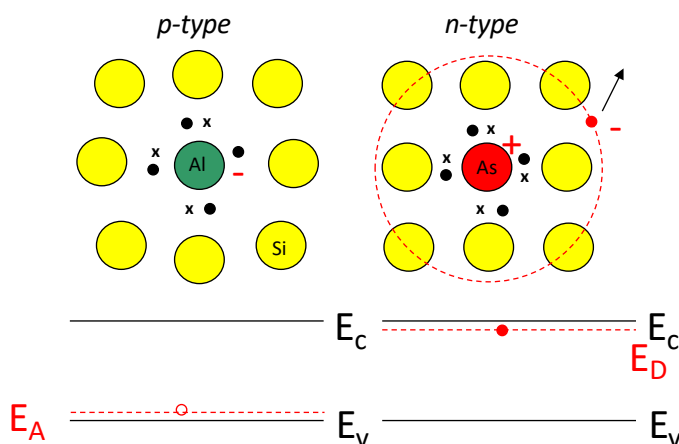
$$= \epsilon_v + \frac{E_g}{2} + \frac{3}{4} K_B T \ln \left(\frac{m_v}{m_c} \right)$$

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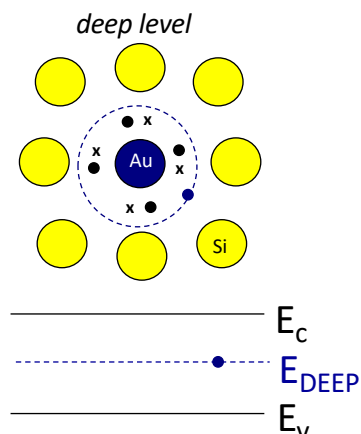
Impurity levels

- Adding impurities can lead to controlled domination of one carrier type
 - n-type is dominated by electrons
 - p-type is dominated by holes
- Adding other impurities can degrade electrical properties

Impurities with close electronic structure to host



Impurities that create deep levels



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Impurity states as “embedded” hydrogen atoms

- Consider the weakly bound 5th electron in phosphorus as a modified hydrogen atom
- For hydrogenic donors or acceptors, we can think of the electron or hole, respectively, as an orbiting electron around a net fixed charge
- We can estimate the energy to free the carrier into the conduction band or valence band by using a modified expression for the energy of an electron in the H atom

$$E_n = \frac{me^4}{8\epsilon_o^2 h^2 n^2} = -\frac{13.6}{n^2} \text{ (eV)}$$

$$E_n = \frac{me^4}{8\epsilon_o^2 h^2 n^2} \xrightarrow{\frac{e^2}{\epsilon_r} = e^2} \frac{m^* e^4}{8\epsilon_o^2 h^2 n^2} \frac{1}{\epsilon_r^2} = -\frac{13.6}{n^2} \frac{m^*}{m} \frac{1}{\epsilon_r^2}$$

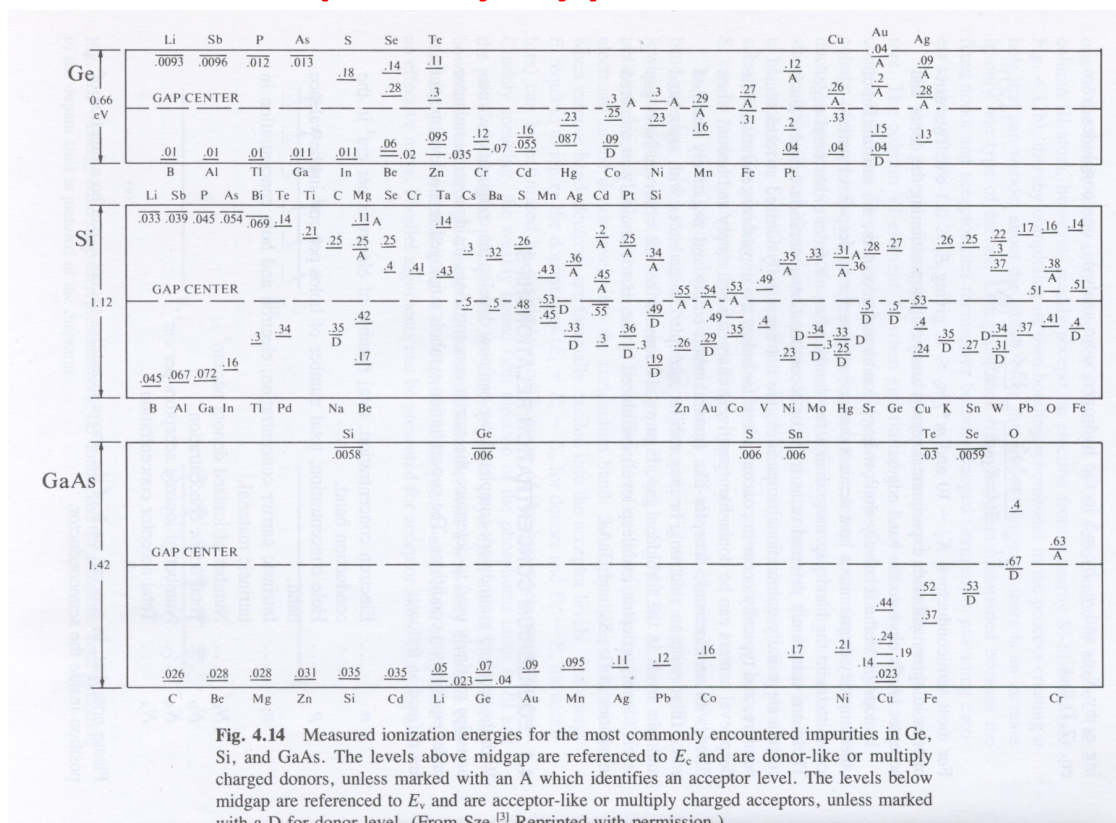
Thus, for the ground state $n=1$, we can see already that since ϵ is of the order of ~ 10 , the binding energy of the carrier to the impurity atom is $< 0.1\text{eV}$

Expect that many carriers are then ionized at room T:

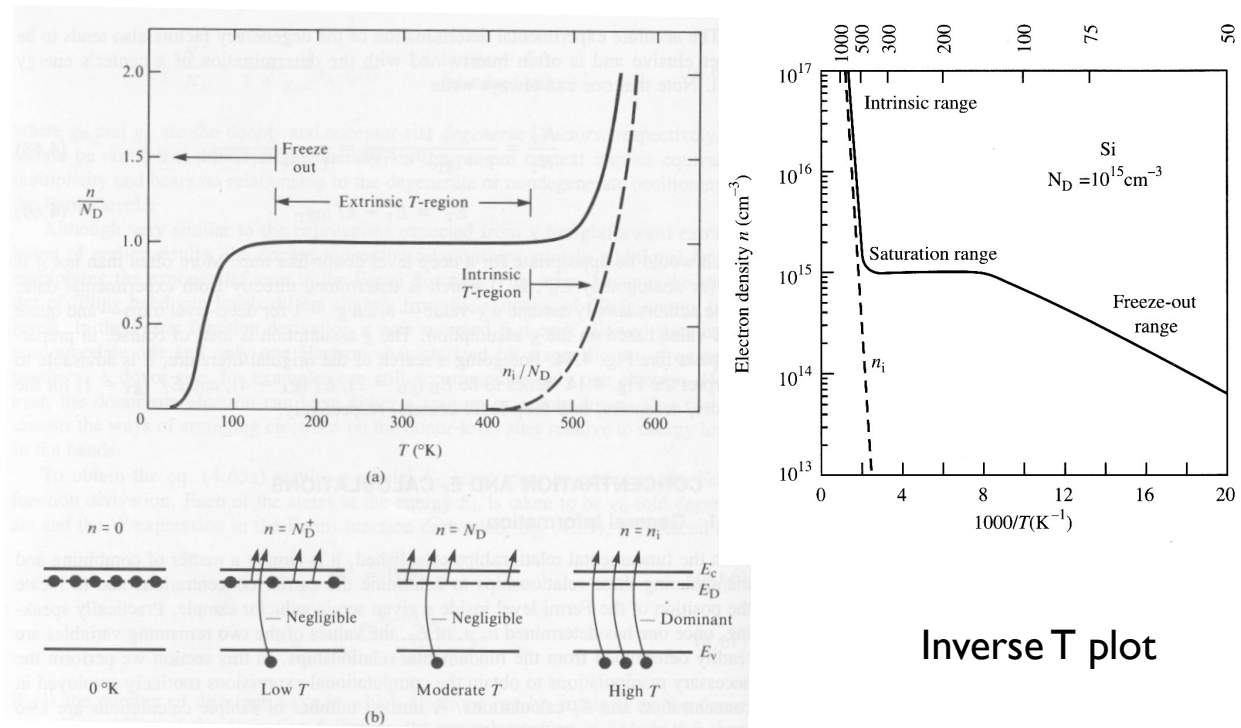
- B acceptor in Si: 0.046 eV
- P donor in Si: 0.044 eV
- As donor in Si: 0.049

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Impurity types, levels



Temperature dependence of majority carriers



Inverse T plot

Conductivity in semiconductors

Conductivity in (doped) semiconductors can be computed as in metals once we know the density of charge carriers (at every T):

$$\sigma = n_c e \mu_e + p_v e \mu_p$$

Table 3 Carrier mobilities at room temperature, in cm²/V-s

Crystal	Electrons	Holes	Crystal	Electrons	Holes
Diamond	1800	1200	GaAs	8000	300
Si	1350	480	GaSb	5000	1000
Ge	3600	1800	PbS	550	600
InSb	800	450	PbSe	1020	930
InAs	30000	450	PbTe	2500	1000
InP	4500	100	AgCl	50	—
AlAs	280	—	KBr (100 K)	100	—
AlSb	900	400	SiC	100	10–20

ELECTRONIC BANDS IN SODIUM CHLORIDE



BY

WILLIAM SHOCKLEY

B.Sc., California Institute of Technology
1932

Submitted in Partial Fulfillment of the
Requirements for the Degree of

DOCTOR OF PHILOSOPHY

from the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
1936

Signature of Author.....

Department of Physics, May 14, 1936.

Signature of Professor
in Charge of Research.....

Signature of Chairman of Department
Committee on Graduate Students.....
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Equilibrium carrier densities of impure/extrinsic/doped semiconductors (simplified)

n-type doping: $N_d \gg N_a$

$$n_c \approx N_d \quad p_v = \frac{n_i^2}{N_d}$$

p-type doping: $N_a \gg N_d$

$$p_v \approx N_a \quad n_c = \frac{n_i^2}{N_a}$$

How does the chemical potential move?

n-type doping: $N_d \gg N_a$

$$\mu = \mu_i + k_B T \ln \left(\frac{N_d}{n_i} \right)$$

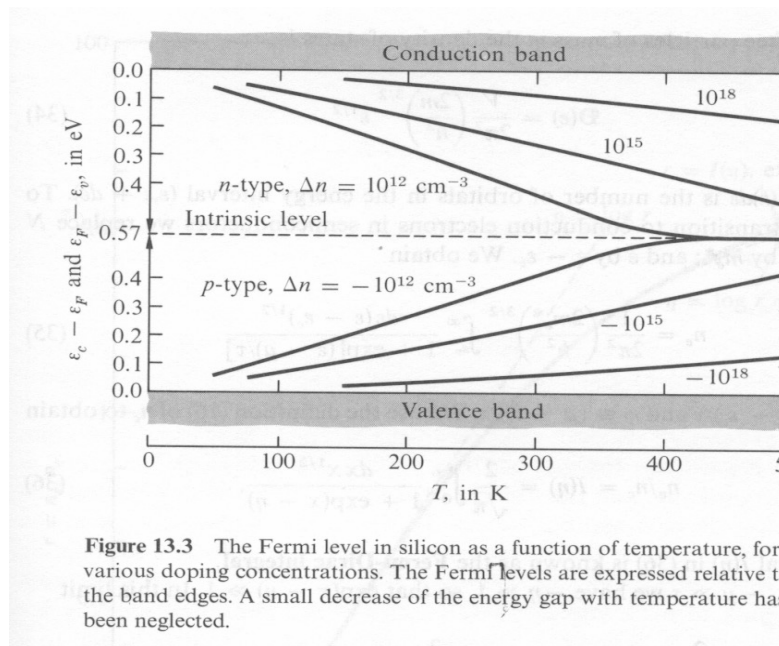
p-type doping: $N_a \gg N_d$

$$\mu = \mu_i - k_B T \ln \left(\frac{N_a}{n_i} \right)$$

$$N_{d/a} \gg n_i$$

Si: n and p type doping

At finite T



Semiconductor carrier engineering

- Silicon at room temperature
 - $n_i: \sim 10^{10} \text{ cm}^{-3}$
 - add 10^{16} cm^{-3} ($\sim 1 \text{ ppm}$) phosphorous donors: $n_c \sim N_d$
 - $n_c \sim 10^{16} \text{ cm}^{-3}$, $p_v \sim 10^4$ (n_i^2/N_d)
 - conductivity is proportional to the # of carriers leading to 6 orders of magnitude change in conductivity!

