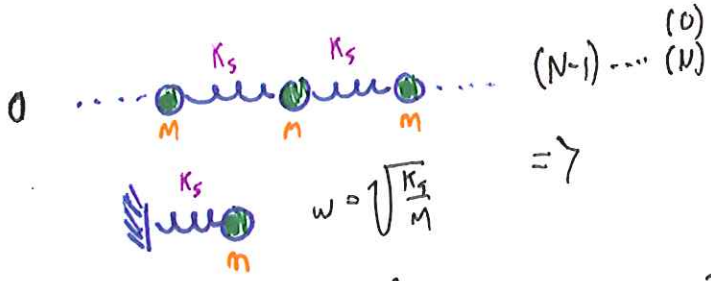
Physics 410/90 – Solid State Physics
Spring 2015
Monday, Week 5:

Review:

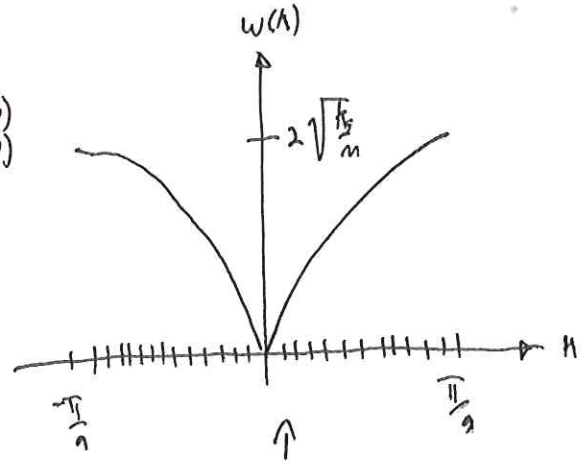
1D Monatomic



$\omega = \sqrt{\frac{K_s}{M}}$

1 frequency

$\Rightarrow$



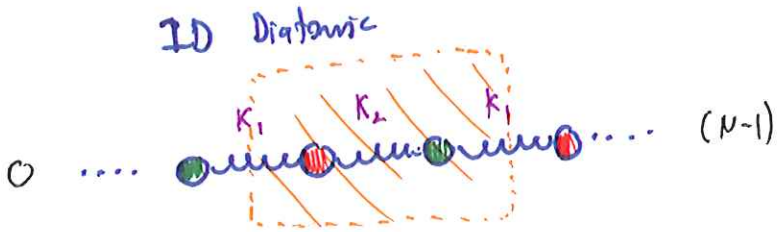
N frequencies; one for each allowed k-vector

For each mode w/ $k_m = \frac{2\pi}{L} \cdot m$, $m \in \mathbb{Z}$, we have $\omega(k_m)$ & energy:

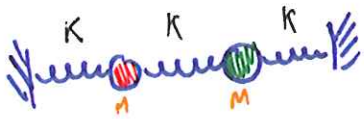
$$E_n = \hbar\omega(k_m)\left(n + \tfrac{1}{2}\right) \qquad n \in \mathbb{Z}^+$$

Each excitation by a step up is called a phonon, which is a discrete quantum of vibration.

1D Diatomic



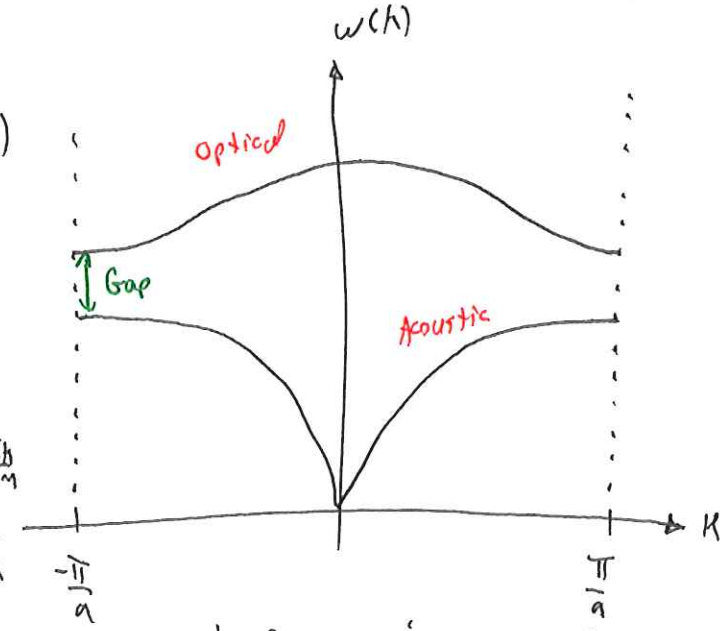
Unit cell



$$\omega = \begin{cases} \sqrt{\frac{K}{M}} \\ \sqrt{\frac{3K}{m}} \end{cases}$$

2 frequencies

A gap



2N frequencies & 2 branches & Gap

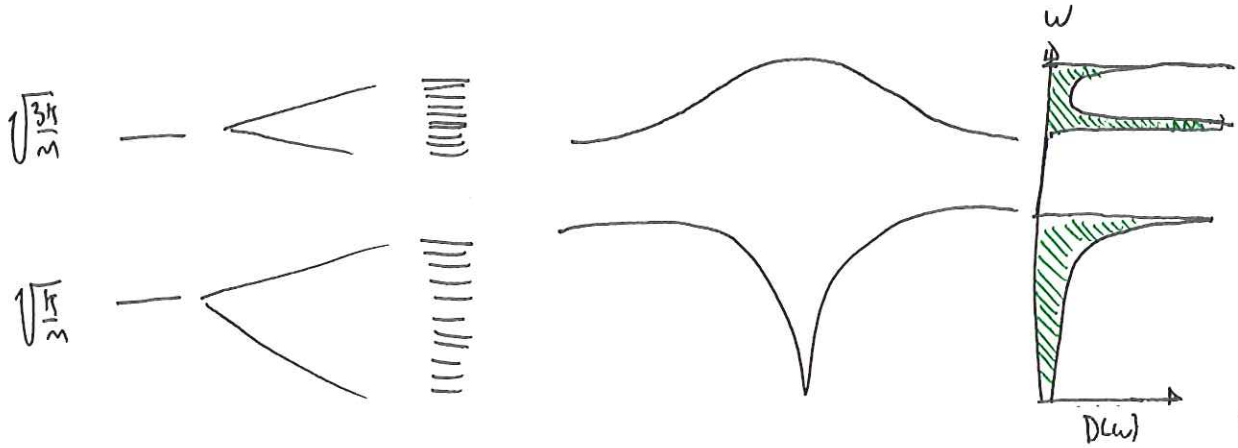
The motion of the basis atoms:

The relative amplitudes (& phases) of a particular $\omega(K)$ are obtained by solving the eigenvalue equation we derived earlier. In general, there will be some complex relationship between the two.

