22. Classical Harmonic Crystal

$$r(R) = R + u(R)$$

$$U = \frac{1}{2}\sum_{R,R'} \phi(R-R') = \frac{N}{2}\sum_{R\neq 0}\phi(R) \quad \text{with } u=0$$

$$U = \frac{1}{2}\sum_{R,R'} \phi\big(r(R)-r(R')\big)$$

$$= \frac{1}{2}\sum_{R,R'} \phi\big(R-R'+u(R)-u(R')\big) \qquad \ldots R\neq R'$$

$$H = \sum_R \frac{P(R)^2}{2M}$$

Expand:

$$U = \frac{N}{2}\sum \phi(R) \leftarrow U_{eq}$$

$$+\frac{1}{2}\sum_{R,R'}\big(u(R)-u(R')\big)\cdot\nabla\phi(R-R') \leftarrow \text{Force in equilibrium} = 0$$

$$+\frac{1}{2!}\frac{1}{2}\sum_{R,R'}\big[(u(R)-u(R'))\cdot\nabla\big]^2\phi(R-R') \quad \nwarrow U_{harm}$$

$$+\mathcal{O}(u^3)$$

$$\boxed{\begin{aligned} U_{harm} &= \frac{1}{4}\sum_{R,R'}\big(u_\mu(R)-u_\mu(R')\big)\,\phi_{\mu\nu}\,\big(u_\nu(R)-u_\nu(R')\big) \\ \phi_{\mu\nu}(r) &= \frac{\partial^2\phi}{\partial r_\mu\,\partial r_\nu}\end{aligned}}$$

$$
\begin{aligned}
U_{harm} = \frac{1}{4}\sum_{R,R'} \; & u_\mu(R)\,\phi_{\mu\nu}(R-R')\,\phi_\nu(R) \\
& u_\mu(R')\,\phi_{\mu\nu}(R-R')\,u_\nu(R') \\
& -u_\mu(R)\,\phi_{\mu\nu}(R-R')\,u_\nu(R') \\
& -u_\mu(R')\,\phi_{\mu\nu}(R-R')\,u_\nu(R)
\end{aligned}
$$

$$
\begin{aligned}
&= \frac{1}{2}\sum_{R} u_\mu(R) \sum_{R''} \phi_{\mu\nu}(R'')\, u_\nu(R) \\
&\quad -\frac{1}{2}\sum_{R,R'} u_\mu(R)\,\phi_{\mu\nu}(R-R')\,u_\nu(R')
\end{aligned}
$$

assuming $\phi_{\mu\nu}(R-R') = \phi_{\mu\nu}(R'-R)$

$$
\boxed{U_{harm} = \frac{1}{2}\sum_{R,R'} u_\mu(R)\, D_{\mu\nu}(R-R')\, u_\nu(R')}
$$

$$
D_{\mu\nu}(R-R') = \delta_{RR'}\sum_{R''}\phi_{\mu\nu}(R-R'') - \phi_{\mu\nu}(R-R')
$$

Adiabatic approx.: Ions move more slowly than electrons.

Law of Dulong & Petit

$$u = \frac{1}{\text{Vol.}} \frac{\int \prod_{R,\mu} du_\mu(R)\, dP_\mu(R)\, H\, e^{-\beta H}}{\int \prod_{R,\mu} du_\mu(R)\, dP_\mu(R)\, e^{-\beta H}}$$

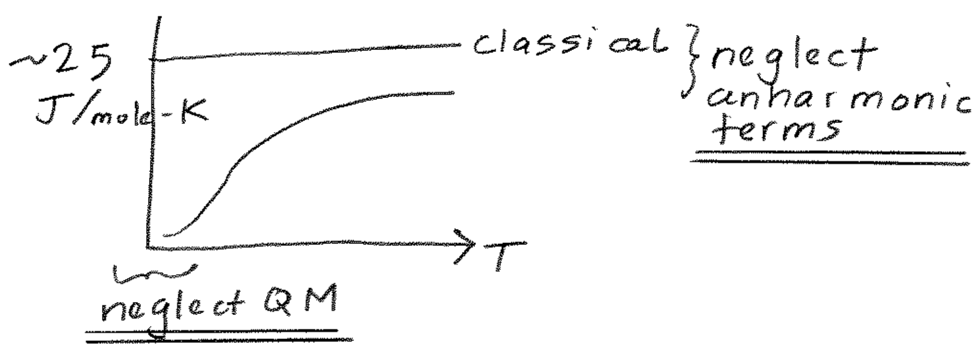
$$= -\frac{1}{V}\frac{\partial}{\partial \beta} \ln \int \prod_{R,\mu} du_\mu(R)\, dP_\mu(R)\, e^{-\beta H}$$

$$= -\frac{1}{V}\frac{\partial}{\partial \beta} \ln \left(e^{-\beta U^{eq}} \beta^{-3N} \times \text{const.} \right)$$

$$\boxed{\begin{aligned} u &= u^{eq} + 3n k_B T \\ c_v &= \frac{\partial u}{\partial T} = 3n k_B \end{aligned}}$$