Impurities at the ppm level drastically change the conductivity (6 orders of magnitude)

Basic electronics: the transistor

The first point contact transistor

William Shockley, John Bardeen, and Walter Brattain
Bell Laboratories, Murray Hill, New Jersey (1947)



December 16, 1947 - Nobel Prize - 1956

Abrupt junction

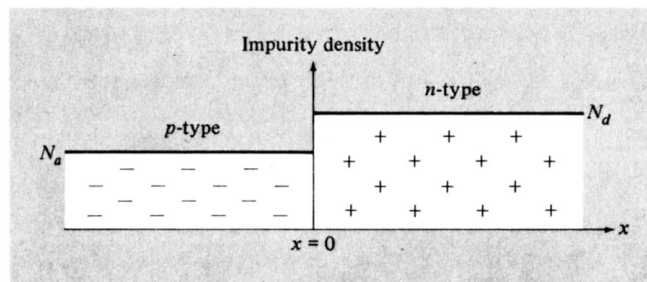


Figure 29.1

The impurity densities along a p - n junction in the case of an “abrupt junction,” for which donor impurities dominate at positive x , and acceptor impurities at negative x . The donors are represented by (+) to indicate their charge when ionized, and the acceptors by (-). For a junction to be abrupt, the region about $x = 0$ where the impurity concentrations change must be narrow compared with the “depletion layer” in which the carrier densities are nonuniform. (Typical plots of the carrier densities are superimposed on this figure in Figure 29.3.)

The p-n junction (diode)

p-type material at equilibrium n-type material at equilibrium

$$p_v \sim N_A$$

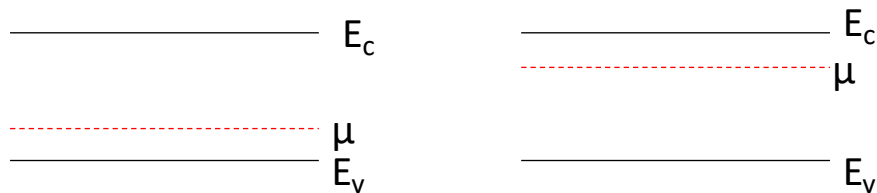
$$n_c \sim n_i^2 / N_A$$

$$n_c \sim N_D$$

$$p_v \sim n_i^2 / N_D$$

$$\mu_p = \mu_i - k_b T \ln \left(\frac{N_A}{n_i} \right)$$

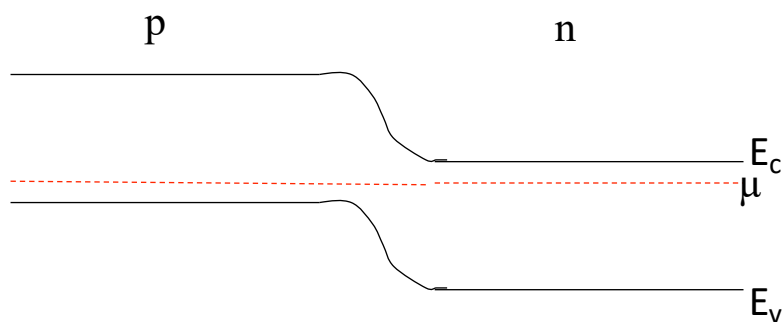
$$\mu_n = \mu_i + k_b T \ln \left(\frac{N_D}{n_i} \right)$$



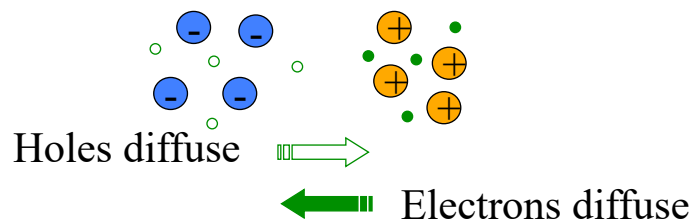
What happens when you join these together?

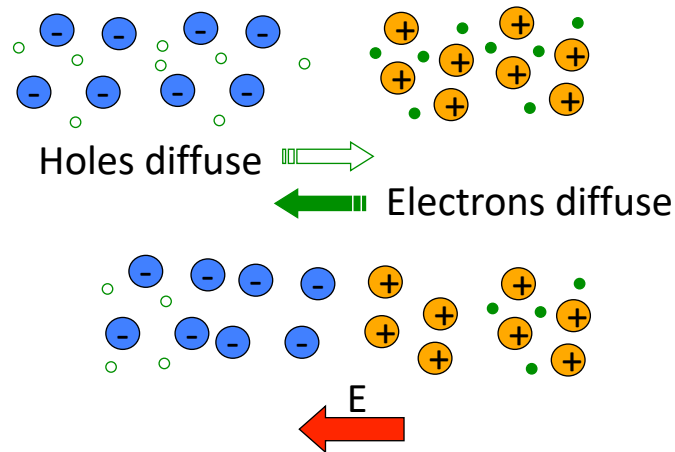
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Joining p and n



Carriers flow under driving force of diffusion until μ is horizontal





An electric field forms due to the deviation from charge neutrality

Therefore, a steady-state balance is achieved where diffusive flux of the carriers is balanced by the drift flux

