Phonon entropy = vibrational entropy = lattice entropy

Debye model heat capacity for $T \ll \Theta_D$

$$C_V = \frac{12\pi^4}{5} N k_B \left(\frac{T}{\Theta_D}\right)^3$$

$$\Theta_D = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3}$$

entropy:

$$\Delta S = \int_{T'=0}^{T} \frac{C_V(T')}{T'}\, dT'$$

$$\frac{N}{V} \equiv n$$

number density

$$S(T) - \cancelto{0}{S(0)} = \frac{12\pi^4}{5} N k_B \frac{1}{\Theta_D^3} \underbrace{\int_0^T (T')^2\, dT'}_{T^3/3}$$

$$S(T) = \frac{\cancelto{4}{12}}{\cancelto{5}{15}} \pi^4 N k_B \left(\frac{T}{\Theta_D}\right)^3$$

More accurate Debye model.

$$v \rightarrow \begin{cases} v_L & \text{longitudinal speed} \\ v_T & \text{transverse speed} \end{cases}$$

Density of states

$$D_{LA}(\omega) = \frac{V\omega^2}{2\pi^2 v_L^3} \quad ; \quad D_{TA}(\omega) = \frac{V\omega^2}{2\pi^2 v_T^3} \times \underset{\substack{\uparrow \\ \text{2 polarizations}}}{2}$$

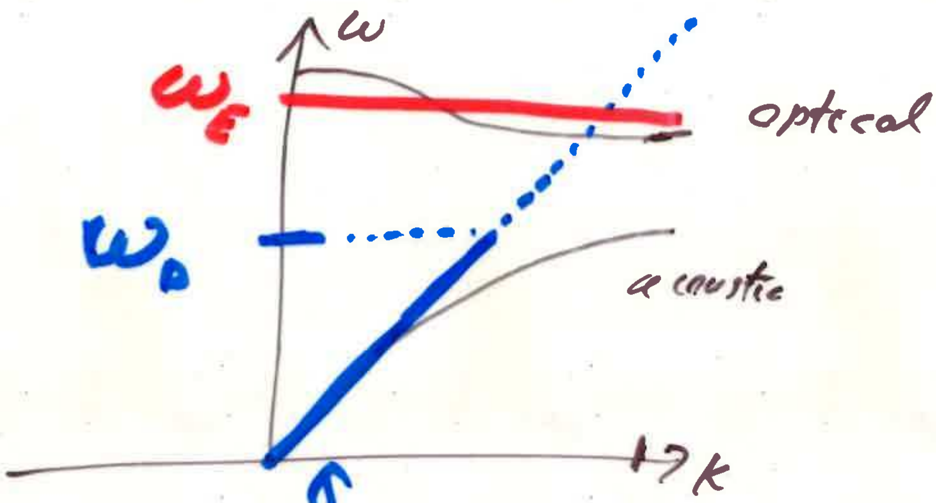
$$D_{tot}(\omega) = D_{LA}(\omega) + D_{TA}(\omega) = \frac{V\omega^2}{2\pi^2}\left(\frac{1}{v_L^3} + \frac{2}{v_T^3}\right)$$

$$3N = \int_0^{\omega_D} \left[D_{LA}(\omega) + D_{TA}(\omega) \right] d\omega$$

$$\Rightarrow \omega_D^3 = \frac{6\pi^2 N}{V}\left[\frac{3}{\frac{1}{v_L^3} + \frac{2}{v_T^3}}\right]$$