$3k_B$ per ion

$c_v^{molar} = 5.96$ cal/mole K



1D Monatomic Bravais Lattice

$$M\ddot{u}(R) = -K(u(R)-u(R-a)) - K(u(R)-u(R+a))$$

Look for soln. $e^{i(qx-\omega t)}$ (Real or Imag part)

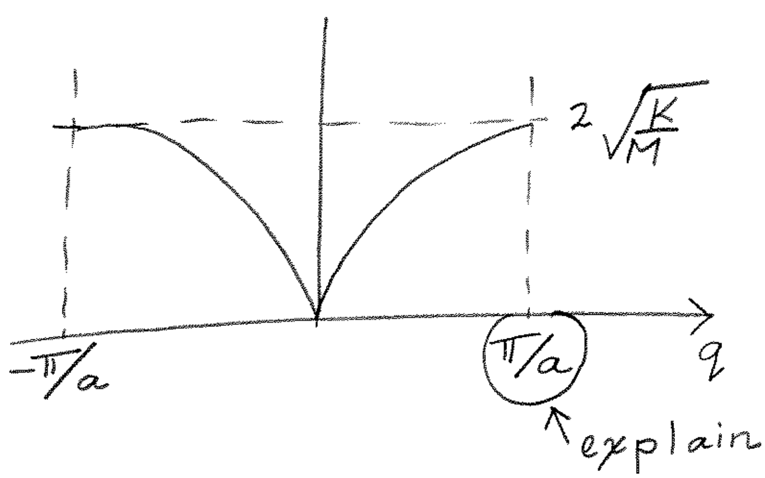
$$-M\omega^2 = -K(2-2\cos qa)$$

$$\omega^2 = \frac{K}{M}(2-2\cos qa)$$

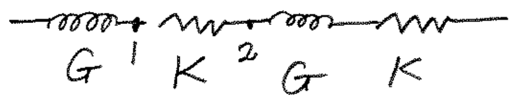
$$= \frac{K}{M} 4\sin^2(qa/2)$$

$$\boxed{\omega = 2\sqrt{\frac{K}{M}}\sin(qa/2)}$$

As $q \to 0$, $\omega \approx \sqrt{\frac{K}{M}}\, qa$ $\qquad \frac{\partial \omega}{\partial q} = \sqrt{\frac{K}{M}}\, a$



1D Lattice w/ Basis



$$M\ddot{u}_1(R) = -K\left(u_1(R) - u_2(R)\right) - G\left(u_1(R) - u_2(R-a)\right)$$

$$M\ddot{u}_2(R) = -K\left(u_2(R) - u_1(R)\right) - G\left(u_2(R) - u_1(R+a)\right)$$

$$u_1(R) = \varepsilon_1 \, e^{i(qR-\omega t)}$$
$$u_2(R) = \varepsilon_2 \, e^{i(qR-\omega t)}$$

$$-M\omega^2\varepsilon_1 = -K(\varepsilon_1 - \varepsilon_2) - G(\varepsilon_1 - \varepsilon_2 e^{-iqa})$$
$$-M\omega^2\varepsilon_2 = -K(\varepsilon_2 - \varepsilon_1) - G(\varepsilon_2 - \varepsilon_1 e^{iqa})$$

$$0 = (M\omega^2 - K - G)\varepsilon_1 + (K + Ge^{-iqa})\varepsilon_2$$

$$0 = (K + Ge^{iqa})\varepsilon_1 + (M\omega^2 - K - G)\varepsilon_2$$

Det = 0

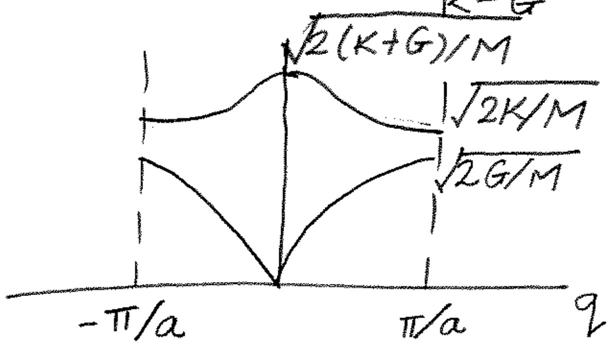
$$\rightarrow (M\omega^2 - K - G)^2 = (K^2 + G^2 + 2KG\cos qa)^2$$

$$\boxed{\begin{gathered}\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2 + G^2 + 2KG\cos qa} \\ \frac{\varepsilon_2}{\varepsilon_1} = -\left(\frac{K + Ge^{iqa}}{M\omega^2 - K - G}\right) = \mp \frac{K + Ge^{iqa}}{|K + Ge^{iqa}|}\end{gathered}}$$

