

Theoretical calculation of the heat capacity

- Principle of equipartition of energy
- Heat capacity of ideal and real gases
- Heat capacity of solids: Dulong-Petit, Einstein, Debye models
- Heat capacity of metals – electronic contribution

Reading: Chapter 6.2 of Gaskell

Degrees of freedom and equipartition of energy

For each atom in a solid or gas phase, three coordinates have to be specified to describe the atom's position – a single atom has 3 **degrees of freedom** for its motion. A solid or a molecule composed of N atoms has 3N degrees of freedom.

We can also think about the number of degrees of freedom as the number of ways to absorb energy. The theorem of **equipartition of energy** (classical mechanics) states that in thermal equilibrium the same **average** energy is associated with each independent degree of freedom and that the energy is $\frac{1}{2} k_B T$. For the interacting atoms, e.g. liquid or solid, for each atom we have $\frac{1}{2} k_B T$ for kinetic energy and $\frac{1}{2} k_B T$ for potential energy - equality of kinetic and potential energy in harmonic approximation is addressed by the virial theorem of classical mechanics.

Based on equipartition principle, we can calculate heat capacity of the ideal gas of atoms - each atom has 3 degrees of freedom and internal energy of $\frac{3}{2} k_B T$. The molar internal energy $U = \frac{3}{2} N_A k_B T = \frac{3}{2} RT$ and the molar heat capacity under conditions of constant volume is $c_v = [dU/dT]_V = \frac{3}{2} R$

In an ideal gas of molecules only internal vibrational degrees of freedom have potential energy associated with them. For example, a diatomic molecule has 3 translational + 2 rotational + 1 vibrational = 6 total degrees of freedom. Potential energy contributes $\frac{1}{2} k_B T$ only to the energy of the vibrational degree of freedom, and $U_{\text{molecule}} = \frac{7}{2} k_B T$ *if all degrees of freedom are “fully” excited.*

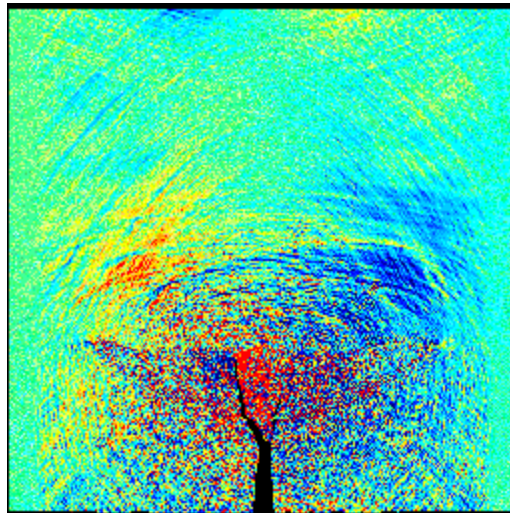
Temperature and velocities of atoms

At equilibrium velocity distribution is Maxwell-Boltzmann,

$$dN(\vec{v}, T) = \left(\frac{m}{2\pi k_B T} \right)^{3/2} \exp \left\{ - \frac{m [v_x^2 + v_y^2 + v_z^2]}{2k_B T} \right\} dv_x dv_y dv_z$$

$$\langle v^2 \rangle_i = 3k_B T/m$$

If system is not in equilibrium it is often difficult to separate different contributions to the kinetic energy and to define temperature.



Acoustic emissions in the fracture simulation in 2D model. Figure by B.L. Holian and R. Ravelo, Phys. Rev. B51, 11275 (1995). Atoms are colored by velocities relative to the left-to-right local expansion velocity, which causes the crack to advance from the bottom up.

Heat capacity of molecules – straightforward application of equipartition principle does not work

Classical mechanics should be used with caution when dealing with phenomena that are inherently quantized.

For example, let's try to use equipartition theory to calculate the heat capacity of water vapor.