Chemical potential

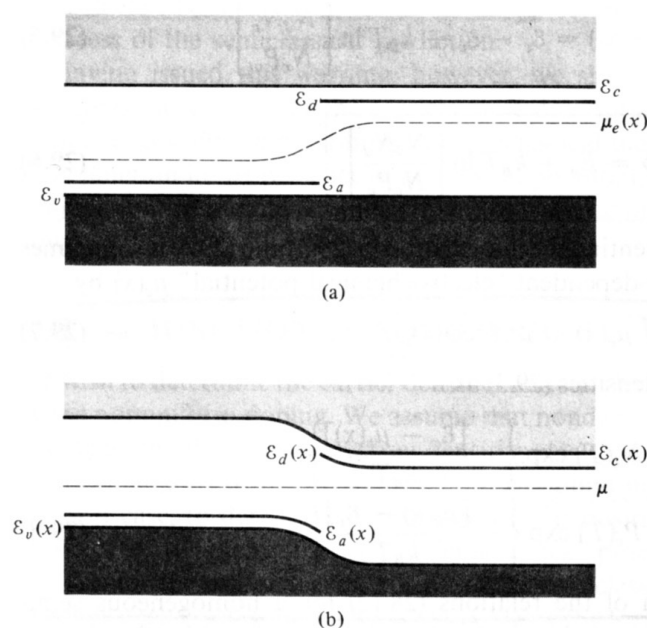


Figure 29.2

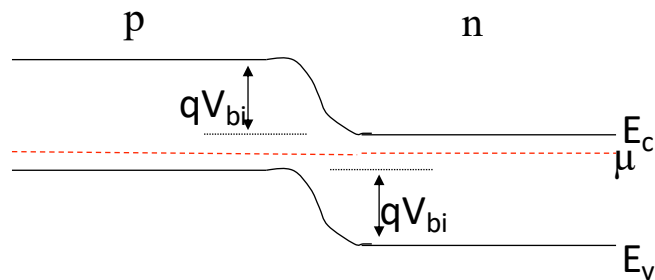
Two equivalent ways of representing the effect of the internal potential $\phi(x)$ on the electron and hole densities of a p - n junction. (a) The electrochemical potential $\mu_e(x) = \mu + e\phi(x)$ is plotted along the p - n junction. The carrier densities at any point x are those that would be found in a uniform semiconductor characterized by the fixed band and impurity energies ϵ_c , ϵ_v , ϵ_d , and ϵ_a , at a chemical potential equal to $\mu_e(x)$. (b) Here $\epsilon_c(x) = \epsilon_c - e\phi(x)$ is the energy of an electron wave packet localized about x formed from levels very near the conduction band minimum, and similarly for $\epsilon_v(x)$. The energies of the local impurity levels are $\epsilon_d(x) = \epsilon_d - e\phi(x)$ and $\epsilon_a(x) = \epsilon_a - e\phi(x)$. The (constant) chemical potential is also shown. The carrier densities at any point x are those that would be found in a uniform semiconductor characterized by band and impurity energies equal to $\epsilon_c(x)$, $\epsilon_d(x)$, $\epsilon_a(x)$, and $\epsilon_v(x)$ at a fixed chemical potential μ .

What is the built-in voltage V_{bi} ?

$$\mu_p = \mu_i - k_b T \ln \left(\frac{N_a}{n_i} \right)$$

$$\mu_n = \mu_i + k_b T \ln \left(\frac{N_D}{n_i} \right)$$

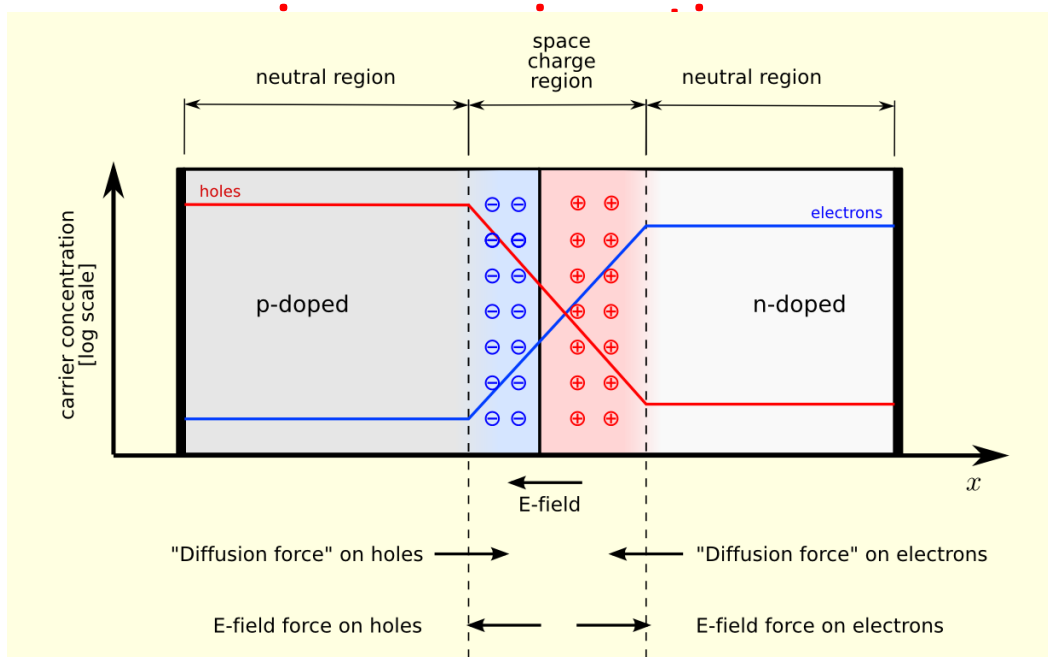
$$eV_{bi} = K_B T \ln \left(\frac{N_D N_A}{n_i^2} \right) = \mu_n - \mu_p$$



The built-in potential is also the one needed to align the Fermi levels!