For $K \to 0$ we have

$$\begin{pmatrix} A_1 \\ A_2 \end{pmatrix} = \begin{cases} \begin{pmatrix} 1 \\ 1 \end{pmatrix} & \text{Acoustic} \\ \begin{pmatrix} 1 \\ -1 \end{pmatrix} & \text{Optical} \end{cases}$$

In the diatomic basis case, the basis already has two distinct allowable frequencies & each one spreads into its own branch or band.



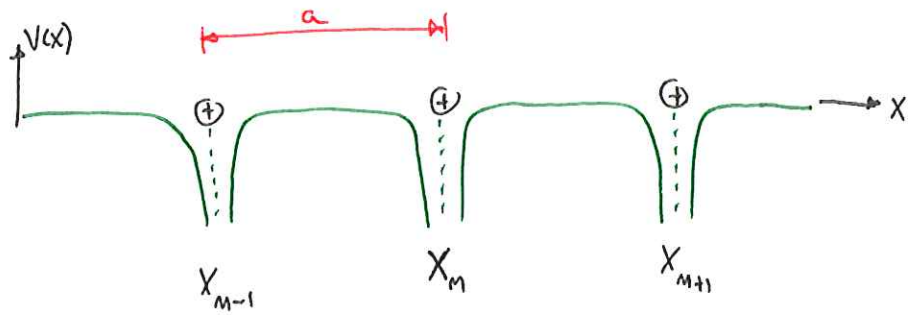
So far we've looked at x-rays, neutrons, & vibrational waves in crystals.

Here are some similarities:

- Bragg reflections at the BZ edges; standing waves.

Since the behavior of waves in periodic environments is similar, let's get a preview of electronic waves:

The Tight-Binding Chain:



Consider an electron in this periodic potential:

$$V_{tot}(x) = \sum_j V(x - x_j)$$

with Hamiltonian,

$$H = \frac{p^2}{2m} + \sum_j V(x - x_j)$$

& Variational trial function

$$|\psi\rangle = \sum \phi_M |M\rangle$$

where $|M\rangle$ are ground state orbitals for $\frac{p^2}{2m} + V(x - x_M)$

& we assume

$$\langle n|M\rangle = \delta_{n,M}$$

& $$\left(\frac{p^2}{2m} + V(x - x_M)\right)|M\rangle = E_{atomic}|M\rangle$$

We derive the variational Schrödinger Eq. the following way:

$$H|\psi\rangle = E|\psi\rangle$$

or $$\sum_i |i\rangle\langle i| \left(H \sum \phi_m |m\rangle = E \sum_m \phi_m |m\rangle \right)$$

$$\langle n| \left(\sum_{i,m} |i\rangle\langle i|H|m\rangle \phi_m = E \sum_{i,m} |i\rangle \underbrace{\langle i|m\rangle}_{S_{im}} \phi_m \right.$$

$$\left. = E \sum_i |i\rangle \phi_i \right)$$

Recall,

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix} = E \begin{pmatrix} \phi_1 \\ \phi_2 \end{pmatrix}$$

$$\sum_{i,m} \underbrace{\langle n|i\rangle}_{S_{ni}} \langle i|H|m\rangle \phi_m = E \sum_i \underbrace{\langle n|i\rangle}_{S_{ni}} \phi_i$$

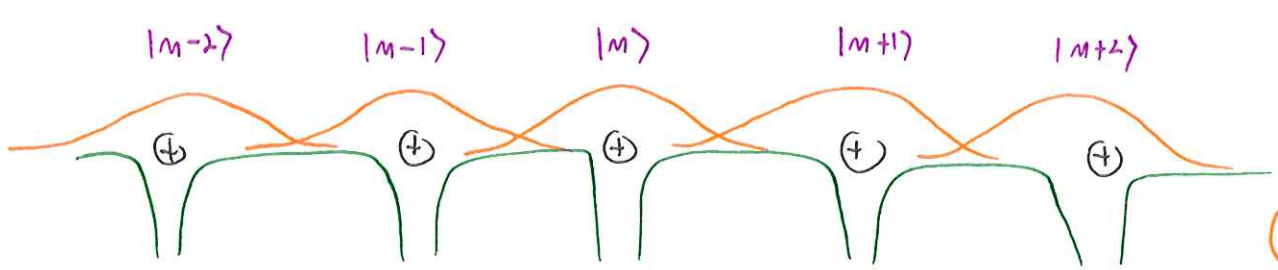
$$\boxed{\sum_m \langle n|H|m\rangle \phi_m = E\phi_n} \quad \text{or} \quad \boxed{\sum_m H_{n,m} \phi_m = E\phi_n} \qquad (1)$$

Now, <u>the matrix elements are</u>:

$$H|m\rangle = \left(\frac{p^2}{2m} + V(x-x_m)\right)|m\rangle + \sum_{j\neq m} V(x-x_j)|m\rangle$$

$$\langle n| \left(H|m\rangle = E_{atomic}|m\rangle + \sum_{j\neq m} V(x-x_j)|m\rangle \right)$$

$$\langle n|H|m\rangle = E_{atomic}\langle n|m\rangle + \sum_{j\neq m} \langle n|V(x-x_j)|m\rangle$$