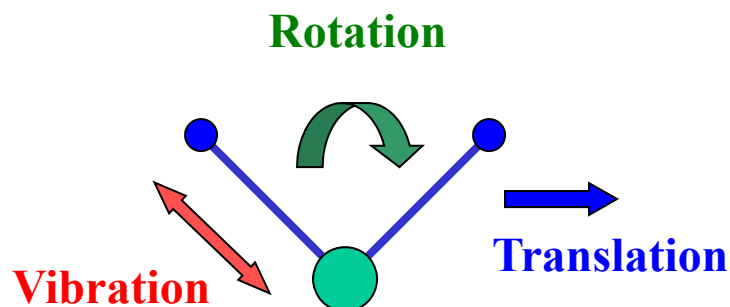
Motion	Degrees of freedom	U	c_v
Translational	3	$3 \times \frac{1}{2} RT$	1.5R
Rotational	3	$3 \times \frac{1}{2} RT$	1.5R
Vibrational	3	$6 \times \frac{1}{2} RT$	3R

$$\text{Total } c_v = 6R$$

But experimental c_v is much smaller.

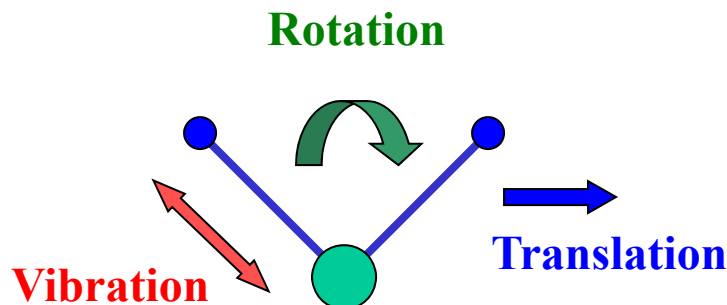
At $T = 298 \text{ K}$ H_2O gas has $c_v = 3.038R$.

What is the reason for the large discrepancy?



Heat capacity of molecules – straightforward application of equipartition principle does not work (continued)

What is the reason for the large difference between the prediction of classical calculations, $c_v = 6R$, and much smaller experimental $c_v = 3.038R$ at 25°C?



The table shows the vibrational frequencies of water along with the population of the first excited state at 600 K.

ν (cm ⁻¹)	$\text{Exp}(-h\nu/k_B T)$
3825	1.0×10^{-4}
1654	1.9×10^{-2}
3936	8.0×10^{-5}

For the high frequency OH stretching motions, there should be essentially no molecules in the first vibrational state even at 600 K. For the lower frequency bending motion, there will be about 2% of the molecules excited.

Contributions to the heat capacity can be considered classically only if $E_n \sim h\nu \ll k_B T$. Energy levels with $E_n \geq kT$ contribute little, if at all, to the heat capacity.

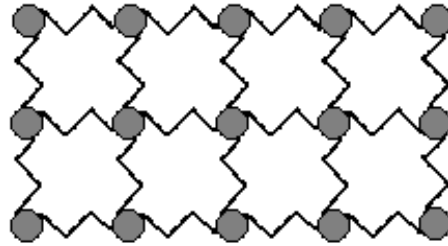
Only translational and rotational modes are excited, the contribution from vibrations is only 0.038R.

Heat capacity of solids – Dulong – Petit law

In 1819 Dulong and Petit found experimentally that for many solids at room temperature, $c_v \approx 3R = 25 \text{ JK}^{-1}\text{mol}^{-1}$

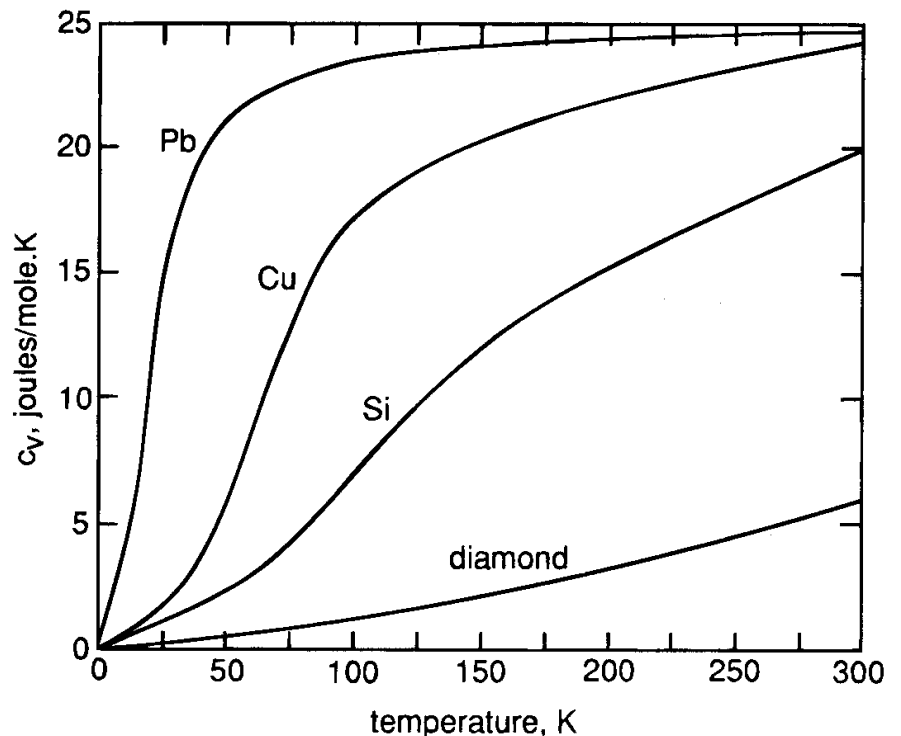
This is consistent with equipartition theory: energy added to solids takes the form of atomic vibrations and both kinetic and potential energy is associated with the three degrees of freedom of each atom.