$$D_{tot}(\omega) = \frac{9N\omega^2}{\omega_D^3}$$

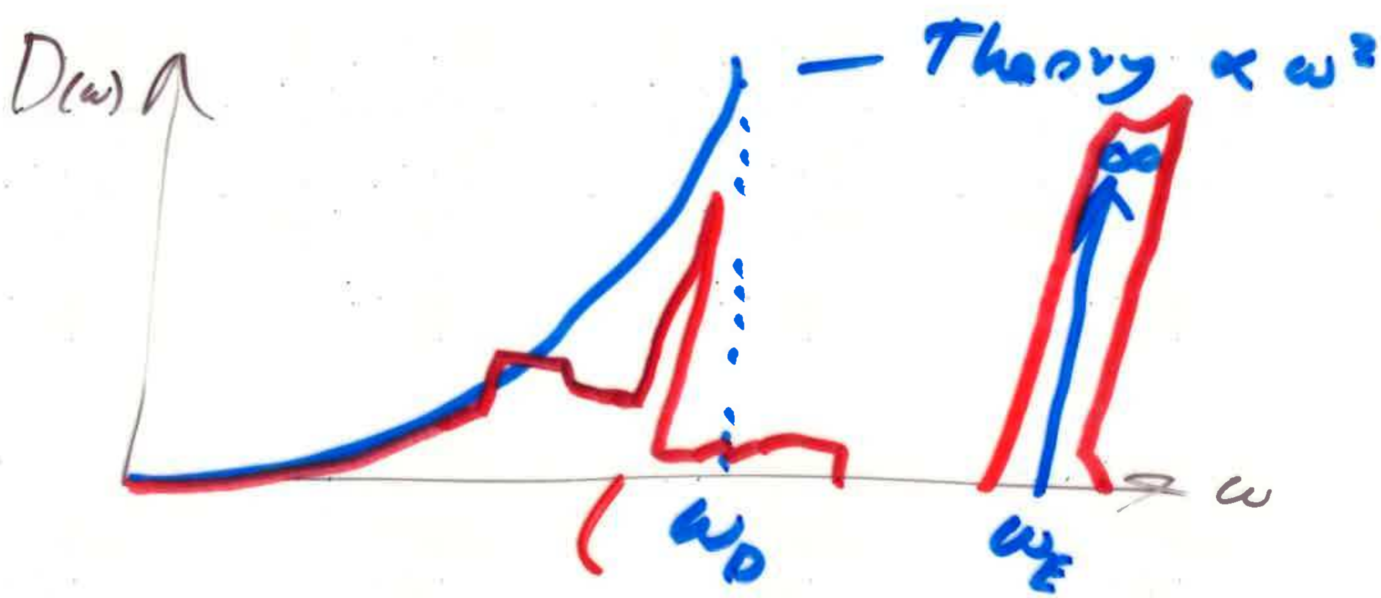
Dispersion Relations for a crystal with a polyatomic basis



Einstein $\omega = \omega_E =$ constant

slope = speed of sound = v

Debye : $\omega = vk$



Data

Spikes in $D(\omega)$ occur when $v = 0$

Van Hove singularities

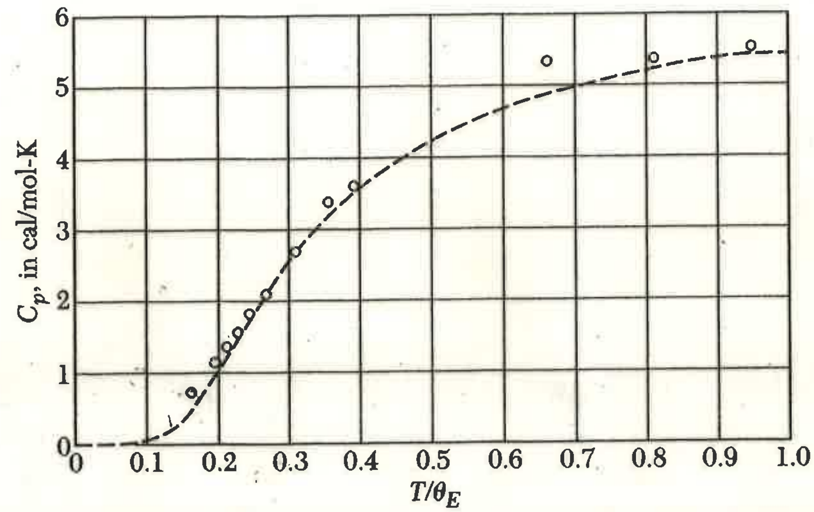


Figure 11 Comparison of experimental values of the heat capacity of diamond with values calculated on the earliest quantum (Einstein) model, using the characteristic temperature $\theta_E = \hbar\omega/k_B = 1320$ K. To convert to J/mol-deg, multiply by 4.186.