So integrals $\langle n | V(x-x_j) | m \rangle$ are negligible if $n > m+1$
$< m-1$

ξ

$$\sum_{j \neq m} \langle n | V(x-x_j) | m \rangle = \begin{cases} V_0 & n = m \\ -t & n = m \pm 1 \\ 0 & \text{otherwise} \end{cases}$$

ξ

$$\boxed{H_{n,m} = (E_{atomic} + V_0)\delta_{n,m} - t\left(\delta_{n+1,m} + \delta_{n-1,m}\right)}$$

Now we know what (1) looks like. We use the trial solution for ϕ_n that is periodic:

$$\phi_n = \frac{e^{-ikna}}{\sqrt{N}}$$

Then the Schrödinger Equation says:

$$(E_{atomic} + V_0)\frac{e^{-ikna}}{\sqrt{N}} - t\left(\frac{e^{-ik(n+1)a}}{\sqrt{N}} + \frac{e^{-ik(n-1)a}}{\sqrt{N}}\right) = E\,\frac{e^{-ikna}}{\sqrt{N}}$$

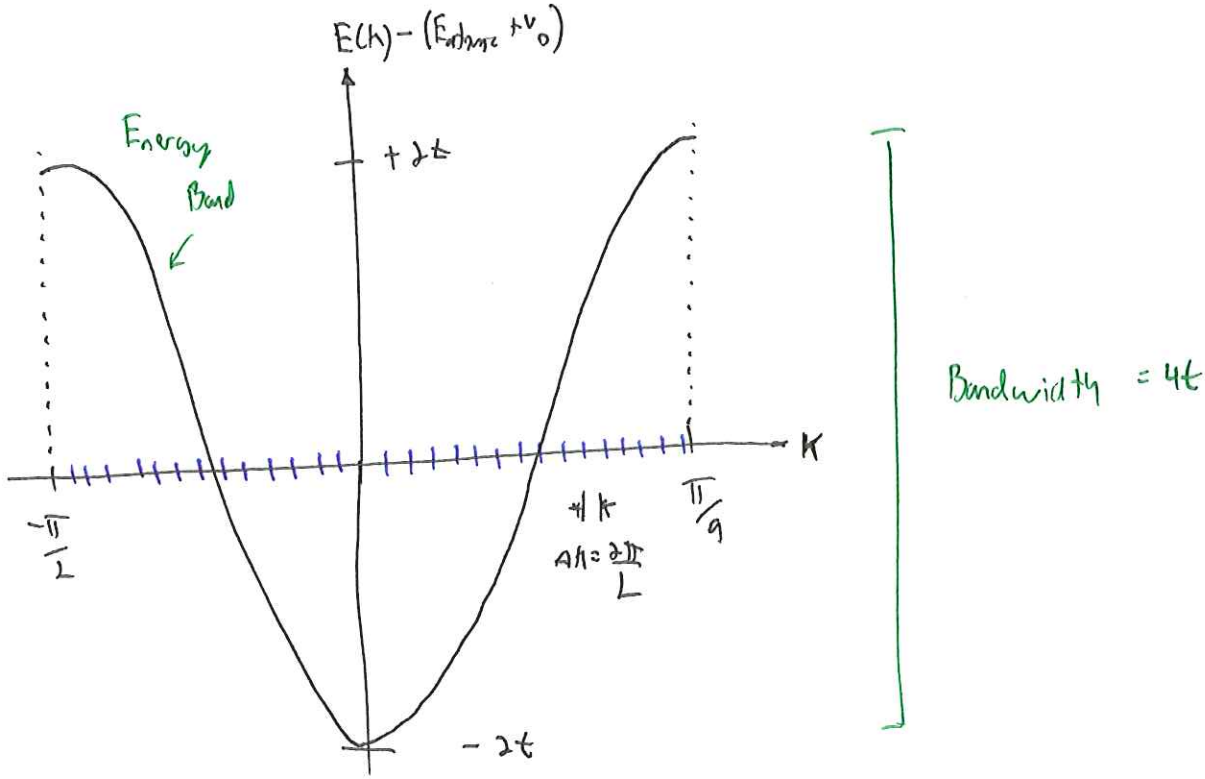
$$(E_{atomic} + V_0) - t\left(e^{-ika} + e^{ika}\right) = E$$

or

$$\boxed{E(k) = (E_{atomic} + V_0) - 2t\cos(ka)}$$

Recall the monatomic chain gave

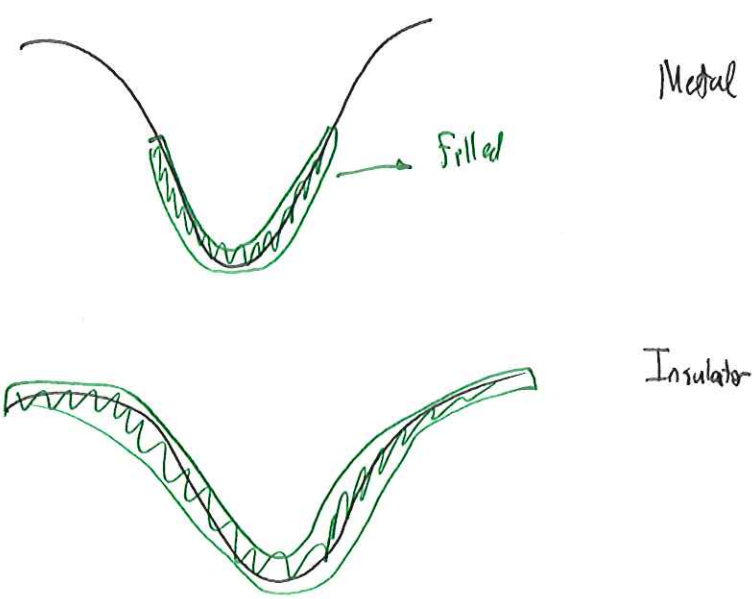
$$\omega^2 = \frac{2\kappa}{m}\left(1 - \cos(ka)\right)$$



$$E(k+g_n) = E(k)$$

The bandwidth $4t$ increases as the atoms become closer together.