$$\langle P(t) \rangle = \langle K(t) \rangle = \frac{3}{2} k_B T$$



The molar internal energy is then $U = 3N_A k_B T = 3RT$ and the molar constant volume heat capacity is $c_v = [\partial U / \partial T]_v = 3R$

Although c_v for many elements at room T are indeed close to $3R$, low- T measurements found a strong temperature dependence of c_v . Actually, $c_v \rightarrow 0$ as $T \rightarrow 0 \text{ K}$.



Heat capacity of solids – Einstein model

The low-T behavior can be explained by quantum theory. The first explanation was proposed by Einstein in 1906. He considered a solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency ν . Quantum theory gives the energy of i^{th} level of a harmonic quantum oscillator as

$$\varepsilon_i = (i + 1/2) h\nu \quad \text{where } i = 0, 1, 2, \dots, \text{ and } h \text{ is Planck's constant.}$$

For a quantum harmonic oscillator the Einstein-Bose statistics must be applied (rather than Maxwell-Boltzmann statistics and equipartition of energy for classical oscillators) and the statistical distribution of energy in the vibrational states gives average energy:

$$\langle U(t) \rangle = \frac{h\nu}{e^{h\nu/k_B T} - 1}$$

There are three degrees of freedom per oscillator, so the total internal energy per mol is

$$U = \frac{3N_A h\nu}{e^{h\nu/k_B T} - 1}$$

Note: you do not need to remember all these scary quantum mechanics equations for tests/exams but you do need to understand the basic concepts behind them.

$$c_V = \left[\frac{\partial U}{\partial T} \right]_V = \frac{3N_A k_B \left(\frac{h\nu}{k_B T} \right)^2 e^{h\nu/k_B T}}{\left(e^{h\nu/k_B T} - 1 \right)^2}$$

The Einstein formula gives a temperature dependent c_V that approaches $3R$ as $T \rightarrow \infty$, and approaching 0 as $T \rightarrow 0$.

The High Temperature Limit of the Einstein Specific Heat

Let's show that Einstein's formula approaches Dulong – Petit law at high T. For high temperatures, a series expansion of the exponential gives

$$e^{h\nu/k_B T} \approx 1 + \frac{h\nu}{k_B T}$$

The Einstein specific heat expression then becomes

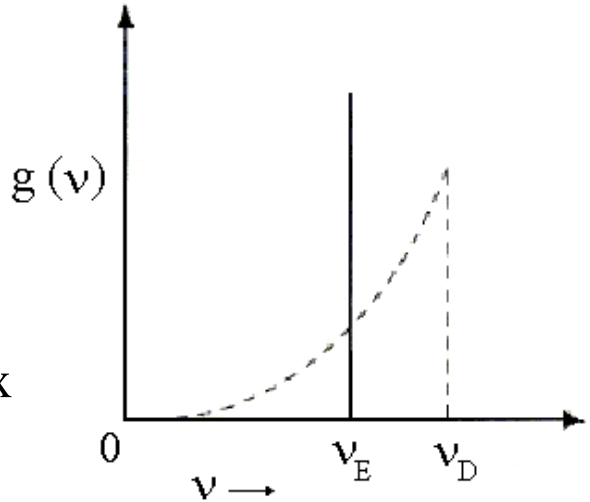
$$\begin{aligned} c_V &= \frac{3 N_A k_B \left(\frac{h\nu}{k_B T} \right)^2 e^{h\nu/k_B T}}{\left(e^{h\nu/k_B T} - 1 \right)^2} \approx \frac{3 N_A k_B \left(\frac{h\nu}{k_B T} \right)^2 \left(1 + \frac{h\nu}{k_B T} \right)}{\left(\frac{h\nu}{k_B T} \right)^2} = \\ &= 3 N_A k_B \left(1 + \frac{h\nu}{k_B T} \right) \approx 3 N_A k_B = 3R \end{aligned}$$