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Carrier concentration



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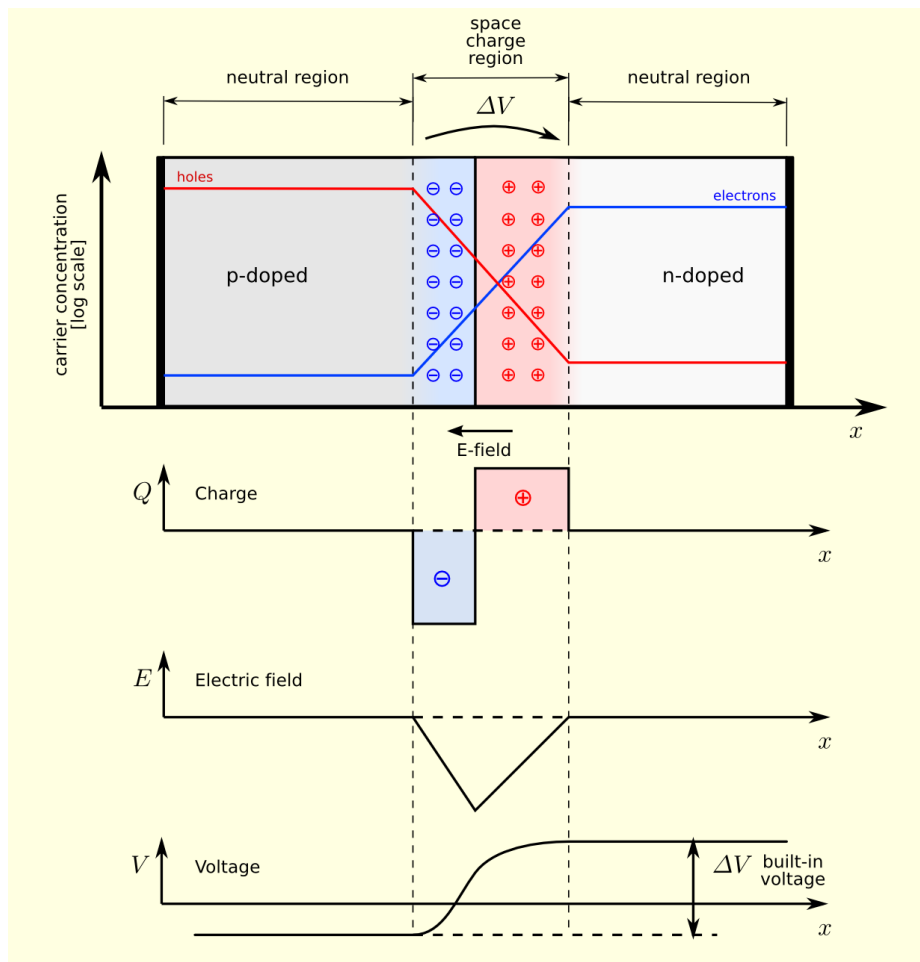
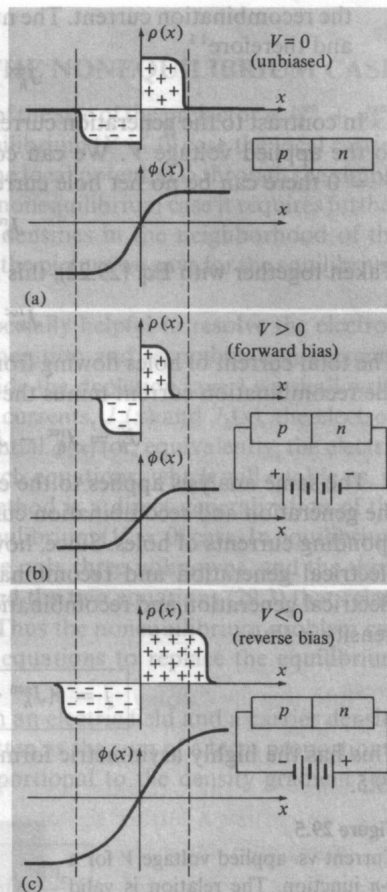


Figure 29.4

The charge density ρ and potential ϕ in the depletion layer (a) for the unbiased junction, (b) for the junction with $V > 0$ (forward bias), and (c) for the junction with $V < 0$ (reverse bias). The positions $x = d_n$ and $x = -d_p$ that mark the boundaries of the depletion layer when $V = 0$ are given by the dashed lines. The depletion layer and change in ϕ are reduced by a forward bias and increased by a reverse bias.

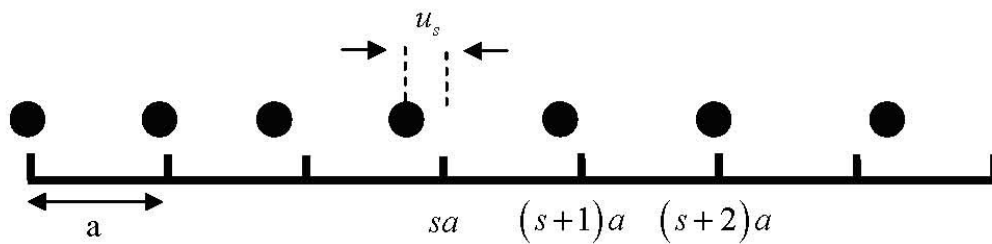


Operation under bias



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1-dimensional monoatomic chain



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Properties

- Unique solutions for k in the first BZ

$$\frac{u_{s+1}}{u_s}$$

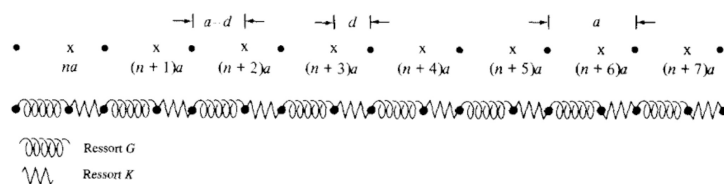
- Phase velocity and group velocity

Properties

- Standing waves
- Long wavelength limit

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1-dimensional diatomic chain



III. Equations of motion

$$M \frac{d^2 u_{1,s}}{dt^2} = K(u_{2,s} - u_{1,s}) + G(u_{2,s-1} - u_{1,s})$$

$$M \frac{d^2 u_{2,s}}{dt^2} = K(u_{1,s} - u_{2,s}) + G(u_{1,s+1} - u_{2,s})$$

IV. Solutions

$$u_{1s} = u_1 e^{iks a} e^{-i\omega t}, \quad u_{2s} = u_2 e^{iks a} e^{-i\omega t}$$

V. Dispersion relations

$$(M\omega^2 - (K + G))u_1 + (K + Ge^{-ika})u_2 = 0$$

$$(K + Ge^{ika})u_1 + (M\omega^2 - (K + G))u_2 = 0$$

The homogenous linear equations have a solution only if the determinant of the coefficients is zero:

$$\begin{vmatrix} M\omega^2 - (K+G) & (K+Ge^{-ika}) \\ (K+Ge^{ika}) & M\omega^2 - (K+G) \end{vmatrix} = 0$$

with solutions:

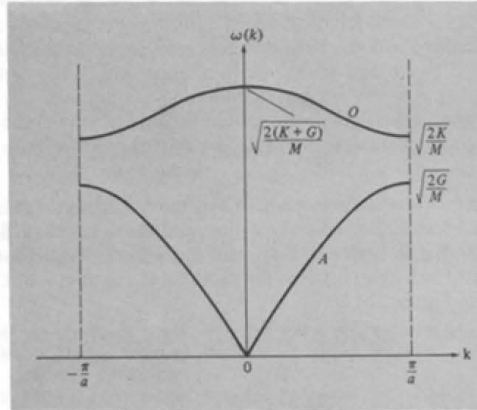
$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M} \sqrt{K^2 + G^2 + 2KG \cos ka}$$

$$\frac{u_1}{u_2} = \mp \frac{K + Ge^{-ika}}{K + Ge^{ika}}$$

for each k there are two solutions which are called the two branches of the dispersion curves.

Figure 22.10

Dispersion relation for the diatomic linear chain. The lower branch is the acoustic branch and has the same structure as the single branch present in the monatomic case (Figure 22.8). In addition, there is now an optical branch (upper branch.)