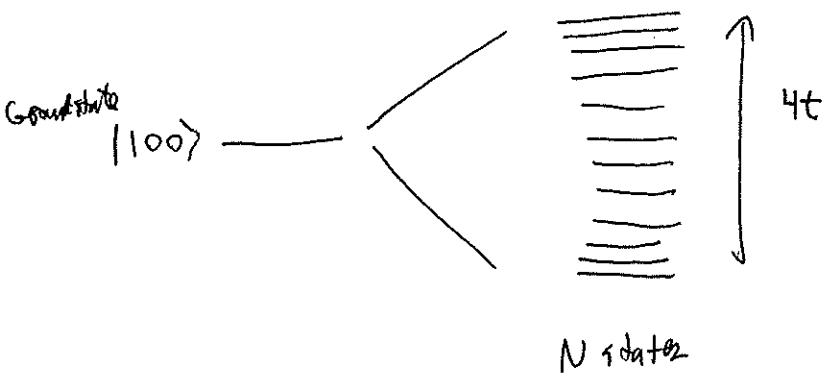
There are still $\underline{N}$ allowed k-states of width $\Delta k = \frac{2\pi}{L}$, but $\underline{2 \text{ electrons}}$ are allowed per k-state. Thus if monovalent:

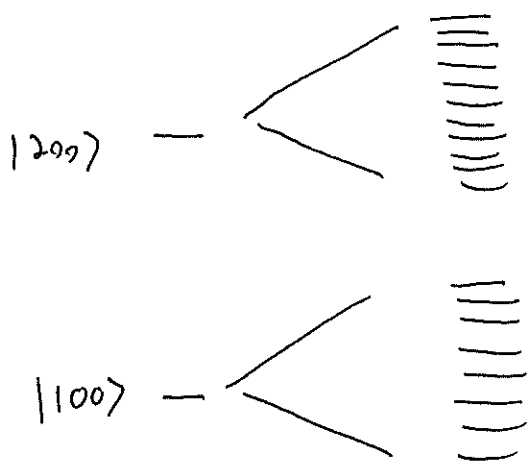


Note a free electron can have any energy

$$E = \frac{\hbar^2 k^2}{2m}$$

but here the electron can have min & max energy. Also the single atomic orbital splits into N levels:





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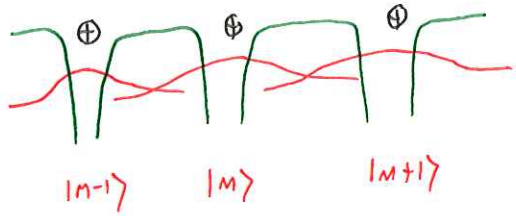
Wednesday, Week 5:

Review:



$$|\psi\rangle = \sum_{m=1}^{N} \phi_m |m\rangle$$

$$H = \frac{p^2}{2m} + \sum_{j=1}^{N} V(x-x_j)$$

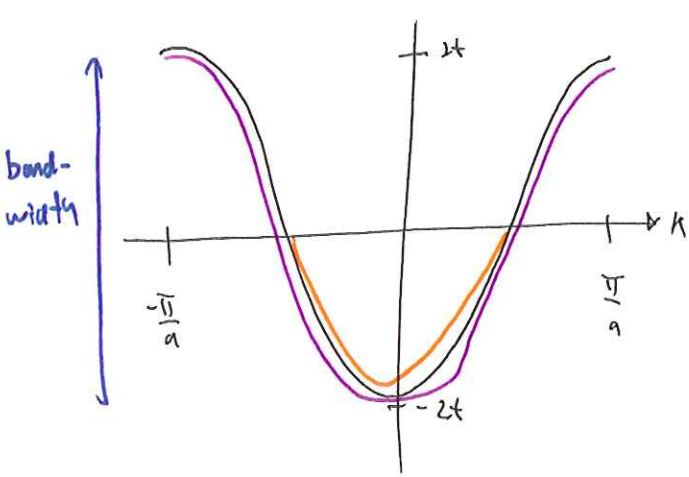
$$\sum_m \langle n|H|m\rangle \phi_m = E\phi_n \Rightarrow \begin{pmatrix} \ddots & \vdots & & & \\ -t & E_0 & -t & & \\ & -t & E_0 & -t & \\ & & -t & E_0 & -t \\ & & & \ddots & \ddots \end{pmatrix} \begin{pmatrix} \phi_1 \\ \vdots \\ \phi_n \\ \vdots \\ \phi_N \end{pmatrix}$$

$$\phi_n = \frac{e^{-ikna}}{\sqrt{N}} \Rightarrow \left(E_{atomic} + V_0\right) - t\left(e^{-ika} + e^{ika}\right) = E$$

$$E(k) = \left(E_{atomic} + V_0\right) - 2t\cos(ka)$$

Measure overlap of $|m\rangle$ w/ all other $V(x-x_j)$'s

Measure overlap of $\langle n|$, $|m\rangle$, & all potentials $V(x-x_j)$ except the mth.