In the Einstein treatment, the appropriate frequency in the expression had to be determined empirically by comparison with experiment for each element. Although the general match with experiment was reasonable, it was not exact. Einstein formula predicts faster decrease of c_V as compared with experimental data. Debye advanced the treatment by treating the quantum oscillators as collective modes in the solid - phonons.

Heat capacity of solids – Debye model

Debye assumed a continuum of frequencies with a distribution of $g(\nu) = a\nu^2$, up to a maximum frequency, ν_D , called the Debye frequency.

This leads to the following expression for the Debye specific heat capacity:



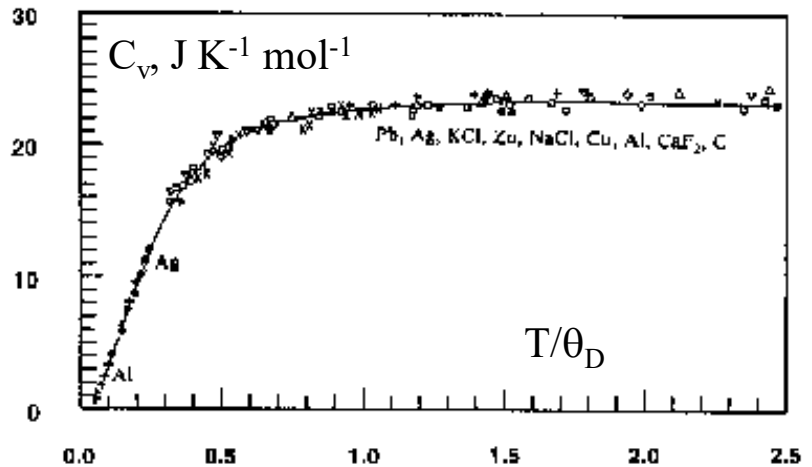
$$c_V = 9N_A k_B \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

where $x = h\nu/k_B T$ and $\theta_D = h\nu_D/k_B$ – Debye characteristic temperature

For low temperatures, Debye's model predicts $c_V = \frac{12\pi^4 N_A k_B}{5} \left(\frac{T}{\theta_D} \right)^3$
 - good agreement with experimental results.

We can see that c_V depends on T/θ_D with θ_D as the scaling factor for different materials.

$\theta_D \sim \nu_D \sim$ strength of the interatomic interaction, $\sim 1/(\text{atomic weight})$.



