Part V Thermal Properties of Materials

20.1 Classical (Atomistic) Theory of Heat Capacity

Average energy of one-dimensional harmonic oscillator

$$E = k_B T$$

Average energy per atom (three-dimensional harmonic oscillator)

$$E = 3k_B T$$

Average kinetic energy of vibrating atom

$$E = \frac{3}{2} k_B T$$

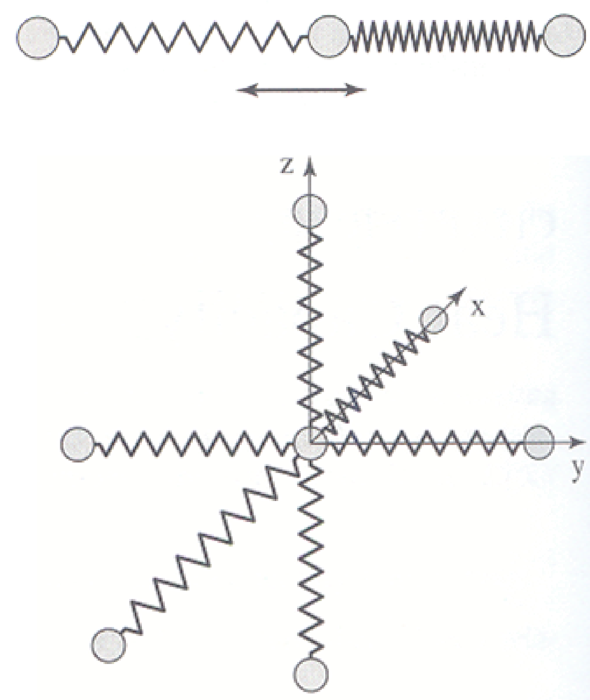


Fig 20.1. (a) A one-dimensional harmonic oscillator and (b) a three-dimensional harmonic oscillator.

20.1 Classical (Atomistic) Theory of Heat Capacity

Average potential energy of vibrating atom has the same average magnitude as the kinetic energy.

So Total energy of vibrating atom has the same average magnitude as the average per atom.

Total internal energy per mole

$$E = 3N_0 k_B T$$

Finally, the molar heat capacity is

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v = 3N_0 k_B$$

Inserting numerical values for N_0 and k_B

$$C_v = 25\ \text{J/mol}\cdot\text{K} = 5.98\ \text{cal/mol}\cdot\text{K}$$

20.2 Quantum Mechanical Considerations-The Phonon

20.2.1 Einstein Model

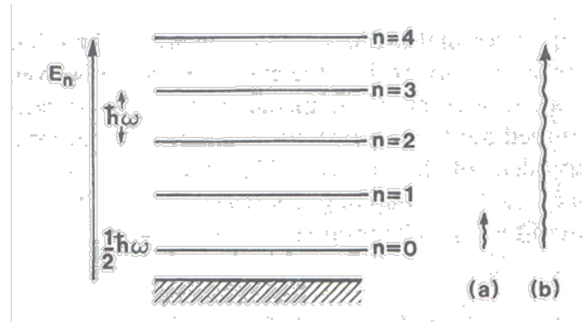


Fig 20.2. Allowed energy levels of a phonon: (a) average thermal energy at low temperatures and (b) average thermal energy at high temperatures.

The energy of the i th energy level of a harmonic oscillator

$$\varepsilon_i = \left(i + \frac{1}{2}\right) hv$$

h = Planck's constant of action

v = frequency of harmonic oscillator

The energy of Einstein crystal (which can be considered to be a system of 3n linear harmonic oscillator)

$$U' = 3\sum n_i \varepsilon_i = 3\sum \left(i + \frac{1}{2}\right) hv \boxed{\left(\frac{ne^{-hv(i+\frac{1}{2})/kT}}{\sum e^{-hv(i+\frac{1}{2})/kT}} \right)}$$

$$n_i = \frac{ne^{-\beta\varepsilon_i}}{P} \quad \text{(P : partition function)}$$

$$= 3nhv \left(\frac{\sum ie^{-hv(i+\frac{1}{2})/kT}}{\sum e^{-hv(i+\frac{1}{2})/kT}} + \frac{\frac{1}{2}\sum e^{-hv(i+\frac{1}{2})/kT}}{\sum e^{-hv(i+\frac{1}{2})/kT}} \right) = 3nhv \left(\frac{\sum ie^{-hvi/kT}}{\sum e^{-hvi/kT}} + \frac{1}{2} \right)$$

$$= \frac{3}{2} nhv \left(1 + \frac{2\sum ie^{-hvi/kT}}{\sum e^{-hvi/kT}} \right)$$

