Density of states

**Isotropic (Debye) model.**

The number of states in between two concentric spherical shells with radii $k$ and $k + dk$

\[
\frac{\frac{4}{3} \pi (k+dk)^3 - \frac{4}{3} \pi k^3}{(2\pi)^3} = \frac{4 \pi k \, dk}{(2\pi)^3} = g(\omega) \, d\omega
\]

\[g(\omega) = \frac{1}{4\pi^2} \, k^2(\omega) \left| \frac{dk}{d\omega} \right| \text{ where } k = k(\omega).
\]

**a) Acoustic mode**

\[\omega = \frac{\omega}{S} k\]

\[\frac{d\omega}{dk} = \frac{\omega}{S}; \quad k = \frac{\omega}{S}\]

\[g(\omega) = \frac{1}{4\pi^2} \, \frac{\omega^2}{S^3}\]

\[(1)\]

**b) Bending mode of 2D elastic membrane**

\[\omega = ak^2\]

2D phase space:

\[\frac{2\pi k \, dk}{(2\pi)^2} = g(\omega) \, d\omega \Rightarrow g(\omega) = \frac{1}{2\pi} \, k \left| \frac{dk}{d\omega} \right|
\]

\[k = \sqrt{\frac{\omega}{a}}; \quad \frac{d\omega}{dk} = 2ak\]

\[g(\omega) = \frac{1}{2\pi} \, \frac{k}{2ak} = \frac{1}{4\pi a}\]

(Reminder: For massive particles, $E = \frac{h^2 k^2}{2m}$, $\alpha = \frac{h^2}{2m}$ and $g = \frac{M}{2\pi h^2}$ per spin orientation.)
Anisotropic case

In this case, one can use two equivalent formulas for the density of states:

**Formula 1**

\[ g(\omega) = \int \frac{d^D k}{(2\pi)^D} \delta(\omega - \omega(k^+)) \]

\( D = \) spatial dimensionality.

**Example:** anisotropic acoustic mode in 3D

\[ \omega^2 = S_x^2 k_x^2 + S_y^2 k_y^2 + S_z^2 k_z^2. \]

\[ g(\omega) = \int \frac{d^3 k}{(2\pi)^3} \delta (\omega - \sqrt{S_x^2 k_x^2 + S_y^2 k_y^2 + S_z^2 k_z^2}) \]

Rescale the components of the wave number as

\[ q_x = S_x k_x, \quad q_y = S_y k_y, \quad q_z = S_z k_z, \]

\[ g(\omega) = \frac{1}{8\pi^3} \int dq_x \int dq_y \int dq_z \delta (\omega - \sqrt{q_x^2 + q_y^2 + q_z^2}) \]

\[ = \frac{1}{8\pi^3} \frac{1}{S_x S_y S_z} \int dq_x \int dq_y \int dq_z \delta (\omega - \mathbf{q}) \]

\[ = \frac{1}{8\pi^3} \frac{1}{S_x S_y S_z} \int d^3 q \delta (\omega - \mathbf{q}) = \frac{1}{S_x S_y S_z} g_{\text{iso}}(\omega), \]

where \( g_{\text{iso}}(\omega) \) is the density of states of an isotropic acoustic mode with the sound velocity equal to 1.

From Eq. (1) on p. 1,

\[ g_{\text{iso}} = \frac{1}{2\pi^2} c^2 \quad \Rightarrow \quad g(\omega) = \frac{1}{2\pi^2} \frac{\omega^2}{S_x S_y S_z}. \]
One more Example: A bending mode in layered crystals

\[ \omega^2 = a (k_x^2 + k_y^2) + s_z^2 k_z^2 \]

(Such a mode is found in layered crystals, where atomic planes can be considered as weakly coupled elastic membranes.)