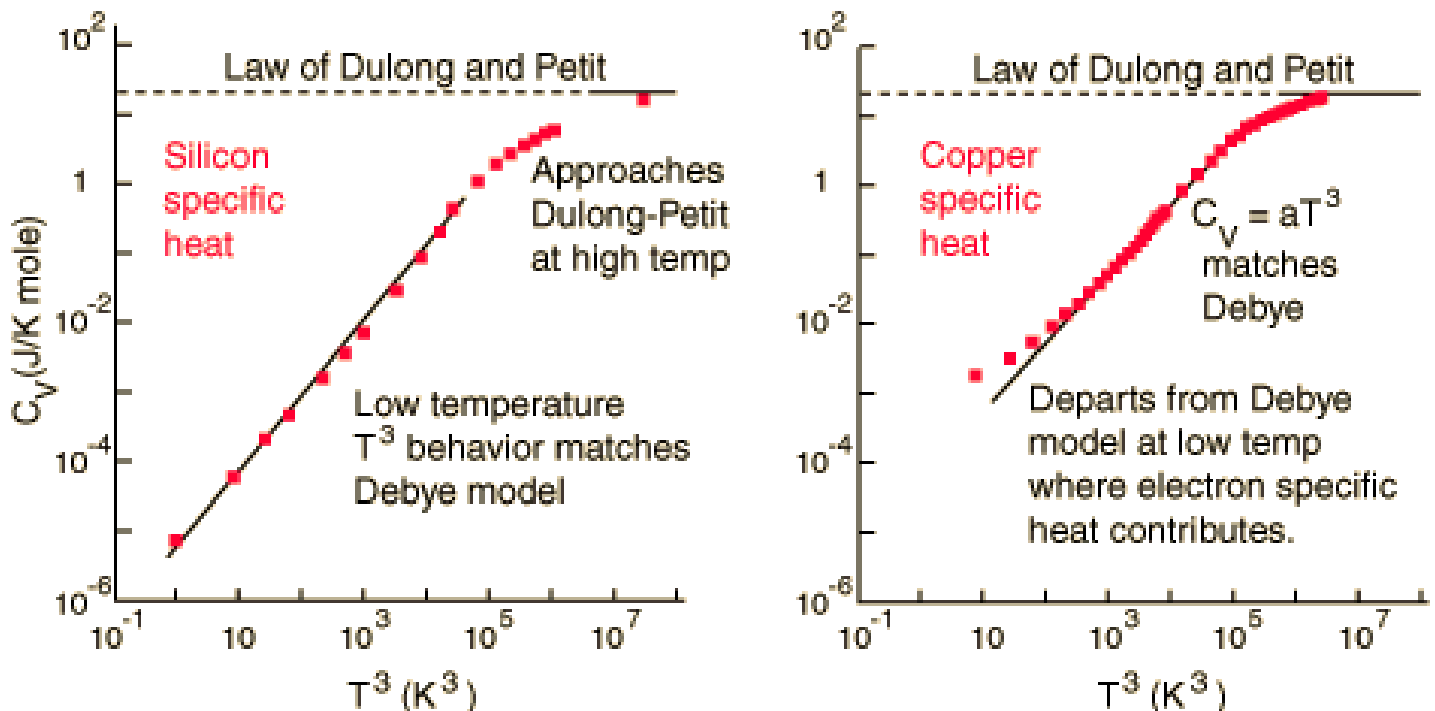
For a harmonic oscillator $\nu = \frac{1}{2\pi} \sqrt{\frac{\text{force constant}}{\text{reduced mass}}}$

Heat capacity of metals – electronic contribution

$c_v = [\partial U/\partial T]_v$ – therefore as soon as energy of electrons are changing with T , they will make contribution to c_v .