$$k_B T_E = \hbar \omega_E$$

$$\theta_E = T_E = \frac{\hbar \omega_E}{k_B}$$

Einstein Temperature

Heat Capacity (Phonons)

p-atomic basis

$$C_V = C_{V_{Debye}} + C_{V_{Einstein}}$$

acoustic

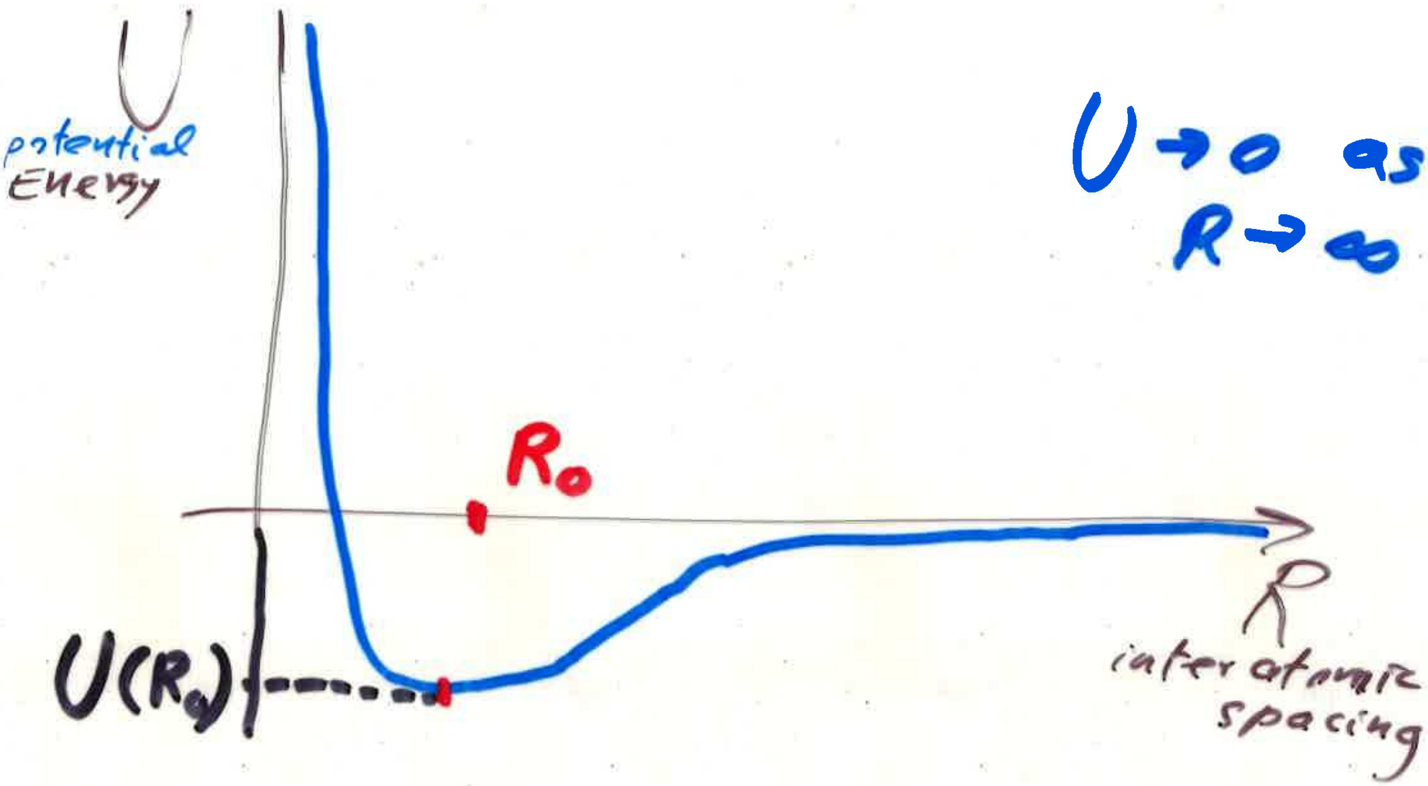
1 Long + 2 Trans.

