Heat Capacity

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1 Heat Capacities of gases

1.1 Monoatomic gases

From 12th grade, the internal energy of monoatomic gases according to the law of equipartition of energy is given as $U = 3(DoF) \times \frac{1}{2}kT$. Since monoatomic gases can only have 3 degrees of freedom and at constant volume $C_v = \frac{dU}{dT}$ we get

$$C_v = \frac{3}{2}RT \; for \; N_A \; particles \; .$$

The experimental results for the heat capacity at constant volume agree with this formulation and hence the quantum theory is not needed in case of monoatomic gases.

1.2 Diatomic gases

From the equipartition theorem we have $C_v = \frac{5}{2}RT$ for diatomic gases as they are assumed to have 5 degrees of freedom, 3 translational and 2 rotational as shown in the figure below.
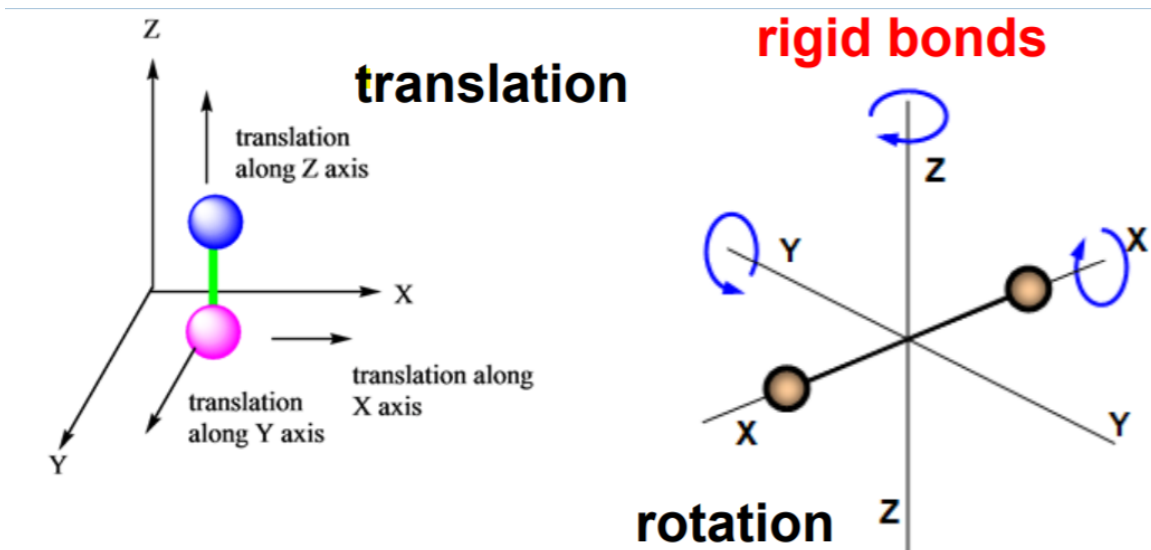

Figure 1: Degrees of freedom of diatomic gases at room temperature.

The classical model assumes the bonds to be rigid at all temperature but in reality they also can oscillate at higher temperatures giving rise to two degrees of vibrational freedom adding on to the initial five. We have two degrees of vibrational freedom due to the kinetic energy of the two atoms as they oscillate and the potential energy of the oscillating bond which can be thought of as a spring connected to two

masses.