20.2 Quantum Mechanical Considerations-The Phonon

Taking

$$\sum ie^{-h\nu i/kT} = \sum ix^{i}$$

where $x = e^{-h\nu/kT}$ **gives,**

$$x(1+2x+3x^{2}+\cdots) = \frac{x}{(1-x)^{2}}$$

and

$$\sum e^{-h\nu i/kT} = \sum x^{i} = 1+x+x^{2}+\cdots = \frac{1}{1-x}$$

in which case

$$U' = \frac{3}{2}nh\nu\left(1+\frac{2x}{1-x}\right) = \frac{3}{2}nh\nu\left(1+\frac{2e^{-h\nu/kT}}{1-e^{-h\nu/kT}}\right)$$

$$= \frac{3}{2}nh\nu + \frac{3nh\nu}{e^{h\nu/kT}-1}$$

20.2 Quantum Mechanical Considerations-The Phonon

Heat capacity at a constant volume

$$C_v = \left(\frac{\partial U'}{\partial T}\right)_v = 3nh\nu(e^{h\nu/kT} - 1)^{-2}\frac{h\nu}{kT^2}e^{h\nu/kT}$$

$$= 3nk\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

Einstein temperature is

$$\theta_E = \frac{h\nu}{k}$$

So,

$$c_v = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

20.2.2 Debye Model

Total energy of vibration for the solid

$$E = \int E_{osc} D(\omega) d\omega$$

E_{osc} = the energy of one oscillator

$$D(\omega) = \frac{3V\omega^2}{2\pi^2 \upsilon_s^3}$$

$$E = \frac{3V}{2\pi^2 \upsilon_s^3} \int_0^{\omega_D} \frac{\hbar\omega^3}{e^{\hbar\omega/kT} - 1} d\omega$$

ω_D = debye frequency

Heat capacity at a constant volume

$$C_v = \frac{3V\hbar^2}{2\pi^2 \upsilon_s^3 k T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\hbar\omega/kT}}{(e^{\hbar\omega/kT} - 1)^2} d\omega$$

Or indicating with Debye temperature θ_D

$$C_v^{ph} = 9kn \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} d\omega \qquad x = \frac{\hbar\omega}{kT} = \frac{hv}{kT}, \qquad \theta_D = \frac{\hbar\omega_D}{k} = \frac{hv_D}{k}$$

20.3 Electronic Contribution to The Heat Capacity

Thermal energy at given temperature

$$E_{\mathrm{kin}} = \frac{3}{2} k_{\mathrm{B}} T dN = \frac{3}{2} k_B T N(E_{\mathrm{F}}) k_{\mathrm{B}} T$$

The Heat capacity of the electrons

$$C_{\mathrm{v}}^{\mathrm{el}} = \left(\frac{\partial E}{\partial T}\right)_{\mathrm{v}} = 3 k_{\mathrm{B}}^2 T N(E_{\mathrm{F}})$$

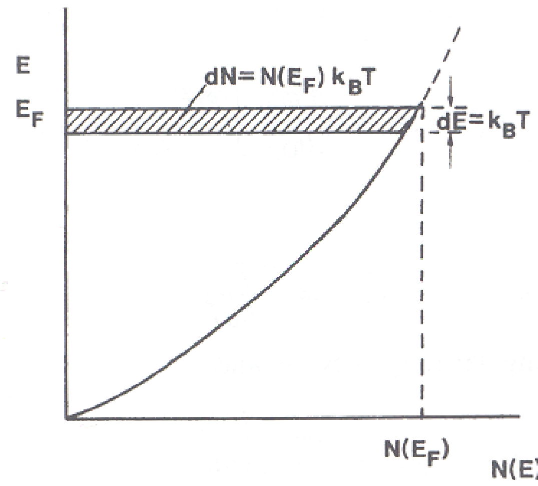


Figure 20.3. Population density as a function of energy for a metal. The electrons within the shaded area below E_{F} can be excited by a thermal energy $k_{\mathrm{B}}T$.