3 branches $\propto T^3$

optical $\propto e^{-\frac{1}{T}}$

$3p-3$ optical branches

$U \to 0$ as $R \to \infty$



$$U(R) = U(R_0) + \cancel{\left.\frac{dU}{dR}\right|_{R_0}(R-R_0)} \to 0$$

Hooke's Law

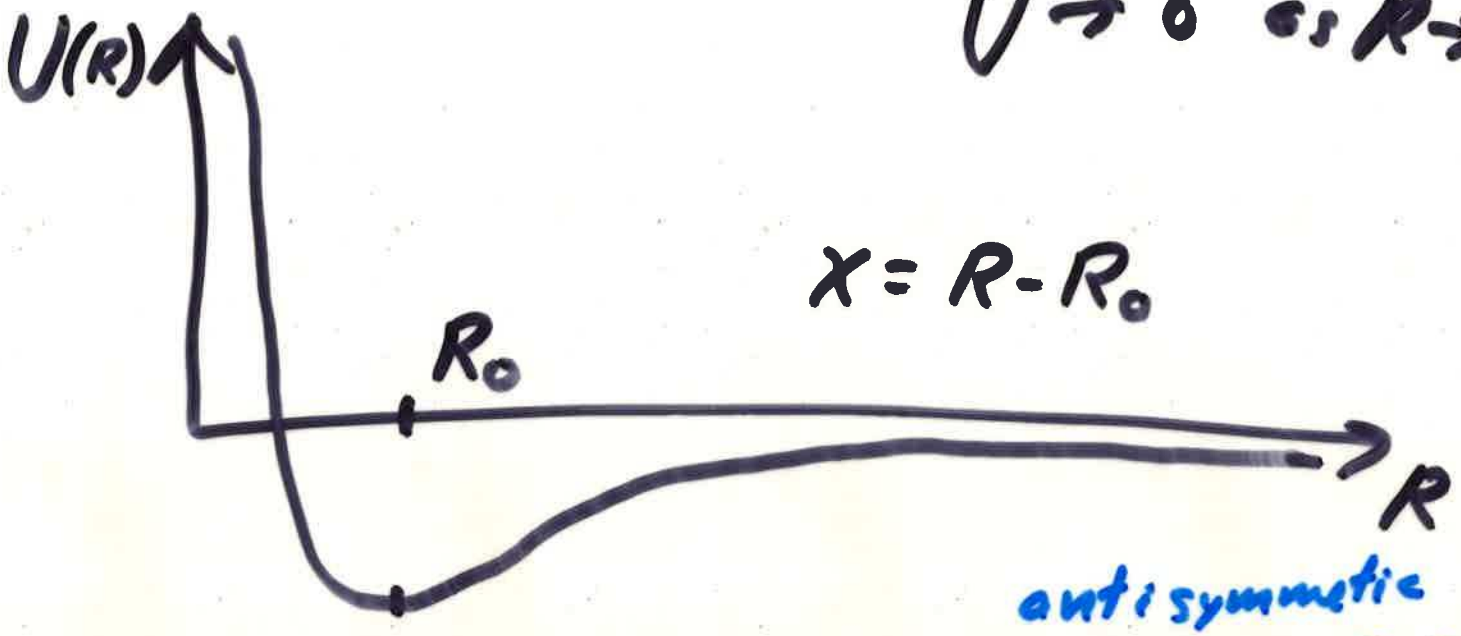
$$c = \boxed{\frac{1}{2!}\left.\frac{d^2U}{dR^2}\right|_{R_0}} \quad + \boxed{\frac{1}{2!}\left.\frac{d^2U}{dR^2}\right|_{R_0}}(R-R_0)^2 \text{ — harmonic}$$

$$-g = \quad + \boxed{\frac{1}{3!}\left.\frac{d^3U}{dR^3}\right|_{R_0}}(R-R_0)^3$$

$$-f = \quad + \boxed{\frac{1}{4!}\left.\frac{d^4U}{dR^4}\right|_{R_0}}(R-R_0)^4, \ldots$$