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The perfectly harmonic crystal

Phonon: lattice vibration of wave-vector $\mathbf{q}$ and frequency $\omega_j(\mathbf{q})$ (j : band index). Frequencies are calculated from the second derivatives of the energy (**interatomic force constants**) versus atomic displacements:

$$C_{\alpha i, \beta j}(\mathbf{R}_L, \mathbf{R}_{L'}) = \left. \frac{\partial^2 E}{\partial u_{\alpha i, L} \partial u_{\beta j, L'}} \right|_{\text{equilibrium}} = C_{\alpha i, \beta j}(\mathbf{R}_L - \mathbf{R}_{L'})$$

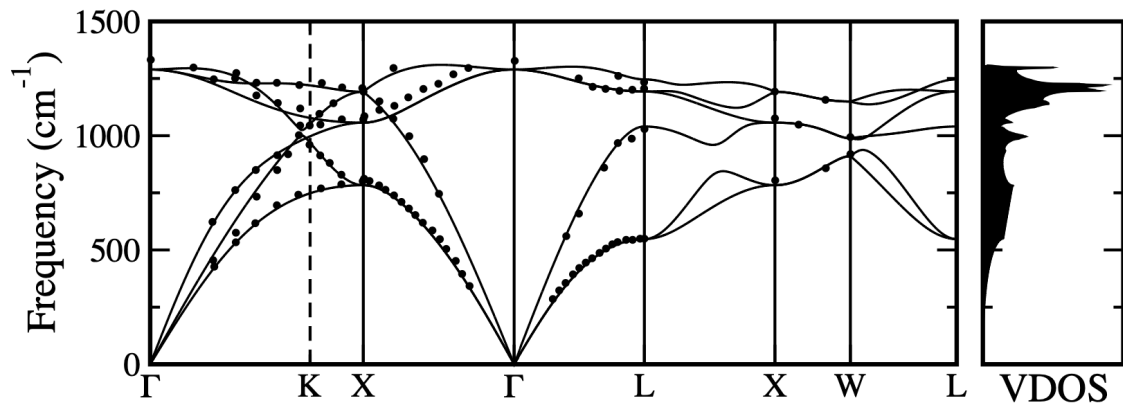
Precisely, phonon frequencies are the eigenvalues of the **dynamical matrix** $\tilde{D}_{\alpha i, \beta j}(\mathbf{q})$, Fourier transform of $C_{\alpha i, \beta j}(\mathbf{R}_L)$:

$$\tilde{D}_{\alpha i, \beta j}(\mathbf{q}) = \sum_L C_{\alpha i, \beta j}(\mathbf{R}_L) e^{-i\mathbf{q} \cdot \mathbf{R}_L}$$

$$\omega^2 u_{\alpha i} = \sum_{\beta j} u_{\beta j} \tilde{D}_{\alpha i, \beta j}(\mathbf{q})$$

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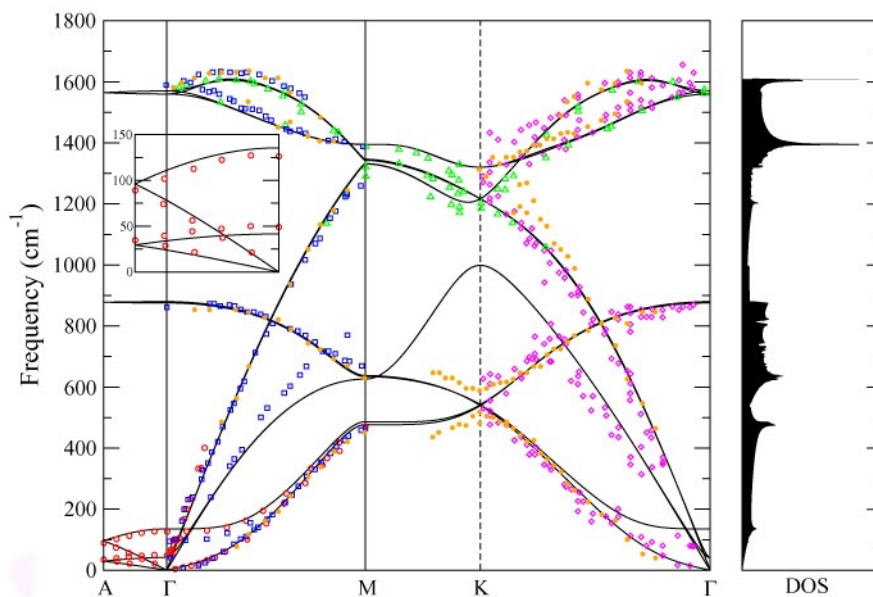
Phonon dispersions in diamond



Mounet PRB 2005

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Phonon dispersions in graphite



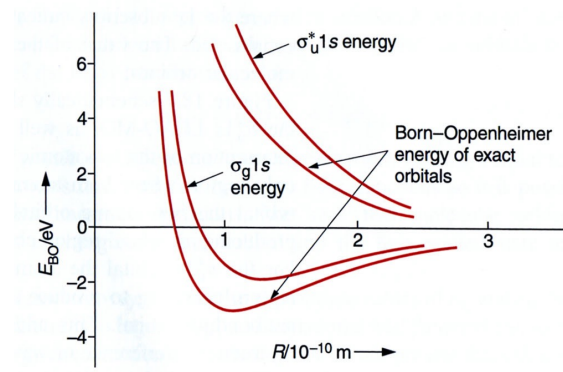
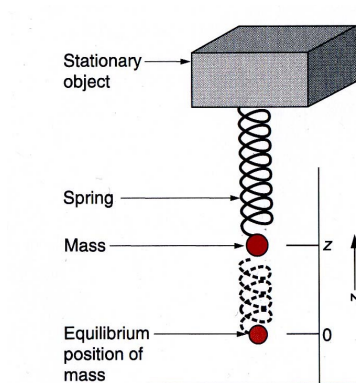
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The quantization of vibrations

- Electrons are much lighter than nuclei ($m_{\text{proton}}/m_{\text{electron}} \sim 1800$)
- Electronic wave-functions always rearrange themselves to be in the ground state (lowest energy possible for the electrons), even if the ions are moving around
- Born-Oppenheimer approximation: electrons in the instantaneous potential of the ions (so, electrons can not be excited – FALSE in general)

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Nuclei have some quantum action...