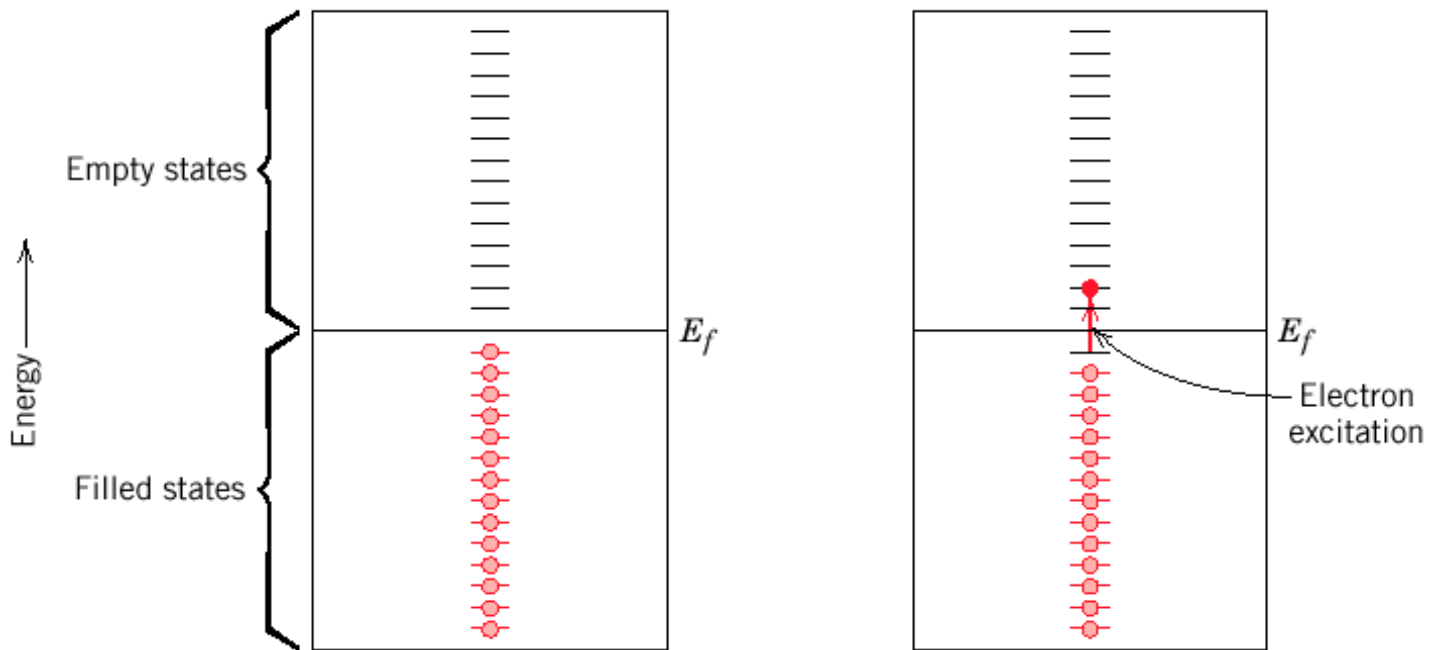
To contribute to bulk specific heat, the valence electrons would have to receive energy from the thermal energy, $\sim k_B T$. But the Fermi energy is much greater than $k_B T$ and the overwhelming majority of the electrons cannot receive such energy since there are no available energy levels within $k_B T$ of their energy.