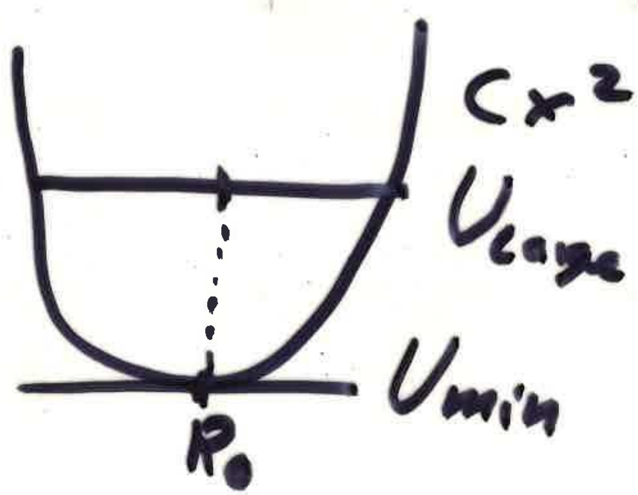
anharmonic

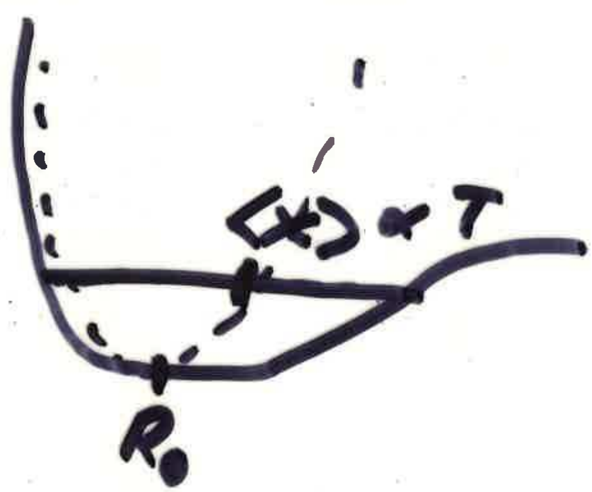
$U \to 0$ as $R \to \infty$

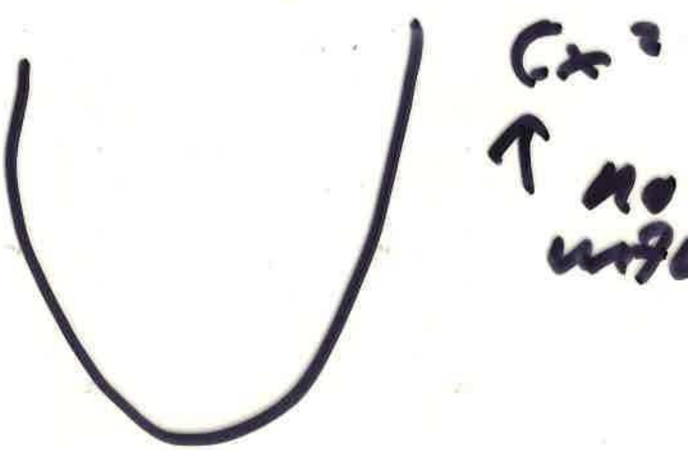


$$X = R - R_0$$

$$U(x) = U_0 + Cx^2 + \underbrace{\overbrace{-gx^3}^{\text{antisymmetric}} \overbrace{- fx^4}^{\text{symmetric}}}_{\text{anharmonic}} + \ldots$$