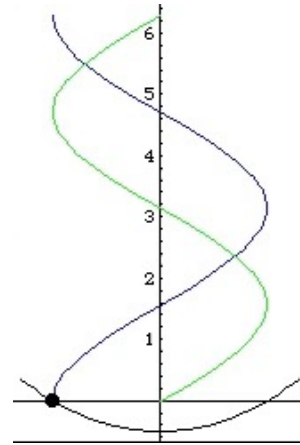


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The quantum harmonic oscillator (I)

$$\left(-\frac{\hbar^2}{2M} \frac{d^2}{dz^2} + \frac{1}{2} k z^2 \right) \varphi(z) = E \varphi(z)$$

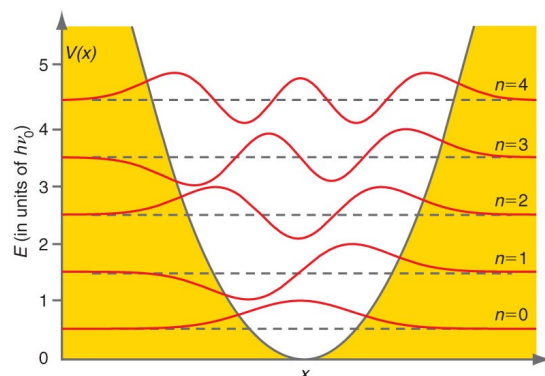
$$\omega = \sqrt{\frac{k}{m}} \quad a = \frac{\sqrt{km}}{\hbar}$$



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The quantum harmonic oscillator (II)

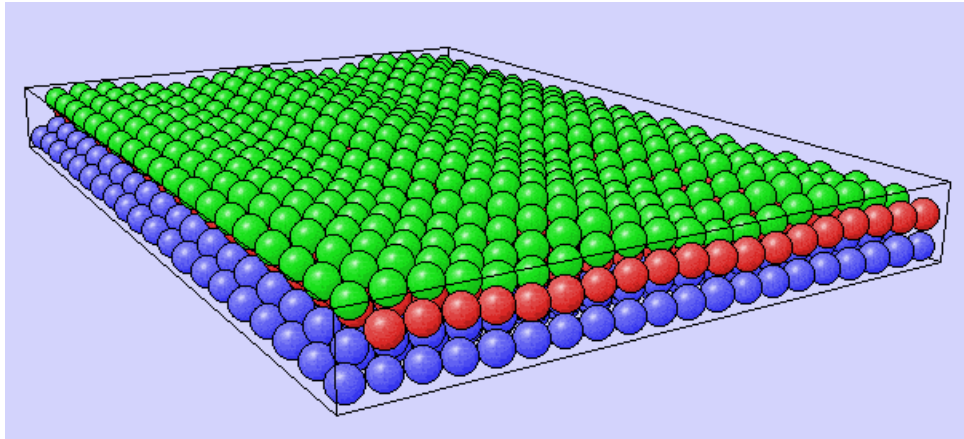
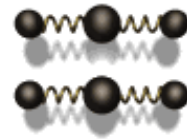
$$\begin{aligned} \psi_0 &= \left(\frac{a}{\pi} \right)^{1/4} e^{-az^2/2} \\ \psi_1 &= \left(\frac{4a^3}{\pi} \right)^{1/4} z e^{-az^2/2} \\ \psi_2 &= \left(\frac{a}{4\pi} \right)^{1/4} (2az^2 - 1) e^{-az^2/2} \end{aligned}$$



$$E = \hbar \omega \left(n + \frac{1}{2} \right)$$

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Quantized atomic vibrations



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Harmonic crystal's free energy

Quantization of phonons' energy:

$$E_j(\mathbf{q}) = \hbar\omega_j(\mathbf{q})\left(n + \frac{1}{2}\right)$$

Partition function of one phonon (microcanonical ensemble - T & V constant):

$$Z_{\mathbf{q},j} = \sum_n \exp\left(-\frac{\hbar\omega_j(\mathbf{q})}{k_B T}\left(n + \frac{1}{2}\right)\right) = \frac{1}{2 \sinh \frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

Total partition function:

$$Z_{total} = \prod_{\mathbf{q},j} Z_{\mathbf{q},j} = \frac{1}{\prod_{\mathbf{q},j} 2 \sinh \frac{\hbar\omega_j(\mathbf{q})}{k_B T}}$$

Free energy: ($\{a_i\}$ = lattice parameters)

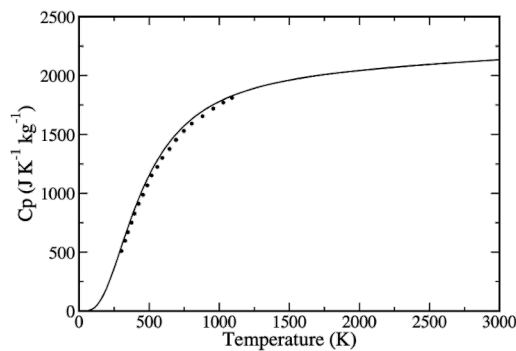
$$\begin{aligned} F(\{a_i\}, T) &= E(\{a_i\}) + F_{vib} \\ &= E(\{a_i\}) - k_B T \ln Z_{total} \\ &= E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar\omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar\omega_{\mathbf{q},j}}{k_B T})) \end{aligned}$$

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Heat capacity

Constant volume heat capacity given by:

$$\begin{aligned} C_v &= -T \frac{\partial^2 F}{\partial T^2} \\ &= \sum_{\mathbf{q},j} c_v(\mathbf{q},j) = k_B \sum_{\mathbf{q},j} \left(\frac{\hbar \omega_{\mathbf{q},j}}{2k_B T} \right) \frac{1}{\sinh^2 \left(\frac{\hbar \omega_{\mathbf{q},j}}{2k_B T} \right)} \end{aligned}$$



$$C_p - C_v = TV_0 B_0 \alpha_V^2$$

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The quasi-harmonic approximation: principle

$$F(\{a_i\}, T) = E(\{a_i\}) + \sum_{\mathbf{q},j} \frac{\hbar \omega_{\mathbf{q},j}}{2} + k_B T \sum_{\mathbf{q},j} \ln(1 - \exp(-\frac{\hbar \omega_{\mathbf{q},j}}{k_B T}))$$

If phonon frequencies assumed constant (harmonic crystal), no dependence of the vibrational free energy on structure

→ no thermal expansion, no temperature dependence of elastic constants, heat capacity reaching a limit at high temperature, ie. **no anharmonic effects**.

Quasi-harmonic approximation: use harmonic expression of the free energy but add additional dependence of the phonon frequencies on the **lattice parameters** $\{a_i\}$.