First, it is convenient to replace \( \delta(\omega - \omega(k^\prime)) \) by \( \delta(\omega^2 - \omega^2(k^\prime)) \). Using the identity

\[ \delta(f(x)) = \sum_j \frac{1}{|f'(x_j)|} \delta(x - x_j), \]

where \( x_j \) are all roots of equation \( f(x_j) = 0 \), we obtain

\[ \delta(\omega^2 - \omega^2(k^\prime)) = \frac{1}{2 |\omega|} \left[ \delta(\omega - \omega(k^\prime)) + \delta(\omega + \omega(k^\prime)) \right] \]

Because \( \omega > 0 \), the second \( \delta \)-function is always \( \equiv 0 \) and

\[ \delta(\omega - \omega(k^\prime)) = 2 \omega \delta(\omega^2 - \omega^2(k^\prime)). \]

Then we have

\[ g(\omega) = \frac{1}{8\pi^3} \int d^3 k \delta(\omega - \omega(k^\prime)) = \frac{1}{8\pi^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(\omega^2 - a k_{11}^2 - s_z^2 k_z^2) \delta_{cyl} \]

where \( \delta_{cyl} \) is the cylindrical coordinate measure

\[ = \frac{\omega}{2\pi^2} \int_{-\infty}^{\infty} dk_z \int_{-\infty}^{\infty} dk_{11} \frac{1}{2} \int_{0}^{\infty} dk_z \delta(\omega^2 - a k_{11}^2 - s_z^2 k_z^2) \]
\[
\begin{align*}
\text{Using the formula for } \psi(x) \text{ again,} & \\
\frac{\omega}{2\pi^2} & \int_0^{\omega} \int_{-\infty}^{\infty} \frac{dk_2}{a^2k_2^2} \delta(k_2^2 - \sqrt{\frac{\omega^2 - \omega_0^2}{\omega - \omega_0}}) \\
& = \frac{\omega}{4\pi^2} \int_{-\infty}^{\omega} \frac{1}{\sqrt{\omega^2 - \omega_0^2 k_2^2}} \theta\left(\frac{\omega^2}{\omega_0^2} - \frac{k_2^2}{\omega_0^2}\right) \\
\text{Notice that } |k_2| & \leq \omega/\omega_0 \\
& = \frac{\omega}{4\pi^2} \int_{-\omega/\omega_0}^{\omega/\omega_0} \frac{2}{a} \int_0^{\omega/\omega_0} \frac{1}{\sqrt{\omega^2 - \omega_0^2 k_2^2}} \\
& = \frac{\omega}{4\pi^2a\omega_0} \int_0^{\pi/2} \frac{1}{\sqrt{1-y^2}} dy = \frac{\omega}{8\pi^2a\omega_0} \\
& = \frac{\pi}{2}
\end{align*}
\]

Formula #2

\[
g(\omega) = \frac{1}{8\pi^3} \oint dA / |\omega|,
\]

where the integral goes over an equipotential surface \( \omega = \omega(x) \).

Proof: Consider two equipotential surfaces at \( \omega \) and \( \omega + d\omega \)

Select two patches of infinitesimal area \( dA \) on each of the two surfaces and find the volume in between them

\[
dV = dA \frac{dk_2}{\text{distance along the normal to the patches}}.
\]
the contribution to the density of states from area $dA$ is

$$\frac{dA}{8\pi^3} \frac{dk}{d\omega} = \frac{dA}{1/\sqrt{\omega}} \frac{1}{8\pi^3}$$

$$\frac{d\omega}{dk} = \frac{1}{\sqrt{\omega}}$$

Then the total density of states is

$$g(\omega) = \frac{1}{8\pi^3} \int \frac{dA}{1/\sqrt{\omega}}$$

Q.E.D.

Example: **Van Hove Singularities**

Suppose that $\omega(k)$ has an extremum at point $k_0$. Choosing the coordinate axes along the principal axes of the quadratic form $\omega(k) = \omega_0 + \sum \delta_{ij} (k_i - k_{0i}) (k_i - k_{0i})$, we write $\omega(k)$ near an extremum as

$$\omega = \omega_0 \pm \frac{i}{2} \left[ a_{xx} (k_x - k_{0x})^2 + a_{yy} (k_y - k_{0y})^2 + a_{zz} (k_z - k_{0z})^2 \right]$$

where $a_{xx}, a_{yy}, a_{zz} > 0$, and corresponds to max, - to min.