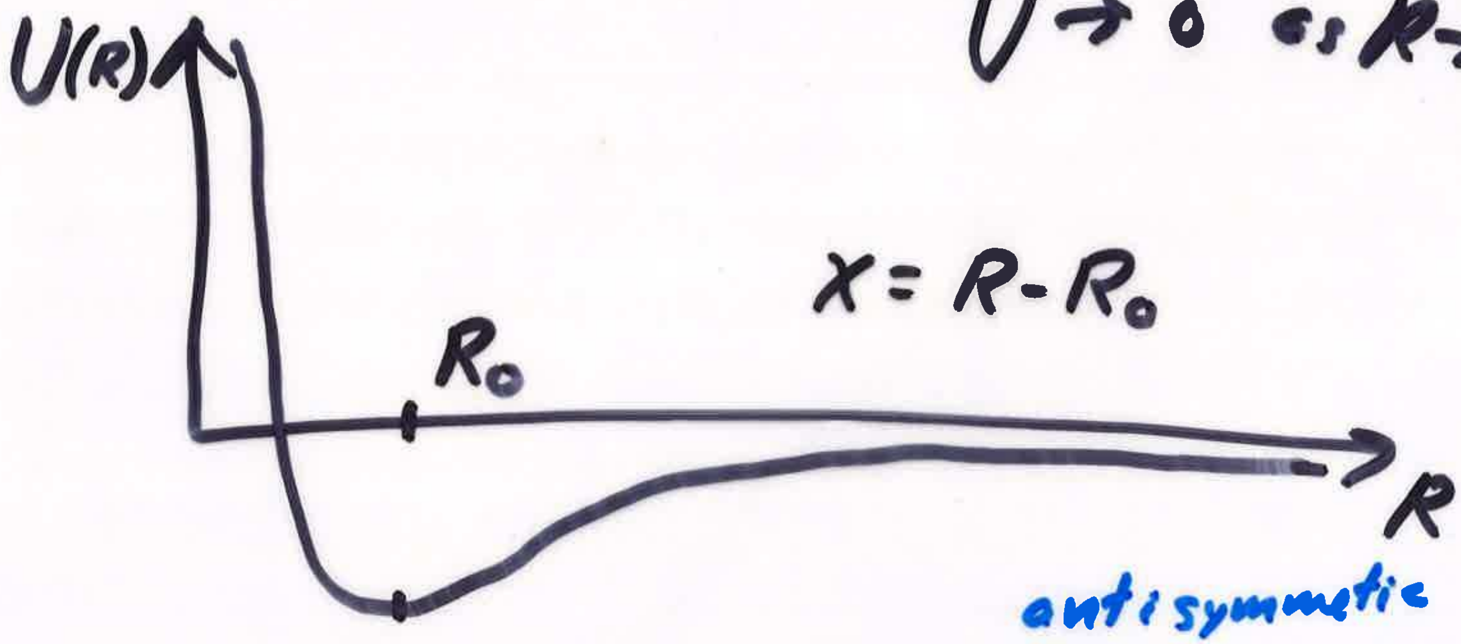






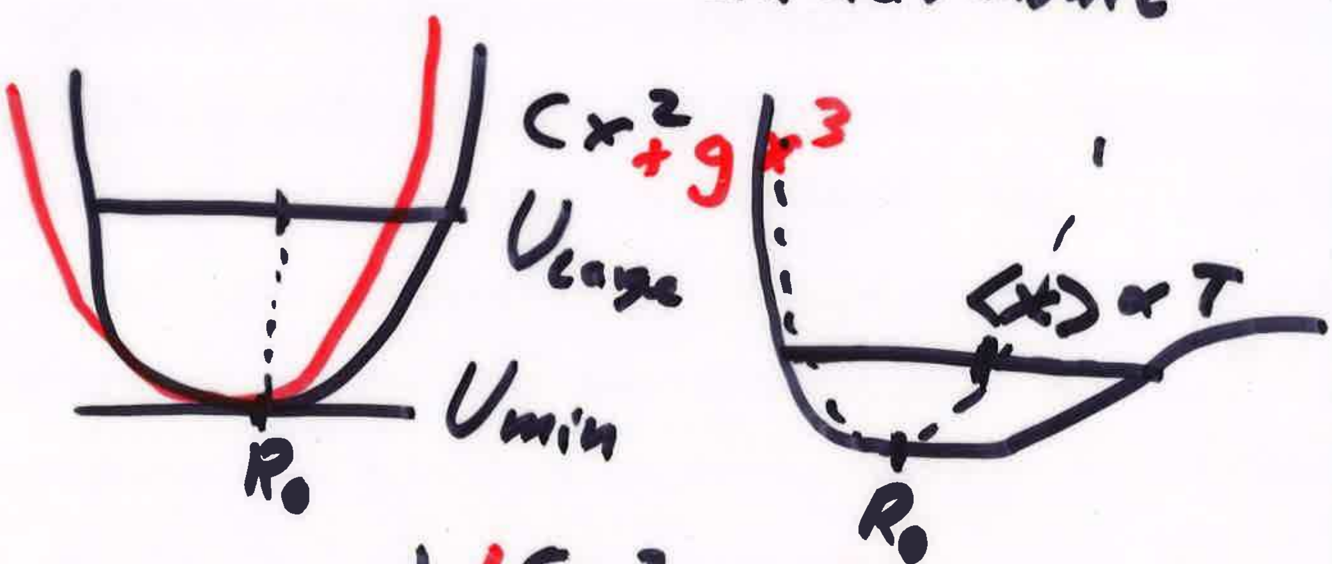
↑ no thermal expansion with only harmonic term