This theory does not agree with the experimental results for the heat capacity of diatomic gases over a large range of temperatures as can be seen in figure below.
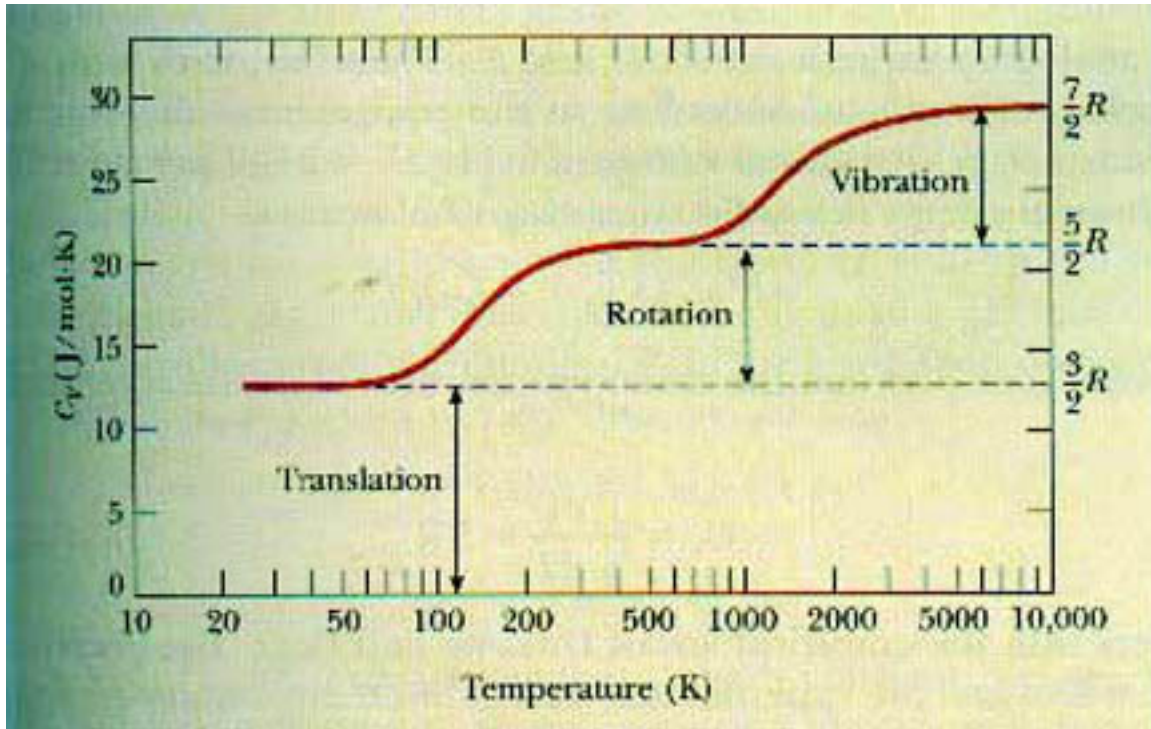

Figure 2: Temperature variation of C_v for diatomic gases

1.3 Quantization of degrees of freedom

As can be seen in the above graph the heat capacity varies with temperature and points towards quantization of motion. Quantum theory determines which degrees of freedom are active at a certain temperature.

Energy Level Picture At low temperatures the translational energy levels are occupied and more and more of them get occupied as temperature increases by small amounts. This is because translational energy levels are quasi-continuous and separated by only 10^{-17}eV. So a small increase in temperature can cause the particles to occupy a significant number of energy levels. Rotational energy levels are more separated as compared to translational, and vibrational energy levels are far apart as can be seen in the image below.
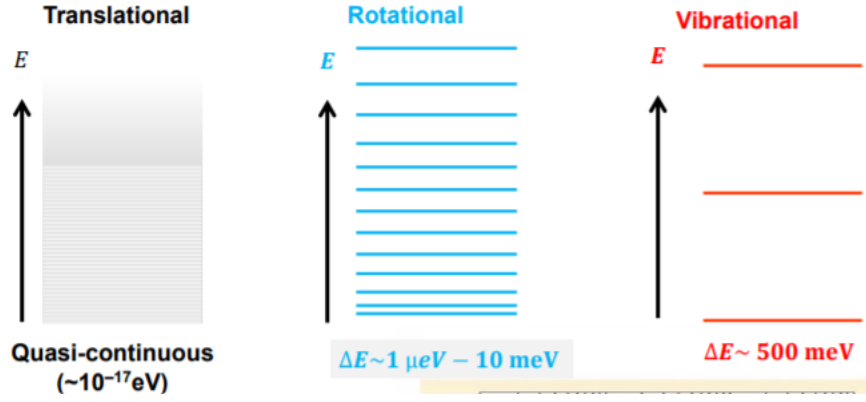
Figure 3: Energy level separation.