Thermal expansion

Minimization of quasi-harmonic free energy vs. lattice parameters $\{a_i\}$:

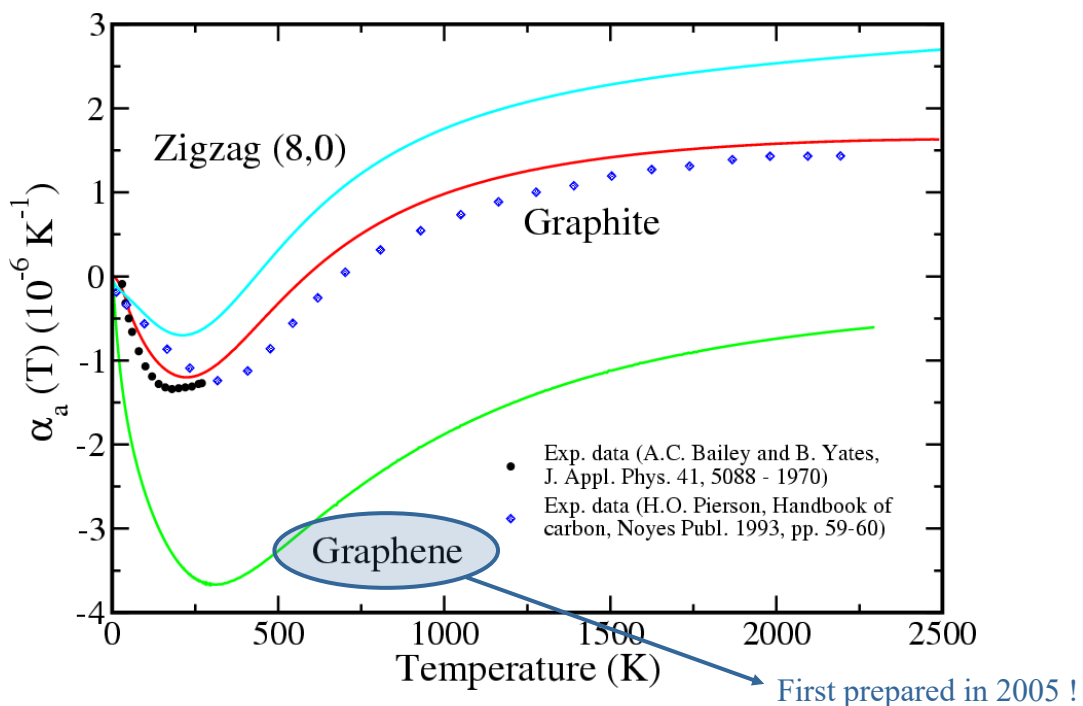
$$F(\{a_i\}, T) = E(\{a_i\}) + \sum_{\mathbf{q}, j} \frac{\hbar \omega_{\mathbf{q}, j}(\{a_i\})}{2} + k_B T \sum_{\mathbf{q}, j} \ln(1 - \exp(-\frac{\hbar \omega_{\mathbf{q}, j}(\{a_i\})}{k_B T}))$$

Equilibrium lattice parameters given by that minimization change with temperature → **Thermal expansion** (or contraction):

$$\alpha_i = \frac{1}{a_i} \frac{\partial a_i}{\partial T}$$

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Thermal Contraction in 2-d and 1-d Carbon

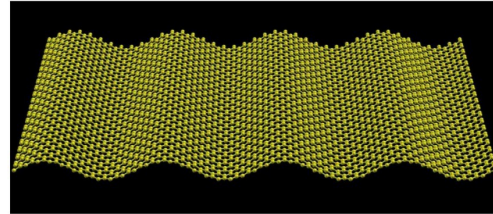
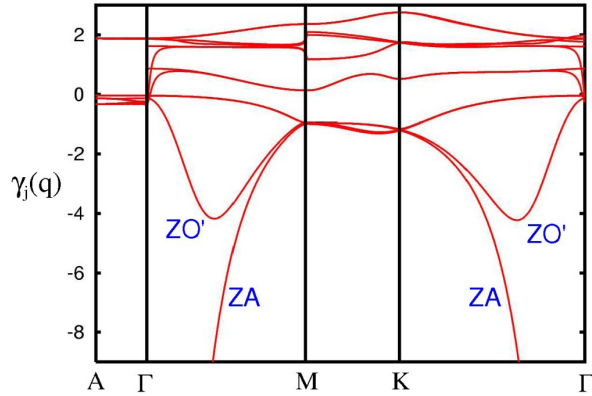


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Grüneisen parameters for graphene

Grüneisen parameters

$$\gamma_k(\mathbf{q}, j) = \frac{-a_{0,k}}{\omega_{0,\mathbf{q},j}} \left. \frac{\partial \omega_{\mathbf{q},j}}{\partial a_k} \right|_0$$

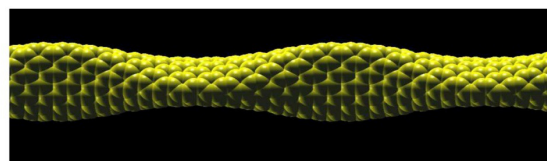
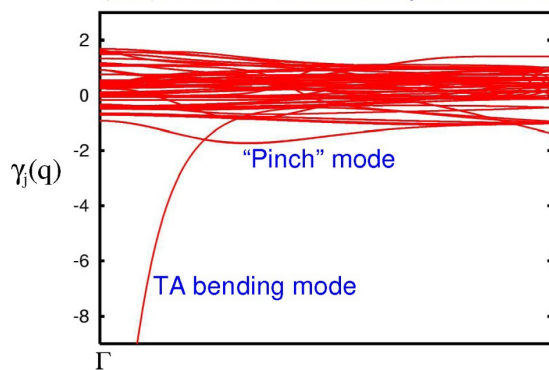


ZA bending mode

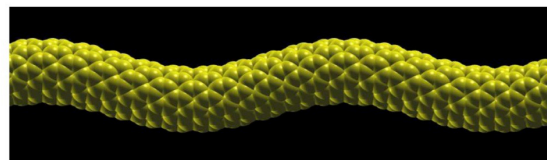
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Grüneisen parameters for SWNT

(8,0) SWNT: Grüneisen parameters

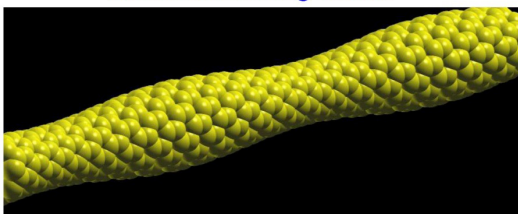


"Pinch" mode

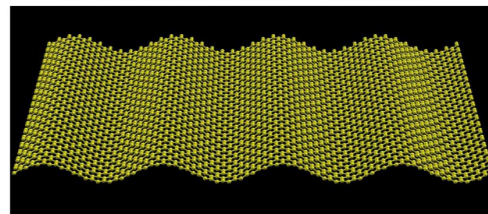


TA bending mode

Radial breathing mode



ZA bending mode of graphite



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