Rescale the variables as

$$q_x = \sqrt{a_{xx}} (k_x - k_{0x}), \ldots, q_z = \sqrt{a_{zz}} (k_z - k_{0z})$$

Then

$$g(\omega) = \frac{1}{8\pi^3} \int \frac{dA_{\mathbf{q}}}{|\sqrt{\mathbf{q} \cdot \omega}|} = \frac{1}{8\pi^3} \int \frac{dA_{\mathbf{q}}}{|\sqrt{\mathbf{q} \cdot \omega}|} \times \frac{1}{\sqrt{a_{xx} a_{yy} a_{zz}}}$$

In $q$-space, $\omega$ is isotropic and given by
\[ \omega = \omega_0 \pm \frac{1}{2} q^2 \Rightarrow \]

\[ |\sqrt{q} \omega| = q \quad \text{solid angle element} \]

\[ \text{while} \quad dA_q = d\xi q^2 \]

\[ g(w) = \frac{1}{8\pi^3} \frac{1}{\sqrt{\omega_0 q q}} \quad \frac{\int dS_2 q}{4\pi} = \frac{1}{2\pi^2 \sqrt{\omega_0 q q}} \]

\[ q(w) = \sqrt{2} |w - \omega_0|^{1/2} \]

Thus

\[ g(w) = \frac{\sqrt{2}}{2\pi^2} \frac{1}{\sqrt{\omega_0 q q}} \quad (w - \omega_0)^{1/2} \]

In the case of max, \( \omega < \omega_0 \).

In the case of min, \( \omega > \omega_0 \).

\[ \text{max} \quad \begin{array}{c}
\sqrt{\omega_0 - w} \\
\omega_0 \end{array} \quad \text{min} \quad \begin{array}{c}
\sqrt{w - \omega_0} \\
\omega_0 \end{array} \]

One should not forget, however, that Eq. (2) is only valid for \( \omega \approx \omega_0 \), because the quartic expansion of the dispersion is only valid near the extremum. Also, there are other modes of the spectrum which do not have the Van Hove singularities. This means that the density of states consists of two parts: 1) regular and 2) singular.
\( g(\omega) = g_{\text{reg}}(\omega) + g_{\text{sing}}(\omega) \)

where \( g_{\text{sing}}(\omega) \) is given by Eq. (2).

For example, if one of the acoustic modes has a maximum

\[
\begin{align*}
\omega & \quad k \\
\hline
-\omega_0 & \quad 0
\end{align*}
\]

then

\[
g(\omega) = A \omega_0^2 + \frac{\sqrt{2}}{\pi n^2} \frac{1}{(a_x a_y a_z)^{1/2}} \sqrt{\omega_0^2 - \omega^2} \quad \Rightarrow \text{see plot}
\]

In addition, van Hove singularities occur at the boundaries of the Brillouin zone, where dispersion has minima or maxima. For example, an optical mode starts from a finite frequency and decreases as \( \omega^2 \)

\[
\omega(\omega) = \omega_0 - \frac{1}{2} (a_x k_x^2 + a_y k_y^2 + a_z k_z^2).
\]

Therefore, the density of states of an optical mode always start with a \( \omega_0 \) root singularity:

\[ g(\omega) \propto \sqrt{\omega_0 - \omega}. \]
Amplitudes of atomic vibrations

Reminder: Simple Harmonic Oscillator

Virial theorem

\[ \langle \text{kinetic energy} \rangle = \langle \text{potential energy} \rangle \]

\[ \langle \frac{1}{2} M \dot{x}^2 \rangle = \langle \frac{1}{2} M \omega^2 x^2 \rangle \]

\[ \langle x^2 \rangle + \langle u \rangle = \langle u \rangle = \frac{1}{2} M \omega (n + \frac{1}{2}) \]

\[ E = \frac{1}{2} M \omega (n + \frac{1}{2}) \]

\[ 2 \langle u \rangle = E = \frac{1}{2} M \omega (n + \frac{1}{2}) \]

\[ M \omega^2 \langle x^2 \rangle = \frac{1}{2} M \omega (n + \frac{1}{2}) \]

\[ \langle x^2 \rangle = \frac{1}{M \omega} (n + \frac{1}{2}) \]

Even in the ground state \((n=0)\), the amplitude of oscillations is non-zero:
\[ \langle x^2 \rangle |_{n=0} = \frac{\hbar}{2 M \omega} = \text{"zero-point motion"} \]