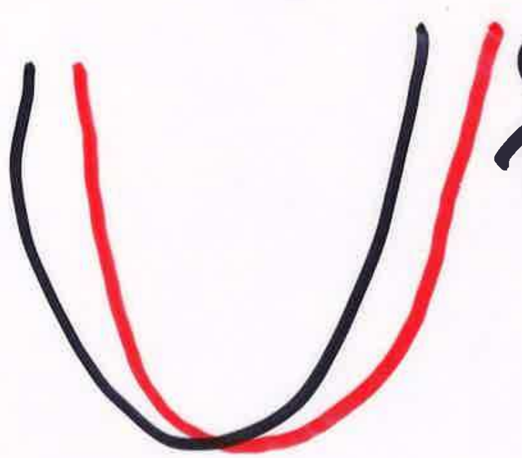
$U \to 0$ as $R \to \infty$



$x = R - R_0$

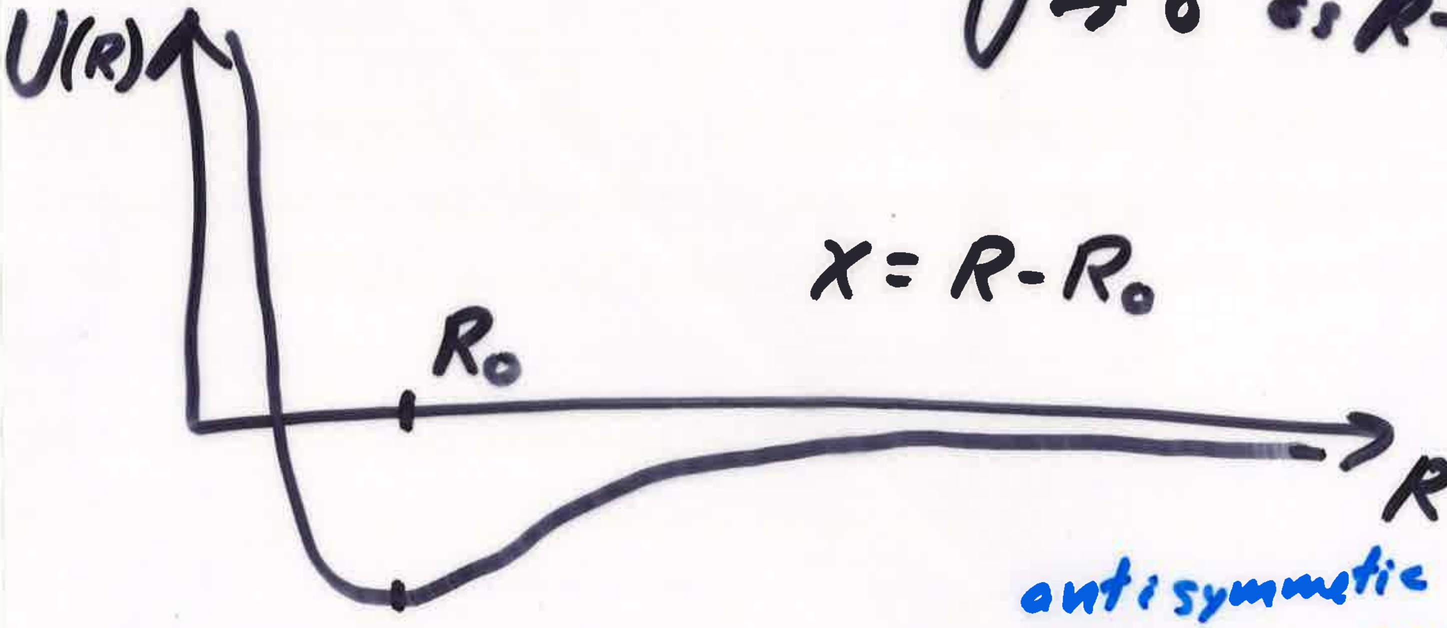
$$U(x) = U_0 + Cx^2 + \underbrace{\overbrace{-gx^3}^{\text{antisymmetric}} \overbrace{- fx^4}^{\text{symmetric}} + \dots}_{\text{anharmonic}}$$