For E < E_F

$$N(E_{\mathrm{F}}) = \frac{3N^*}{2E_{\mathrm{F}}} \left(\frac{\text{electrons}}{\mathrm{J}}\right)$$

$N^* =$ number of eletrons which have an energy equal to or smaller than E_{F}

$$C_{\mathrm{v}}^{\mathrm{el}} = \left(\frac{\partial E}{\partial T}\right)_{\mathrm{v}} = 3 k_{\mathrm{B}}^2 T \frac{3N^*}{2E_{\mathrm{F}}} = \frac{9}{2} \frac{N^* k_{\mathrm{B}}^2 T}{E_{\mathrm{F}}} \quad \left(\frac{\mathrm{J}}{\mathrm{K}}\right)$$

So far, we assumed that the thermally excited electrons behave like a classical gas.

20.2 Quantum Mechanical Considerations-The Phonon

In reality, the excited electrons must obey the Pauli principle. So,

$$C_{\mathrm{v}}^{\mathrm{el}} = \frac{\pi^2}{2} \frac{N^* k_{\mathrm{B}}^2 T}{E_{\mathrm{F}}} = \frac{\pi^2}{2} N^* k_{\mathrm{B}} \frac{T}{T_{\mathrm{F}}}$$

If we assume a monovalent metal in which we can reasonably assume one free electron per atom, N^* can be equated to the number of atoms per mole.

$$C_{\mathrm{v}}^{\mathrm{el}} = \frac{\pi^2}{2} \frac{N_0 k_{\mathrm{B}}^2 T}{E_{\mathrm{F}}} = \frac{\pi^2}{2} N_0 k_{\mathrm{B}} \frac{T}{T_{\mathrm{F}}} \qquad \left(\frac{\mathrm{J}}{\mathrm{K} \cdot \mathrm{mol}} \right)$$

Below the Debye temperature, the heat capacity of metals is sum of electron and phonon contributions.

$$C_{\mathrm{v}}^{\mathrm{tot}} = C_{\mathrm{v}}^{\mathrm{el}} + C_{\mathrm{v}}^{\mathrm{ph}} = \gamma T + \beta T^3$$

$$\therefore \ \frac{C_{\mathrm{v}}^{\mathrm{tot}}}{T} = \gamma + \beta T^2$$

$$\gamma = 3k_B^2 N(EF)$$

$$\beta = 9kn \left(\frac{1}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} d\omega$$

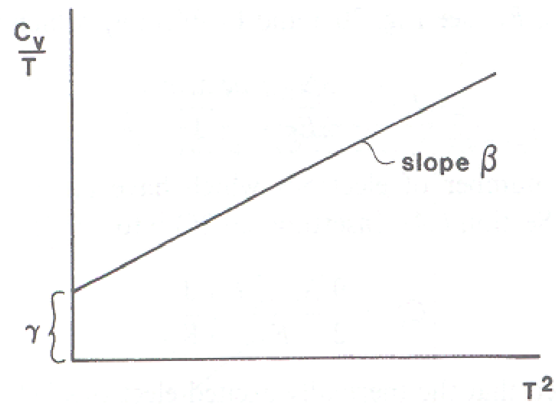


Figure 20.4. Schematic representation of an experimental plot of C_v/T versus T^2.

20.2 Quantum Mechanical Considerations-The Phonon

Thermal effective mass

$$\frac{m_{th}^*}{m_0} = \frac{\gamma(\text{obs.})}{\gamma(\text{calc.})}$$

Table 20.1. Calculated and Observed Values for the Constant γ, see (20.31).