Quantization of atomic displacements in solids

Normal modes:
\[
X^{l\mu}_{n}(t) = \frac{1}{\sqrt{N}} \sum_{k \mu m} (a_{km} \psi_{m}(k) e^{i (\mathbf{k} \cdot \mathbf{r}_p - \omega_m(k)t)}) + \text{c.c.}
\]

atom \#n in prim. cell \#\mu

Normal coordinates
\[
a_{km} = \frac{\hbar \omega_m(k)}{2 \sqrt{M}} (\omega \mathbf{Q}_{km} + i \mathbf{P}_{km}) \sim \text{classical} \quad \text{"coordinates"} \quad \text{and \"momentum\"}
\]

\[ \mathbf{Q}_{km} \rightarrow \hat{\mathbf{Q}}_{km} \]

\[ \mathbf{P}_{km} \rightarrow \hat{\mathbf{P}}_{km} \]

quantum operators of coordinate and momentum

\[ [\hat{\mathbf{Q}}_{km}, \hat{\mathbf{P}}_{km}'] = i \hbar \delta_{km} \delta_{km'} \]
\[ a_{km} \rightarrow \hat{a}_{km} \]

Operators \( \hat{a}_{km} \) and \( \hat{a}^+_{km} \) are proportional to creation and annihilation operators.

\[
\begin{align*}
C_{km} &= \frac{1}{\sqrt{2 \hbar \omega_m(k)}} \left( \omega_m(k) \hat{a}_{km} + i \hat{p}_{km} \right) \\
C^+_{km} &= \frac{1}{\sqrt{2 \hbar \omega_m(k)}} \left( \omega_m(k) \hat{a}^+_{km} - i \hat{p}_{km} \right)
\end{align*}
\]

\[
\begin{align*}
\hat{a}_{km} &= \frac{1}{2 \sqrt{M \omega_m(k^2)}} \left( \omega_m(k) \hat{q}_{km} + i \hat{p}_{km} \right) \\
&= \frac{1}{2 \sqrt{M \omega_m(k)} \sqrt{2 \hbar \omega_m(k)}} \left( \omega_m(k) \hat{q}_{km} + \frac{i}{\sqrt{2 \hbar \omega_m(k^2)}} \hat{p}_{km} \right) \\
&= \frac{\hbar}{\sqrt{2 M \omega_m(k)}} \cdot \hat{C}_{km}
\end{align*}
\]

Likewise,

\[
\hat{a}^+_{km} = \sqrt{\frac{\hbar}{2 M \omega_m(k)}} \cdot \hat{C}^+_{km},
\]

and the operator of displacement becomes

\[
\begin{align*}
\vec{u}_{np}(t) &= \sqrt{\frac{\hbar}{2 MN}} \sum_{km} \frac{1}{\sqrt{\omega_m(k)}} \left( \hat{C}_{km} \vec{e}_{nm} \right) e^{i (k^2 \hbar - \omega_m(k^2) t)} + \text{h.c.}
\end{align*}
\]

The expectation value of \( u_{np} \) is

\[
\left\langle \left\langle u_{np}^2(t) \right\rangle \right\rangle = \text{thermodynamic average of thermal distribution of phonons}
\]

\( u_{np} \) averaging over a state with \( n \) vibrational quanta (n phonons)
In the product \( \langle \hat{C}_{km} \hat{C}_{km}' | n \rangle \) only the terms that contain one \( c \) and one \( c^+ \) survive

\[
\langle \langle n | \hat{C}_{km} \hat{C}_{km}' | l \rangle \rangle = \delta_{kk'} \delta_{mm'} (N_B + 1)
\]

\[
\langle \langle n | c_{km} c_{km}' | l \rangle \rangle = \delta_{kk'} \delta_{mm'} N_B,
\]

where

\[
N_B = \frac{1}{e^{\frac{\text{E}}{k_0 T}} - 1}
\]

indeed, recalling the algebra of \( c \) and \( c^+ \)

\[
\langle n-1 | c | n \rangle = \langle n | c^+ | n-1 \rangle = \sqrt{n}
\]

\[
\langle n | c^+ | n - 1 \rangle = \langle n | c | n + 1 \rangle = \langle n + 1 | c^+ | n \rangle = (\sqrt{n + 1})^2 = n + 1
\]

\[
\langle n | c^+ | n - 1 \rangle = \langle n | c | n \rangle - \langle n-1 | c | n \rangle = (\sqrt{n})^2 = n.
\]

Averaging \( n \) over statistical distribution gives \( N_B \).