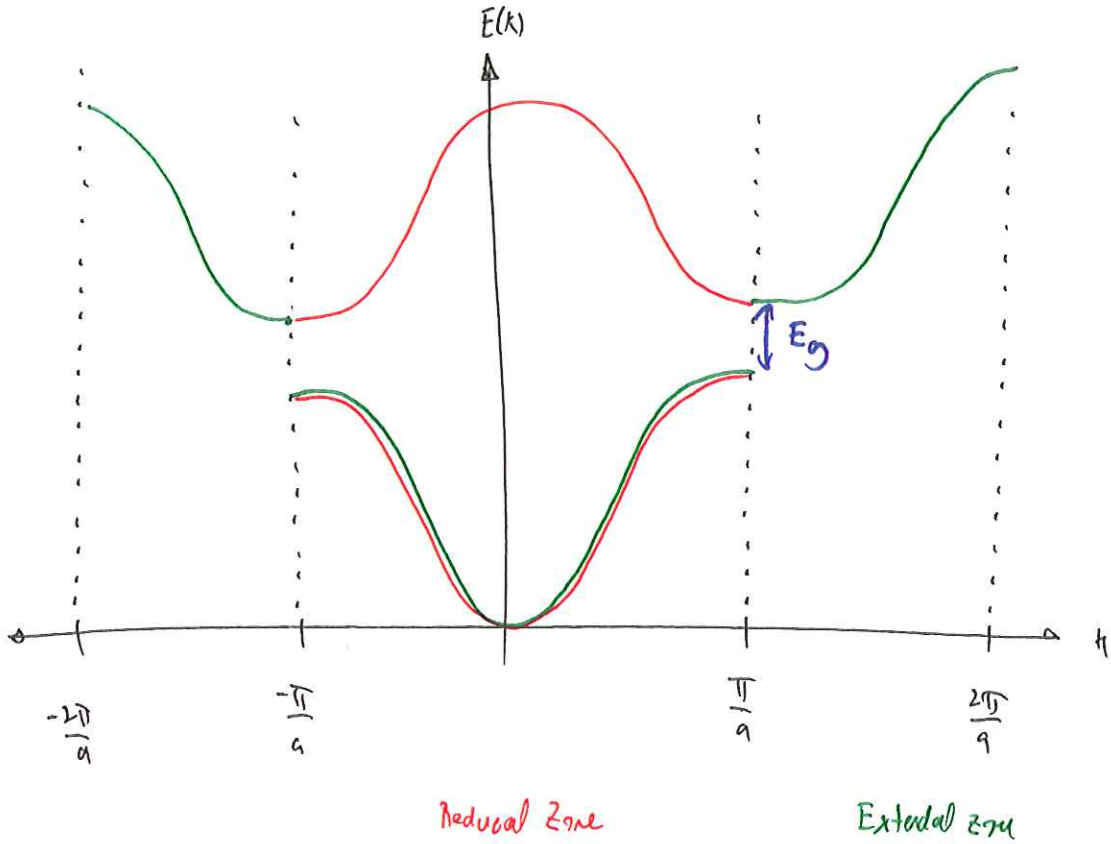


— = Monovalent Metal

— = Divalent Band insulator

The bandwidth $4t$ grows as the lattice spacing decreases.

Much like the diatomic chain gave a frequency gap, if our basis, in this case a single atom, has more than one energy level (frequency), then we'll get a second band & there will be a band gap at the BZ edges:



<u>Effective Mass:</u> The energy of a free electron is $E_k = \frac{\hbar^2 k^2}{2m}$

In the crystal, the electron has min & max energy. If we taylor expand our tight-binding E(k) at min:

$$E(k) = E(0) + \frac{1}{2}\frac{d^2E}{dk^2}\bigg|_{k=0} \cdot k^2$$

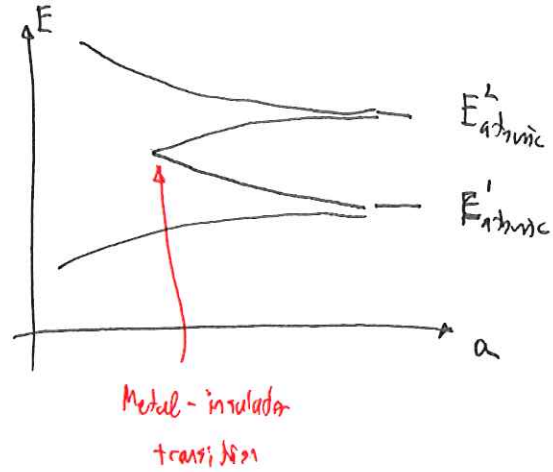
Then

$$\frac{1}{2}\frac{d^2E}{dk^2} = \frac{\hbar^2}{2m^*} \quad \text{or} \quad \boxed{m^* = \hbar^2 \frac{1}{d^2E/dk^2}}$$ Effective Mass

Here

$$m^* = \frac{\hbar^2}{2ta^2}$$

Compressing a solid, reducing the lattice constant increases the band width, which in the case of multiple bands can lead to the metal-insulator transition:



So electron waves behave similarly to x-rays, neutrons, & phonons in periodic environments. We'll return to electrons again later & cover the topics in greater detail. For now, let's return to thermal properties of solids.

Thermal Properties of Solids:

- How much energy is stored in phonons at a temperature T?
  - If we add energy ΔU to solid, what is ΔT?
- If we heat up a crystal, why does it expand or contract?
- How do phonons transport energy accross a thermal gradient?

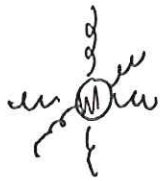
Heat Capacity:

$$C = 3Nk_B \qquad [\text{Dulong-Petit}]$$
$$= 3nR$$

C/R per mole

Material	C/R
Al	2.91
Cu	2.94
Au	3.05
Ag	2.99
C-dia	0.735

Boltzmann proposed model,



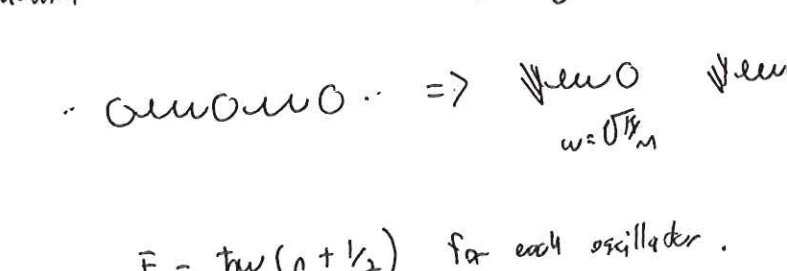
6 quadratic degrees of freedom,

$$U = 6 \times \frac{1}{2} k_B \cdot T \cdot N$$

$$= 3 k_B T N$$

$$\frac{dU}{dT} = 3 k_B N \quad \blacksquare$$

But, this doesn't work at low T (or for diamond @ room T). Einstein modeled the solid as a array of harmonic oscillators w/ freq. ω. In 1D:



$$E_n = \hbar\omega(n + 1/2) \quad \text{for each oscillator.}$$

Then for a single 1D oscillator:

$$Z_{1D} = \sum_{n \geq 0} e^{-\beta\hbar\omega(n+1/2)} \qquad \text{where } \beta \equiv \frac{1}{k_B T}$$

$$= e^{-\beta\hbar\omega/2} \sum_{n \geq 0}^{\infty} \left(e^{-\beta\hbar\omega}\right)^n$$

used $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} \quad x \leq 1$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}$$

$$= \frac{1}{e^{\beta\hbar\omega/2}\left(1 - e^{-\beta\hbar\omega}\right)}$$

$$= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}}$$

$$= \frac{1}{2\sinh\left(\beta\hbar\omega/2\right)}$$

The expectation value of the energy is:

Recall $Z = \sum e^{-\beta E_i}$

$$\langle E \rangle = \frac{-1}{Z_{1D}} \frac{\partial Z_{1D}}{\partial \beta}$$

$$\frac{\partial Z}{\partial \beta} = \sum -E_i e^{-\beta E_i} = -Z \cdot \langle E \rangle$$

$$= -\frac{1}{Z_{1D}} \frac{1}{2} \left(-\frac{\cosh(\beta\hbar\omega/2)}{\sinh(\beta\hbar\omega/2)^2} \right) \cdot \frac{\hbar\omega}{2}$$

$$= \frac{\hbar\omega}{2} \frac{\cosh(-)}{\sinh(-)}$$

$$= \frac{\hbar\omega}{2} \coth\left(\frac{\beta\hbar\omega}{2}\right)$$

gives $\langle E \rangle = \hbar\omega(n_B + 1/2)$ ✓

$$= \hbar\omega \left(n_B(\beta\hbar\omega) + \frac{1}{2} \right) \quad \text{where } n_B(\beta\hbar\omega) \equiv \frac{1}{e^{\beta\hbar\omega} - 1}$$

The heat capacity for a single oscillator is:

$$C = \frac{\partial \langle E \rangle}{\partial T} = k_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}$$

In 3D,

$$Z_{3D} = \sum_{n_x, n_y, n_z} e^{-\beta\hbar\omega[(n_x + 1/2) + (n_y + 1/2) + (n_z + 1/2)]}$$

$$= \sum_{n_x} e^{-\beta\hbar\omega(n_x + 1/2)} \cdot \sum_{n_y} (-) \cdot \sum_{n_z} (-)$$

$$= (Z_{1D})^3$$

$$\langle E_{3D} \rangle = 3 \langle E_{1D} \rangle$$

$$\Rightarrow \boxed{C = 3N k_B (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}}$$

ω is only fitting parameter

Einstein Heat Capacity for N oscillators

In the limit $k_B T \gg \hbar\omega$, $\beta \to 0$ &

$$C = 3Nk_B (\beta\hbar\omega)^2 \frac{(1+\beta\hbar\omega+\cdots)}{(1+\beta\hbar\omega+\cdots-1)^2}$$

$$\approx 3Nk_B(1+\beta\hbar\omega)$$

$$= 3Nk_B \quad \square$$

which is the Dulong-Petit Law. ★ Show PPT of $C(T)$.

Recall our previous enumeration of modes:

$$U_{tot} = \sum_k \hbar\omega(k)\left(n(\beta\hbar\omega(k)) + \tfrac{1}{2}\right)$$

$$= \frac{L}{2\pi}\int dk\, \underset{\omega}{\hbar\omega(k)}\left(\underset{\omega}{n(\omega(k))} + \tfrac{1}{2}\right) = \frac{Na}{2\pi}\cdot\frac{2\pi}{a}\hbar\omega\left(n(\beta\hbar\omega)+\tfrac{1}{2}\right)$$

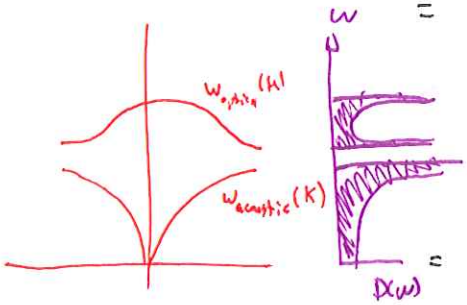
Einstein

$$= N\cdot\hbar\omega\left(n_B+\tfrac{1}{2}\right)$$

$$= \int D(\omega')\hbar\omega'\left(n(\beta\hbar\omega')+\tfrac{1}{2}\right)d\omega'$$

U_{tot} for a single polarization with the dispersion $D(\omega)$, which will depend on the branch & the real total energy is

$$U = \sum_{\text{polarizations}} U_{tot}^{\text{Polarization}}$$



$$\downarrow$$

$$N\delta(\omega-\omega') \quad \text{Einstein } D(\omega)$$

$$= N\hbar\omega\left(n_B+\tfrac{1}{2}\right)$$

· 3D diatomic

$U = 3(U^{optical} + U^{acoustic})$

In general, Einstein's calculation is good for most T, especially for small ω:

$$k_B T > \hbar\omega$$

When $k_B T \ll \hbar\omega$, the Einstein calc. deviates significantly from experiment.

Namely, at low T, $C(T) \propto T^3$. ★ Show PPT

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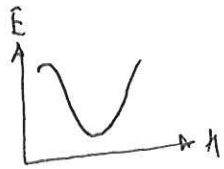
Friday, Week 5:

Review:

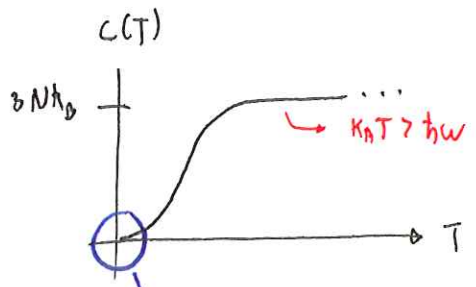
Effective Mass: $m^* \equiv \dfrac{\hbar^2}{d^2E/dk^2}$



Heat Capacity: $C \to 3Nk_B$ @ higher T

Einstein: $$C(T) = 3Nk_B \left(\frac{\hbar\omega}{k_BT}\right)^2 \frac{e^{\hbar\omega/k_BT}}{\left(e^{\hbar\omega/k_BT}-1\right)^2} \qquad [3D]$$

$\times 3N$



Has T^3 dependence for many crystals.