The small fraction of electrons which are within $k_B T$ of the Fermi level (defined by Fermi-Dirac statistics) does make a small contribution to the specific heat. This contribution is proportional to temperature, $c_v^{el} = \gamma T$ and becomes significant at very low temperatures, when $c_v = \gamma T + AT^3$ (for metals only).

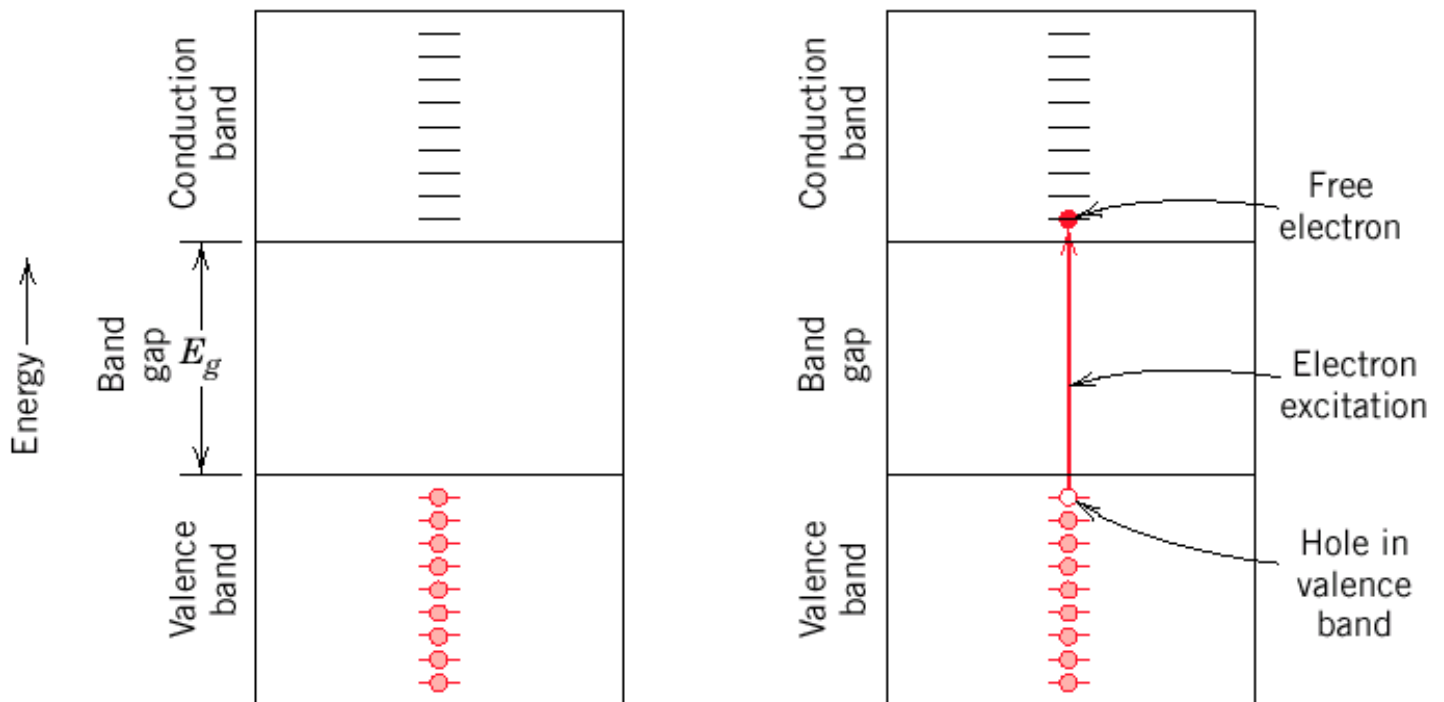


Energy Band Structures

Metals



Semiconductors and Insulators



Summary (1)

Make sure you understand language and concepts:

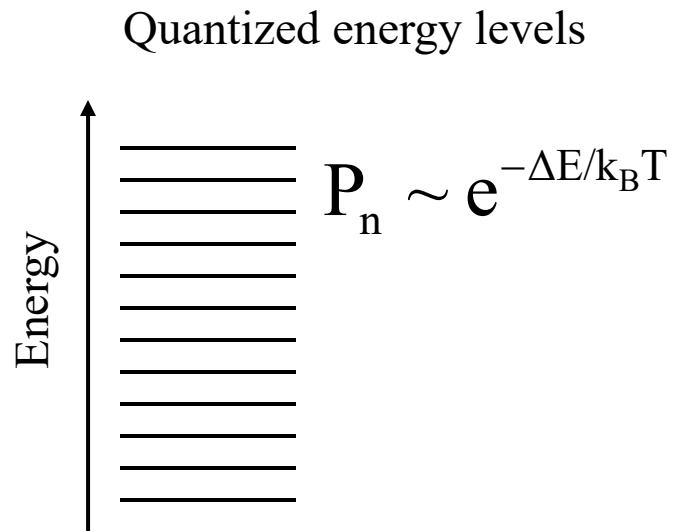
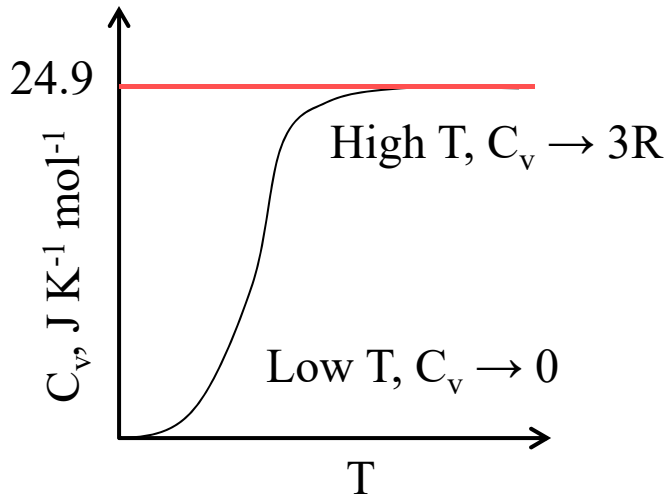
- Degrees of freedom
- Equipartition of energy
- Heat capacity of ideal gas
- Heat capacity of solids: Dulong-Petit law
- Quantum mechanical corrections: Einstein and Debye models

Heat capacity of gas, solid or liquid tends to increase with temperature, due to the increasing number of excited degrees of freedom, requiring more energy to cause the same temperature rise.

The theoretical approaches to heat capacities, discussed in this lecture, are based on rather rough approximations (anharmonicity is neglected, phonon spectrum is approximated by ν^2 in Debye model, etc.). In practice $c_p(T)$ is normally measured experimentally and the results are described analytically, e.g. $C_p = A + BT + CT^2$ for a certain range of temperatures.

Summary (2)

Equipartition theory is only valid if all degrees of freedom are “fully” excited.



$\Delta E \ll k_B T$ - classical behavior

$\Delta E \geq k_B T$ - quantum behavior