Consider, for simplicity, the monochromatic basis case, when

polarization vectors of \( \phi \) three acoustic modes are orthogonal

\[
\vec{e}_m \cdot \vec{e}_{m'} = \delta_{mm'}
\]

Then (\( \alpha = 1 \))

\[
\langle \langle n \phi \alpha^2 | n \rangle \rangle \equiv u^2 = \frac{1}{2MN} \sum_k \sum_{m=1}^{\mathcal{D}} \frac{1}{c_\omega (k)} (2N_B + 1)
\]

\[
= \frac{1}{2MN} \sqrt{\int d \vec{P}_k} \sum_{m=1}^{\mathcal{D}} \frac{1}{c_\omega (k)} (2N_B + 1)
\]

\[
\mathcal{D} \text{ dimensions}
\]
In the product $\langle n l \hat{c} \hat{c}^+ l n \rangle$ only the terms that contain one $\hat{c}$ and one $\hat{c}^+$ survive.

Indeed, recalling the algebra of $\hat{c}$ and $\hat{c}^+$

$$\langle n-1|\hat{c}\hat{c}^+|n \rangle = \langle n - 1 \hat{c}^+ | n \rangle = \sqrt{n},$$

we have

$$\langle n l \hat{c} \hat{c}^+ l n \rangle = \langle n l \hat{c} l n+1 \rangle \langle n+1 \hat{c}^+ l n \rangle = (\sqrt{n+1})^2 = n+1$$

and

$$\langle n l \hat{c}^+ \hat{c} l n \rangle = \langle n l \hat{c}^+ l n-1 \rangle \langle n-1 \hat{c} l n \rangle = (\sqrt{n})^2 = n.$$

Averaging $n$ over statistical distribution gives the Bose function

$$\langle n \rangle_{WB} = \frac{1}{e^{\frac{\epsilon_m k_B T}{h \omega_0}} - 1}.$$

Thus

$$\langle \langle n l \hat{c} \hat{c}^+ l n \rangle \rangle = \delta_{k_k' \delta_{m m'}} (N_B + 1)$$

and

$$\langle \langle n l \hat{c}^+ \hat{c} l n \rangle \rangle = \delta_{k_k'} \delta_{m m'} N_B.$$

From now on, consider for simplicity the case of a monotonically basis, when polarization vectors of the three acoustic modes are orthonormal

$$\hat{e}_{m}, \hat{e}_{m'}^\dagger, \hat{e}_{n}^\dagger l_{n} = \delta_{m m'}, \delta_{n n'} = 1.$$
\[ \langle \langle n | u_p | n \rangle \rangle = \bar{u}^2 = \frac{\hbar}{2MN} \sum_{\kappa} \sum_{m=1}^{3} \frac{1}{\omega_m(\mathbf{k}^2)} (2N_B + 1) \]

\[ = \frac{\hbar}{2MN} \cdot \nabla \cdot \int d^3k \frac{1}{(2\pi)^3} \sum_{m=1}^{3} \frac{1}{\omega_m(\mathbf{k}^2)} (2N_B + 1) \]

\[ \rho = \frac{MN}{V} = \text{mass density} \]

\[ = \frac{\hbar}{\rho} \int d^3k \frac{1}{(2\pi)^3} \sum_{m=1}^{3} \frac{1}{\omega_m(\mathbf{k}^2)} \left( N_B + \frac{1}{2} \right) \]

Contribution of zero-point motion

Debye model \( \omega_D = s \kappa \)

\[ \int d^3k \frac{1}{(2\pi)^3} \rightarrow \int d\omega \quad g(\omega) ; \quad g(\omega) = \frac{1}{2\pi^2} \frac{\omega^2}{\nu^3} \]

\[ \bar{u}^2 = 3 \frac{\hbar}{\rho} \int d\omega \frac{\omega^2}{\nu^3} \frac{1}{\omega} \left( \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} + \frac{1}{2} \right) \]

High T: \( k_B T \gg \hbar \omega_D \)

\[ \frac{1}{e^{\frac{\hbar \omega}{k_B T}} - 1} \approx \frac{k_B T}{\hbar \omega_D} \gg 1 \]

Neglect \( \frac{1}{2} \)

\[ \langle u^2 \rangle = 3 \frac{\hbar \ k_B T}{\rho} \int d\omega \frac{\omega^2}{\nu^3} \frac{1}{\omega} = \frac{3 k_B T}{\rho \nu^3} \omega_D \]

The r.m.s. amplitude \( \sqrt{\langle u^2 \rangle} \propto T^{1/2} \)
NB: this scaling explains linear scaling of the resistivity with $T$ in metals.

\[ \sigma = \frac{n_e^2 T}{m} \]

\[ \frac{1}{\sigma} = \tau_F \cdot N_s \cdot A \]

- $\tau_F$: effective scattering cross-section.
- $N_s$: number of scattering centers/unit volume.