In the Einstein calculation, ω is a fit parameter.

The failure is at low T, where it fails to predict T^3 behavior.

Debye Model:

$$U = \sum_k \hbar\omega(k)\left(n(p\hbar\omega(k)) + \tfrac{1}{2}\right)$$

$$= \left(\frac{L}{2\pi}\right)\int dk\, \hbar\omega(k)\left(n(\omega(k)) + \tfrac{1}{2}\right)$$

$$= \int D(\omega)\,\hbar\omega\left(n(\omega) + \tfrac{1}{2}\right)d\omega$$

Debye improved on Einstein's calculation by allowing the oscillators to couple, so that there will be a distribution of frequencies.

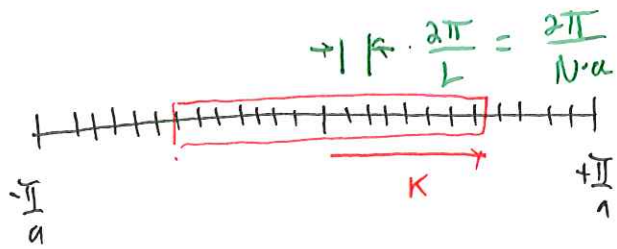
So the energy in a polarization (transverse, longitudinal) is: ★ Show PDF

$$U = \int D(\omega)\hbar\omega\left(n_B(\beta\hbar\omega) + \tfrac{1}{2}\right) d\omega \qquad \text{[Per Polarization]}$$

Density of states.

Debye modelled the $D(\omega)$ differently:

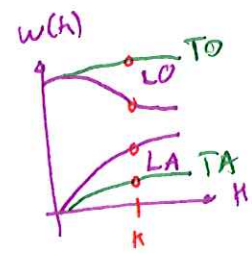
Recall in 1D:



One way to get $D(\omega)$ is to consider # states in a 1D sphere (line) of radius K:

Length of specimen

$$N_{sk} = \left(\frac{L}{2\pi}\right) \cdot 2K$$



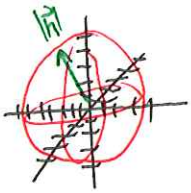
So density of states in ω-space:

$$D(\omega) = \boxed{\frac{dN}{d\omega} = 2 \cdot \left(\frac{L}{2\pi}\right)\frac{dk}{d\omega} = 2 \cdot \left(\frac{L}{2\pi}\right)\frac{1}{|d\omega/dk|}} \quad \square$$

In 3D: The density of states in K-space is $\left(\frac{L}{2\pi}\right)^3 = \frac{V}{(2\pi)^3}$ → Volume of specimen

For each polarization & each branch.

& $N(\leq|\vec{k}|) = \frac{V}{(2\pi)^3} \cdot \frac{4\pi}{3} k^3$



radius of sphere.

$$D(\omega) = \frac{dN}{dk} = \frac{4\pi V}{(2\pi)^3} \cdot k^2 \cdot \frac{dk}{d\omega}$$

For each polarization assuming $d\omega/dk$ constant over sphere. $\omega(\vec{k}) = \omega(k)$

Also, recall that

$$\sum_k \to \int \left(\frac{L}{2\pi}\right) dk \qquad [1D]$$

constant $\omega(\vec{k})$ because we want # states between $\omega(\vec{k})$ & $\omega(\vec{k})+d\omega$ which is $\equiv D(\omega)d\omega$

$$\boxed{D(\omega) = \frac{V}{(2\pi)^3}\int \frac{dS_\omega}{|\vec{\nabla}_k \omega(\vec{k})|}}$$

So now,

$$\sum_{\vec{k}} \to \int \left(\frac{L}{2\pi}\right)^3 d\vec{k}$$

$$= \frac{V}{(2\pi)^3}\int d\vec{k} = \frac{V}{(2\pi)^3}\iint_{S_\omega} dS_\omega\, dk = \int_{S_\omega}\int \frac{V}{(2\pi)^3}\frac{dS_\omega}{|\vec{\nabla}_k \omega(\vec{k})|}\, d\omega$$

Surface element of constant $\omega(\vec{k})$

$\omega(\vec{k}) = \omega(k)$

Spherically symmetric in $\vec{k}$-space

$$= \frac{V}{(2\pi)^3}\cdot 4\pi \int k^2\, dk \qquad [\text{spherical}]$$

$$= \int \underbrace{D(\omega)}_{\frac{4\pi}{(2\pi)^3} V k^2 \frac{1}{(d\omega/dk)}} d\omega$$

as before ☑

<u>Debye used a simple form of $\omega(k)$:</u> (Assumed spherically symmetric)

$$\omega(k) = V_{sound}\cdot k = V_s \cdot k \qquad d\omega/dk = V_s$$

$$\therefore\ D(\omega) = \frac{4\pi\cdot V}{(2\pi)^3}\frac{k^2}{V_s} = \frac{4\pi\cdot V}{(2\pi)^3}\left(\frac{\omega}{V_s}\right)^2\frac{1}{V_s}$$

So with <u>3 polarizations</u>,

$$\langle E\rangle = U = 3\cdot\frac{4\pi V}{(2\pi)^3}\int_0^\infty \left(\frac{\omega}{V_s}\right)^2 \frac{1}{V_s}\hbar\omega\left(n_B(\beta\hbar\omega)+\tfrac{1}{2}\right)d\omega$$