2 Heat capacities of solids

2.1 Classical theory

Classical theory states that the atoms in a solid oscillate about their mean position and oscillation in each direction has an average energy of $k_B\text{T}$ hence in three directions the average energy was $3k_B\text{T}$. If we consider one mole of the solid there are N_A atoms thus the internal energy is

$$U = 3k_B T \times N_A = 3RT$$

hence we get

$$C_v = 3R.$$

This means that the heat capacity of solids is independent of temperature however the experimental results were quite different.
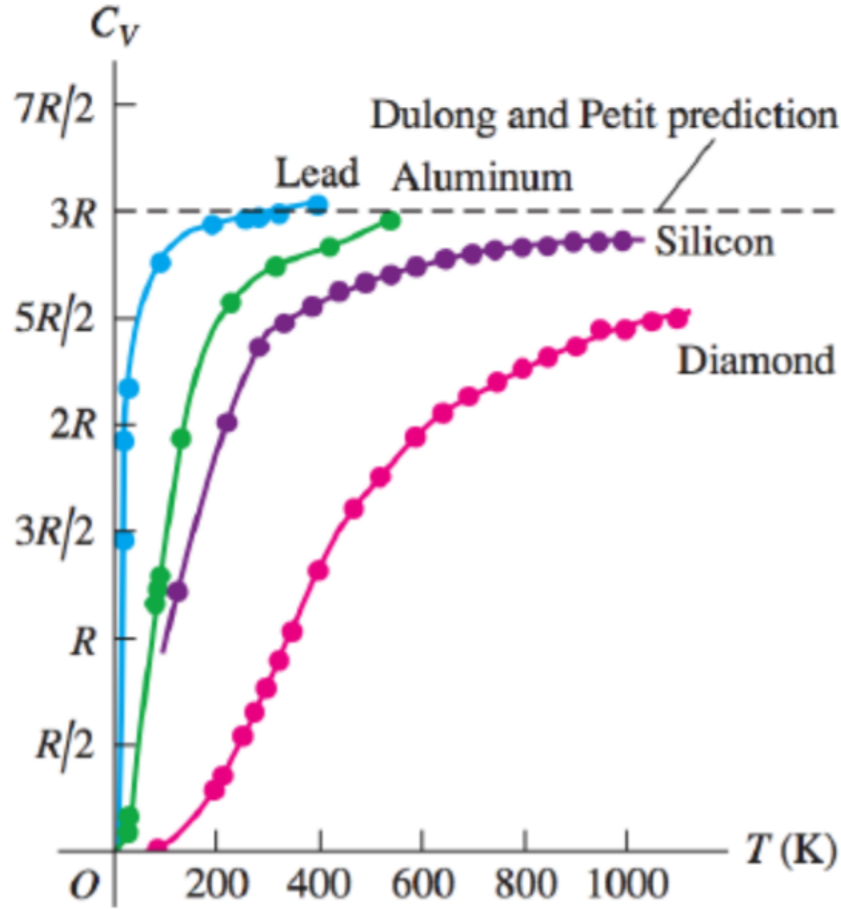
Figure 4: Experimental results for heat capacity of conductors, semi-conductors and insuators.

2.2 Dulong-Petit's law

The law considers atoms in a solid to be classical harmonic oscillators which move in all directions. The equipartition theorem and Boltzmann distributuion gave rise to $< E >= k_B$T. Hence the specific heat of all solids was proposed to be

$$C_v = 3R.$$

This however is true only at high temperatures.

2.3 Einstein model(1906)

- 3N quantized harmonic oscillators in the solid.

- Oscillate independent of each other and with the same characteristic (natural) frequency ν_E.

- Energy of the oscillators is quantized as $E_n = (n + \frac{1}{2})h\nu_E = 1, 2, 3, ...$

- $< E >= \dfrac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}$

- For 3N oscillators,

$$U = \frac{3Nh\nu}{e^{\frac{h\nu}{k_B T}} - 1} = \frac{3Nk_B\theta_E}{e^{\frac{\theta_E}{T}} - 1}$$

Einstein temperature(θ_E)=$\frac{h\nu}{k_B}$. This is a measure of the rigidity of the lattice.

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Case 1: $T >> \theta_E$.

$$exp(\frac{\theta_E}{T}) \approx 1 + \frac{\theta_E}{T}$$

$$\implies U = 3RT \implies C_v = 3R$$

So in limits of very high temperature the Einstein model reduces to the Dulong-Petit law.