Substance	γ, observed $\left(\frac{\text{J}}{\text{mol} \cdot \text{K}^2}\right)$	γ, calculated $\left(\frac{\text{J}}{\text{mol} \cdot \text{K}^2}\right)$	$\frac{m_{th}^*}{m_0}$
Ag	0.646×10^{-3}	0.645×10^{-3}	1.0
Al	1.35×10^{-3}	0.912×10^{-3}	1.48
Au	0.729×10^{-3}	0.642×10^{-3}	1.14
Na	1.3×10^{-3}	0.992×10^{-3}	1.31
Fe	4.98×10^{-3}	—	—
Ni	7.02×10^{-3}	—	—

Part V Thermal Properties of Materials

Chap. 18 Introduction

Chap. 19 Fundamentals of Thermal Properties

Chap. 20 Heat Capacity

Chap. 21 Thermal Conduction

Chap. 22 Thermal Expansion

21.3 Thermal Conduction in Metals and Alloys Classical Approach

From the kinetic theory of gases

$$E_1 = z \cdot \frac{3}{2} k_B (T_o + l(-\frac{dT}{dx})) = \frac{n_V v}{6} \frac{3}{2} k_B (T - l\frac{dT}{dx})$$

$$(\because \ z = \frac{1}{6} n_V v, \quad n_V = \frac{N}{V})$$

$$E_2 = \frac{n_V v}{6} \frac{3}{2} k_B (T + l\frac{dT}{dx})$$

$$J_0 = E_2 - E_1 = -\frac{n_V v}{6} \frac{3}{2} k_B (2l\frac{dT}{dx}) = -\frac{n_V v}{2} k_B l \frac{dT}{dx}$$

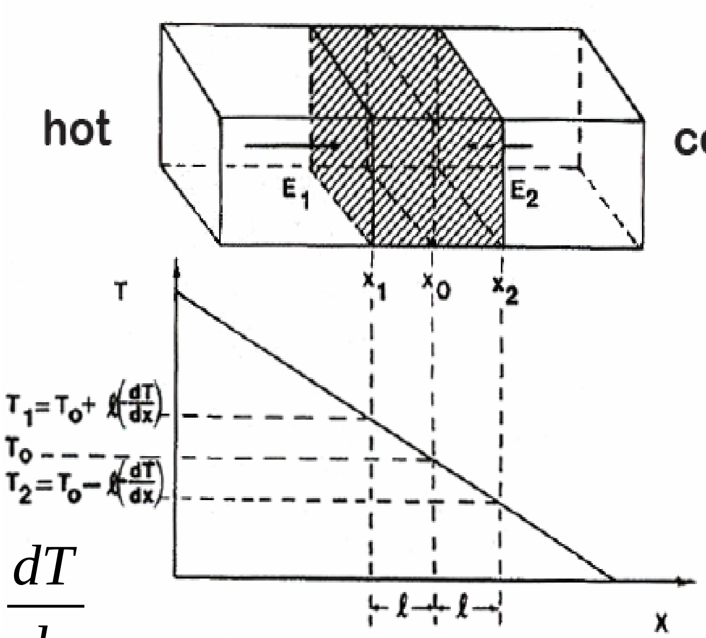


Fig 21.1. For the derivation of the heat conductivity in metals. Note that (dT/dx) is negative for the case shown in the graph.

21.3 Thermal Conduction in Metals and Alloys Classical Approach

$$J_Q = -\frac{n_V v}{2} k_B l \frac{dT}{dx}$$

$$J_Q = -K \frac{dT}{dx}$$

$$\boxed{K = \frac{n_V v k_B l}{2}}$$

Relation between the heat conductivity and C_v^{el}

$$E = n_V \tfrac{3}{2} k_B T \quad , \quad C_V^{el} = \left(\frac{dE}{dT}\right)_V = n_V \tfrac{3}{2} k_B$$

$$\boxed{K = \frac{1}{3} C_v^{el} v l}$$

21.2 Thermal Conduction in Metals and Alloys-Quantum Mechanical Considerations

Do all the electrons participate in the heat conduction?