↑ as the usual expansion with only harmonic term

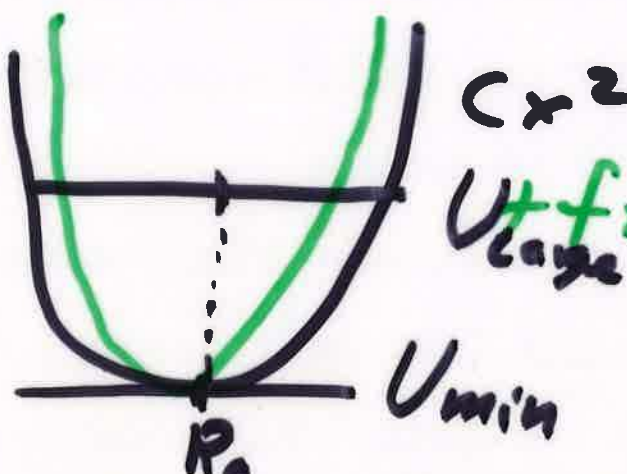
$U \to 0$ as $R \to \infty$

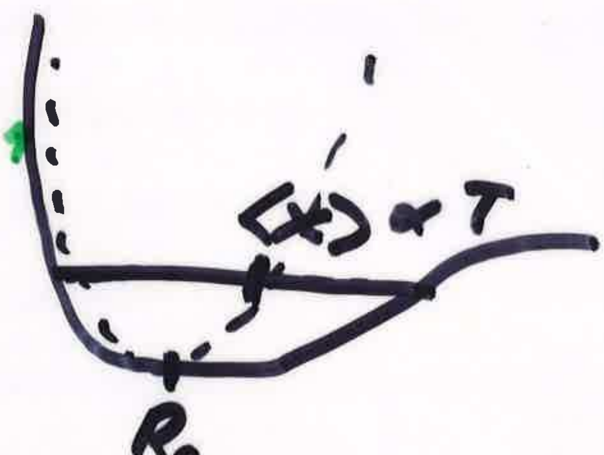


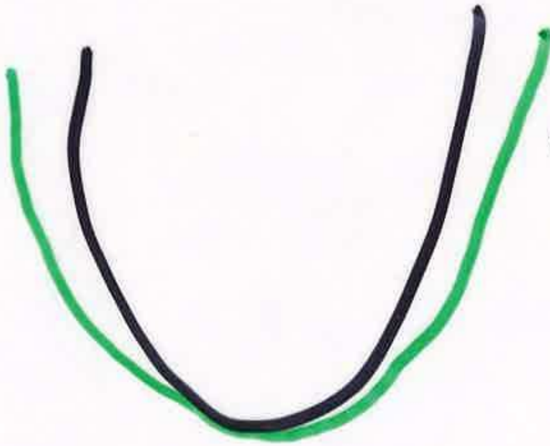
$x = R - R_0$

$$U(x) = U_0 + Cx^2 + \overbrace{-gx^3}^{\text{antisymmetric}} \overbrace{- fx^4}^{\text{symmetric}} + \dots$$

$\underbrace{-gx^3 - fx^4}_{\text{anharmonic}}$







do the usual expansion with only harmonic term

Define $x = R - R_0$ set $U(R_0) = 0$

$$U(x) = cx^2 - gx^3 - fx^4 + \cdots$$

Average Displacement

$$\langle x \rangle = \frac{\sum x\,p(x)}{\sum P(x)} = \frac{\int_{-\infty}^{+\infty} x\, e^{-\frac{U(x)}{k_B T}}\,dx}{\int_{-\infty}^{+\infty} e^{-\frac{U(x)}{k_B T}}\,dx}$$

Numerator

$$x\, e^{-\frac{cx^2 - gx^3 - fx^4}{k_B T}} = x\, e^{-\frac{cx^2}{k_B T}} \cdot e^{\frac{gx^3 + fx^4}{k_B T}}$$

Taylor expand last term

$$\approx x\, e^{-\frac{cx^2}{k_B T}} \left[1 + \frac{gx^3}{k_B T} + \frac{fx^4}{k_B T} + \cdots\right]$$

$$= e^{-\frac{cx^2}{k_B T}} \left[x + \frac{gx^4}{k_B T} + \frac{fx^5}{k_B T} + \cdots\right]$$

Denominator

$$e^{-\frac{U(x)}{k_BT}} = e^{-\frac{cx^2}{k_BT}} \cdot e^{\frac{gx^3+fx^4}{k_BT}}$$

Taylor expand

$$\approx e^{-\frac{cx^2}{k_BT}}\left[1+\dots\right]$$

Num. $\int x\, e^{-\frac{U}{k_BT}}\,dx = \frac{3\sqrt{\pi}}{4}\,\frac{g}{(\sqrt{c})^5}\cdot\left(\sqrt{k_BT}\right)^3$

Den. $\int e^{-\frac{U}{k_BT}}\,dx = \sqrt{\frac{\pi k_BT}{c}}$

$$\langle x\rangle \approx \frac{3g}{4c^2}\cdot k_BT$$

$\langle x\rangle$ would be 0 without anharmonic terms.

Gaussian Integrals

$$I = \int_{x=-\infty}^{+\infty} e^{-x^2} dx = ?$$

$$I^2 = \int_{x=-\infty}^{+\infty} e^{-x^2} dx \int_{y=-\infty}^{+\infty} e^{-y^2} dy$$

$$I^2 = \iint_{x\ y\ -\infty}^{+\infty} e^{-(x^2+y^2)} dx\, dy$$ Cartesian $\longrightarrow$ Polar

$$I^2 = \int_{r=0}^{\infty} \int_{\varphi=0}^{2\pi} e^{-r^2} r\, dr\, d\varphi$$

$$I^2 = \underbrace{\int_{r=0}^{\infty} e^{-r^2} r\, dr}_{-\frac{1}{2} e^{-r^2} \Big|_{r=0}^{\infty}} \cdot \underbrace{\int_{\varphi=0}^{2\pi} d\varphi}_{2\pi} = \frac{1}{2}(2\pi) = \pi$$

$$I = \sqrt{\pi}$$