Case 2: $T << \theta_E \to exp(\frac{\theta_E}{T}) >> 1$. Therefore,

$$U = 3Nk_B\theta_E e^{\frac{-\theta_E}{T}}$$

$$C_v = \frac{\partial U}{\partial T} = 3Nk_B e^{\frac{-\theta_E}{T}} (\frac{\theta_E}{T})^2$$

2.4   Debye Model

Solid consists of quantized harmonic oscillators however they are not of the same frequency. Oscillators have energy from a zero to a max value v_D which is called the Debye cut-off frequency.

$$\lambda_d = 2d, \quad \text{where d is the distance between atoms}$$

All these frequencies are modes of vibration. Single atoms do not oscillate in a solid but all the atoms are part of quantized vibrations which pass through the solid and are known as **phonons**. Each atom is a part of the imaginary "string" oscillating throughout the solid
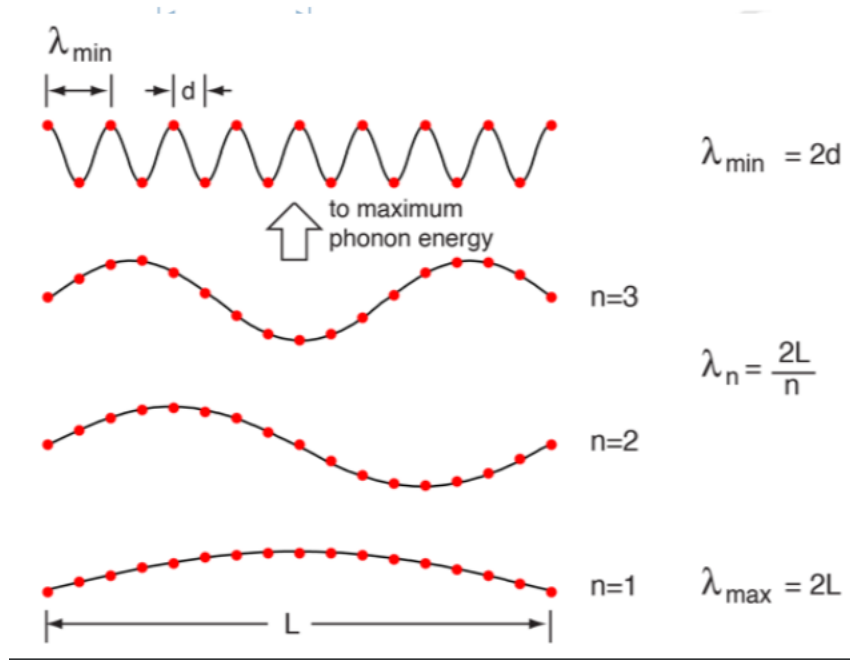

Figure 5: Modes of phonons.

Case 1: At higher temperature, $C_v = 3R$

Case 2: At low temperatures, $C_v = \beta T^3$. β is a constant which can be determined by experiment and is specific to each material. This is known as the Debye third power law. This law however is not applicable to metals, while in non-metals the phonons transfer heat through the solid, in metals the electrons have a dominant contribution in thermal conductivity and at lower temperatures the electron specific heat becomes even more significant. For more details see **electron specific heat.**
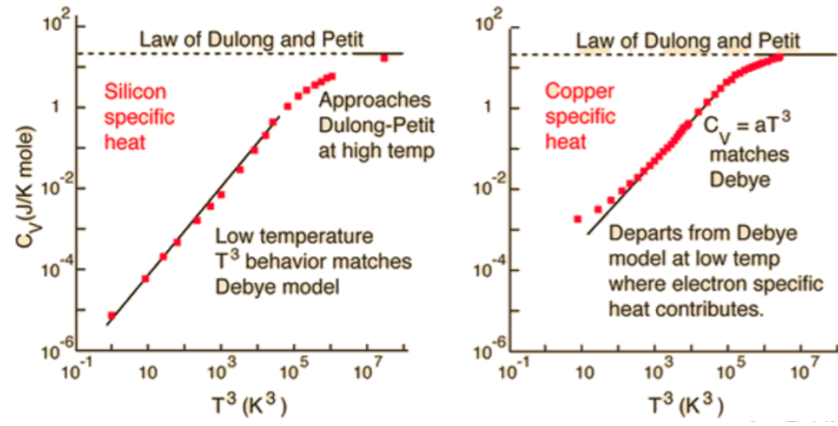
Figure 6: Debye third power law in case of metalloid and metal.