- *No, Only those electrons which have an energy close to the Fermi energy participate in the heat conduction*

$$E_F = \frac{1}{2} m v_F^2$$

$$C_V^{el} = \frac{\pi^2}{2} \frac{N_f k_B^2 T}{E_F} = \frac{1}{3} \frac{\pi^2}{2} \frac{N_f k_B^2 T}{E_F} v_F l_F = \frac{\pi^2 N_f k_B^2 T v_F l_F}{6 E_F}$$

$$K = \frac{1}{3} C_V^{el} v_F l_F$$

21.2 Thermal Conduction in Metals and Alloys-Quantum Mechanical Considerations

$$\boxed{K = \frac{\pi^2 N_f k_B^2 T \tau}{3m^*}}$$

$$\sigma = \frac{N_f e^2 \tau}{m^*}$$

$$\frac{K}{\sigma T} = L = \frac{\pi^2 k_B^2}{3e^2} \; (= 2.443 \times 10^{-8} \; J\text{-}\Omega / K^2 \cdot s$$

$$= 5.8 \times 10^{-9} \; cal\text{-}\Omega / K^2 \cdot s)$$

(Lorentz number)

21.3 Thermal Conduction in Dielectric Materials

Heat conduction in dielectric materials occurs by a flow of phonons.

$$\boxed{K = \frac{1}{3} C_v^{ph} v l}$$

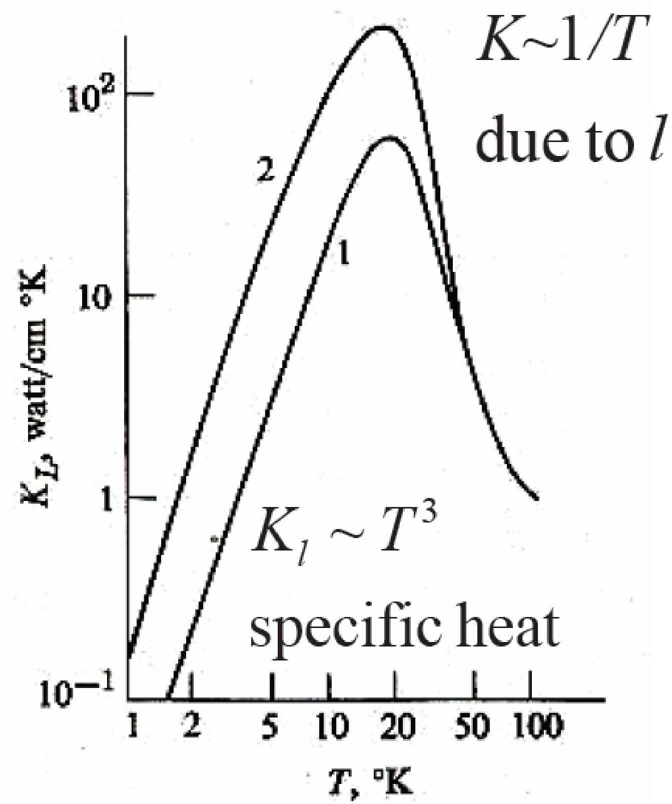
At low temperatures

Only a few phonons exist, the thermal conductivity depends mainly on the heat capacity C_v^{ph} which increses with the low temperatures.

At higher temperature

The phonon-phonon interactions are dominant, the phonon density increases with increasing T.

Thus the mean free path and the thermal conductivity decreases for temperatures



21.3 Thermal Conduction in Dielectric Materials

Umklapp Process

When two phonons collide, a third phonon results in a proper manner to conserve momentum. Phonons can be represented to travel in k-space.

$$\overrightarrow{a_1} + \overrightarrow{a_2} = \overrightarrow{a_3} + \overrightarrow{G}$$