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

$$= \int N\left[\frac{12\pi}{(2\pi)^3 n V_s^3}\right]\omega^2\cdot\hbar\omega\left(n_B(\beta\hbar\omega)+\tfrac{1}{2}\right)d\omega$$

$\omega_D^3 = 6\pi^2\cdot n\cdot V_s^3$

$$= \int N\cdot\frac{9\omega^2}{\omega_D^3}\hbar\omega\left(n_B(\beta\hbar\omega)+\tfrac{1}{2}\right)d\omega$$

Debye-frequency

$$= \frac{9N\hbar}{\omega_D^3}\left[\int_0^\infty \frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega + \underbrace{\int_0^\infty \frac{1}{2}\omega^3\,d\omega}_{\text{No T-dependence... will ignore.}}\right]$$

$x \equiv \beta\hbar\omega$

$\frac{dx}{\beta\hbar} = d\omega$

$$= \frac{9N\hbar}{\omega_D^3}\frac{1}{(\beta\hbar)^4}\int_0^\infty \frac{x^3}{e^x-1}\,dx$$

$$= 9N\frac{(k_BT)^4}{(\omega_D\hbar)^3}\cdot\frac{\pi^4}{15}$$

Similar to Planck's Quantum Energy of photons where $\omega = ck$

& use $2\times$ for 2 polarizations of phonons

vs. $3\times$ " 3 " phonons

$$C = \frac{\partial\langle E\rangle}{\partial T}$$

$$= Nk_B\left(\frac{k_BT}{\omega_D\hbar}\right)^3\cdot\frac{12\pi^4}{5} = Nk_B\left(\frac{T}{T_{Debye}}\right)^3\cdot\frac{12\pi^4}{5}$$

$$\boxed{T_D \equiv \frac{\hbar\omega_D}{k_B}}$$ [Debye Temperature]

$\propto T^3$

$\downarrow$

Get T^3 Law

But now, $C \to \infty$ @ $T \to \infty$!!!

T_D (K)	Material
1850	C (diamond)
625	Si
315	Cu
215	Ag
88	Pb

Higher T_D materials deviate from Dulong-Petit Law at $T < T_D$.

To fix T^3 power at high T, Debye introduced cutoff frequency determined by # of modes in 3D of N atoms:

$$3N = 3\int_0^{\omega_{cutoff}} D(\omega)\,d\omega$$

$$= 3\cdot\frac{4\pi\cdot V}{(2\pi)^3}\frac{1}{v_s^3}\int_0^{\omega_{cutoff}} \omega^2 d\omega$$

$$= (\cdots)\frac{1}{3}\omega_{cutoff}^3$$

$$= \frac{3\,V}{6\pi^2 v_s^3}\frac{N}{N}\omega_{cutoff}^3$$

$$= 3N\cdot\frac{\omega_{cutoff}^3}{6\pi^2 n v_s^3}$$

$$\Rightarrow \quad \boxed{\omega_{cutoff}^3 = \omega_D^3 = 6\pi n v_s^3}$$

Then

$$\langle E\rangle = \frac{9N\hbar}{\omega_D^3}\int_0^{\omega_D}\frac{\omega^3}{e^{\beta\hbar\omega}-1}\,d\omega \quad + \quad \text{T-Independent term}$$

$$C = \frac{\partial\langle E\rangle}{\partial T} = \frac{9N\hbar^2}{6\pi^2 n v_s^3}\frac{1}{k_B T^2}\int_0^{\omega_D}\frac{\omega^4 e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega}-1)^2}\,d\omega$$

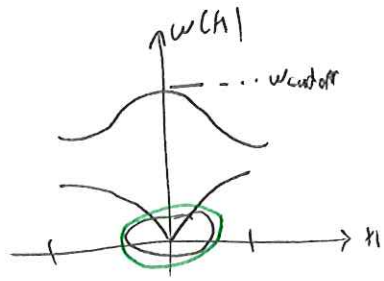
$\downarrow x = \beta\cdot\hbar\omega$

$$= 9Nk_B\left(\frac{T}{T_0}\right)^3\underbrace{\int_0^{x_D=\beta\hbar\omega_D=\hbar\omega_D/k_BT}\frac{x^4 e^x}{(e^x-1)^2}\,dx}_{\text{Now depends on Temperature!!}}$$

☆ Show POT of C

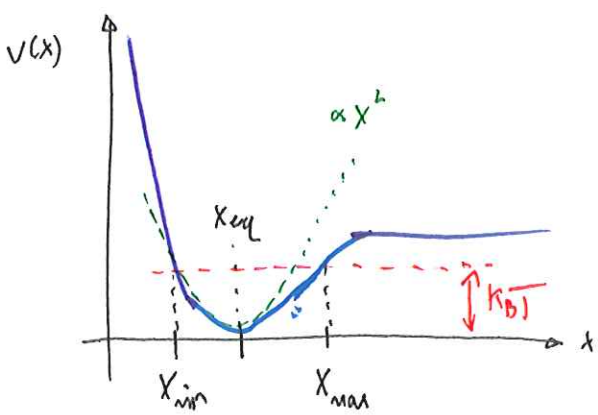
Remarks:

- T^3 behavior occurs when $T \ll T_D$:
  - Here $\omega \ll \omega_D = \omega_{cutoff}$, which is where acoustic phonon line & the Debye approximation hold, $\omega = v_s \cdot k$:



- For Metals, $C = \gamma T + \alpha T^3$

Thermal Expansion:



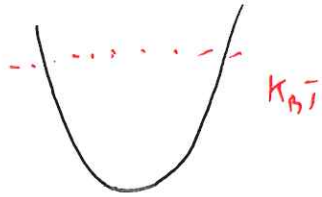
$V(x_{min}) = V(x_{max}) = k_B T$

$|x_{max} - x_{eq}| > |x_{min} - x_{eq}|$

so $\langle x \rangle > x_{eq}$ because of asymmetric potential.

& $\langle x \rangle$ will increase for higher T's

If only $\frac{1}{2} k x^2$



$\langle x \rangle = 0$.