$q \to 0$: $\quad \omega^2 = \frac{K+G}{M} \pm \frac{1}{M}|K+G| = 0, \frac{2(K+G)}{M}$

$q \to \frac{\pi}{a}$: $\quad \omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\underbrace{|K-G|}_{K-G} = \frac{2G}{M}, \frac{2K}{M}$

$(K > G)$



$\boxed{q \ll \frac{\pi}{a}}$: $\quad \cos(qa) \approx 1 - \frac{(qa)^2}{2}$

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2+G^2+2KG - KG(qa)^2}$$

$$= \frac{K+G}{M}\Big(1 \pm \underbrace{\sqrt{1 - \frac{KG}{(K+G)^2}(qa)^2}}_{1-\frac{1}{2}\frac{KG}{(K+G)^2}(qa)^2}\Big)$$

$$= \frac{2(K+G)}{M} - \mathcal{O}(qa)^2 \qquad (+\text{ case})$$

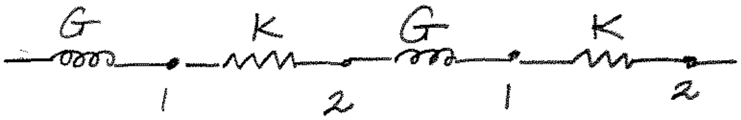
$$= \frac{1}{2}\frac{KG}{(K+G)}(qa)^2 \qquad (-\text{ case})$$

$$\omega \approx \sqrt{\frac{2(K+G)}{M}} - \mathcal{O}(qa)^2$$ optical, out of phase (+ case), $\frac{\varepsilon_2}{\varepsilon_1} = -1$

$$\omega \approx \sqrt{\frac{KG}{2(K+G)}}\,(qa)$$ (− case), $\frac{\varepsilon_2}{\varepsilon_1} = +1$ acoustic, in phase

$\boxed{q = \frac{\pi}{a}}$: + case $\quad \omega = \sqrt{\frac{2K}{M}}$, $\frac{\varepsilon_2}{\varepsilon_1} = -1$

− case $\quad \omega = \sqrt{\frac{2G}{M}}$, $\frac{\varepsilon_2}{\varepsilon_1} = +1$



− case:  acoustic

+ case: 

Symmetry 1: $D_{\mu\nu}(R-R') = D_{\nu\mu}(R'-R)$

$$D_{\mu\nu} = \frac{\partial^2 U}{\partial u_\mu(R)\,\partial u_\nu(R')}$$

Symmetry 2: $D_{\mu\nu}(R-R') = D_{\mu\nu}(R'-R)$

$D(R) = D(-R)$

inversion symmetry

Symmetry 3: $\sum_R D_{\mu\nu}(R) = 0$

$\sum_R D(R) = 0$

energy not changed by translation

$$\rightarrow M\ddot{u}_\mu(R) = -\frac{\partial U^{harm}}{\partial u_\mu(R)} = -\sum_{R'\nu} D_{\mu\nu}(R-R')u_\nu(R')$$

$$M\ddot{u}(R) = -\sum_{R'} D(R-R')u(R')$$

$$u(R,t) = \vec{\varepsilon}\, e^{i(k\cdot R-\omega t)}$$

$$M\omega^2\vec{\varepsilon} = D(k)\vec{\varepsilon}$$

$$D(k) = \sum_R D(R)\, e^{-ik\cdot R}$$

$$= \frac{1}{2}\sum_R D(R)\left[e^{-ik\cdot R} + e^{ik\cdot R} - 2\right]$$

$$= \sum_R D(R)\left[\cos(k\cdot R) - 1\right]$$

$$= -2\sum_R D(R)\sin^2\left(\tfrac{1}{2}k\cdot R\right)$$

$D(k)$ symmetric, even in k, real

$$D(k)\,\vec{\varepsilon}_s = \lambda_s\,\vec{\varepsilon}_s(k)$$

$$\varepsilon_s(k)\cdot\varepsilon_{s'}(k) = \delta_{ss'}$$

$$\omega_s = \sqrt{\frac{\lambda_s(k)}{M}}$$

$k \to 0 \quad \sin^2\left(\frac{1}{2}k\cdot R\right) \approx \left(\frac{1}{2}k\cdot R\right)^2$

$$D(k) \approx -\frac{k^2}{2}\sum_R (\hat{k}\cdot R)^2 D(R) \qquad \hat{k} = k/|k|$$

$$\omega_s(k) = c_s(\hat{k})\,k$$

$c_s(\hat{k})$ sq. roots of eigenvalues of

$$-\frac{1}{2M}\sum_R (\hat{k}\cdot R)^2 D(R)$$