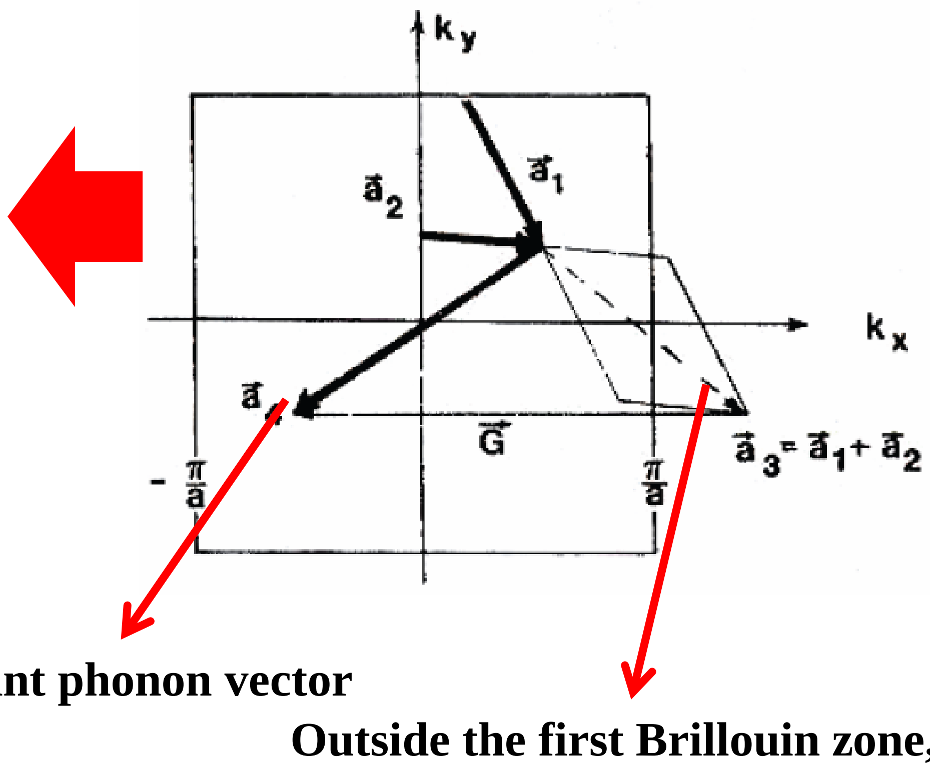


Fig 21.2. Schematic representation of the thermal conductivity in dielectric materials as a function of temperature.

After the collision in a direction that is almost opposite to a_2

Part V Thermal Properties of Materials

Chap. 18 Introduction

Chap. 19 Fundamentals of Thermal Properties

Chap. 20 Heat Capacity

Chap. 21 Thermal Conduction

Chap. 22 Thermal Expansion

22 Thermal Expansion

α_L : **Coefficient of linear expansion**

The length L of a rod increases with increasing temperature

$$\frac{\Delta L}{L} = \alpha_L \Delta T \quad , \quad \frac{\Delta V}{V_o} = \alpha_v \Delta T$$

Atomistic point of view

For small temperature
: a atom may rest in its equilibrium position

As temperature increases
the amplitudes of the vibrating atom increases

Because potential curve is not symmetric, a atom moves farther apart from its neighbor

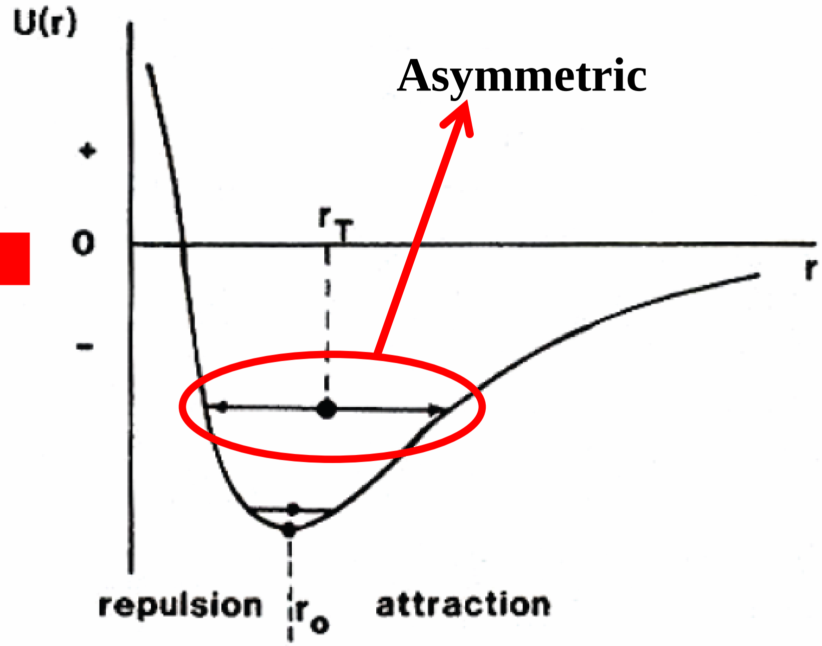


Fig 22.1. Schematic representation of the potential energy, $U(r)$, for two adjacent atoms as a function of internuclear separation, r.