Each atom is displaced from its equilibrium position and thus scatters electrons.

\[ N_s = N_{\text{atoms}} = \frac{2}{Z} \frac{n_e}{V} \]

$A$ is the effective area covered by an atom in thermal motion.

\[ A \sim (\sqrt{2} \bar{u})^2 \sim \bar{u}^2 \propto T \]

Therefore, \[ \frac{1}{\sigma} \propto T \]

\[ \rho = \frac{1}{\sigma} \propto \frac{1}{T} \propto T \]
Q: When does thermal motion lead to melting?

A: 
\[ \bar{u}^2 \sim a \]

atomic spacing

\[ \bar{u}^2 \sim \frac{k_B T}{g s^2} \quad \omega_d \sim \frac{k_B T}{M s^2} \quad a^3 \omega_d \sim a^2 \frac{k_B T}{M s^2} \quad S \sim 1. \]

\[ \rho \sim \frac{M}{a^3} \quad \omega_d \sim \frac{S}{a^2} \]

\[ = k_B T_m \sim M s^2. \]

Reminder: 
\[ s = \sqrt{\frac{K}{M}} \]

\[ K = U''(a) \sim \frac{U_0}{a^2} \]

\[ M s^2 \sim M \frac{K}{a^2} \sim \frac{M}{M} \cdot \frac{U_0}{a^2} \sim \frac{U_0}{a^2} \sim \text{few eV}. \]

Too crude estimate for two reasons:
1) anharmonicity becomes important at high \( T \)
2) crystals melt when \( \sqrt{\bar{u}^2} \sim 0.2 \div 0.3 a \)

In actual materials, 
\[ T_m \sim 10^3 K. \]
Los T:

Separate $u^2$ into the thermal part and zero-point part

$$u^2 = u^2_T + u^2_0$$

$$u^2_T = 3 \, \frac{\hbar}{\rho} \int_0^{\infty} dw \, \frac{w}{s^3} \cdot \frac{1}{\frac{tw}{k_B T} - 1} \approx$$

For $k_B T \ll \omega$

$$\approx 3 \, \frac{\hbar}{\rho} \int_0^{\infty} dw \, \frac{w}{s^3} \cdot \frac{1}{\frac{tw}{k_B T} - 1} \propto T^2$$

$u^2_T$ vanishes as $T \to 0$.

$$u^2_0 = \frac{3}{2} \, \frac{\hbar}{\rho} \int_0^{\omega_D} dw \, \frac{w^2}{s^3} = \frac{3}{2} \, \frac{\hbar}{\rho} \frac{\omega_D^2}{s^3}$$

Remain finite as $T \to 0$.

Estimate:

$$\frac{u^2_0}{M} \sim \frac{\hbar}{M} a^3 \left( \frac{S}{a} \right)^2 \frac{1}{s^3} \sim \frac{\hbar}{M} \frac{a}{s} \sim$$

$$\sim a^2 \frac{\hbar}{MSa}$$

$s \sim \sqrt{\frac{k}{M}} a \sim \sqrt{\frac{U_0}{a^2 M}} a \sim \sqrt{\frac{U_0}{M}}$

$(u^2_0)^{1/2} \sim \alpha \cdot \left( \frac{\frac{\hbar}{M}}{(U_0)^{1/2} a} \right)^{1/2} \sim a \left( \frac{m}{M} \right)^{1/4}$

$U_0 \approx \frac{\hbar^2}{m a^2}$

$\epsilon$: electron mass
\[ M = \frac{M_p}{\text{motion mass}} \approx 10 m A = \frac{4}{10} m_A. \]

\[ (\overline{u^2})^{1/2} = a \frac{1}{(10^4 A^{1/10})^{1/4}} \approx \frac{a}{10} \cdot (\frac{10}{A})^{1/4}. \]

In typical solids, \( A \sim 10 \)

\[ (\overline{u^2})^{1/2} \sim 0.1 a \ll a \]

NaCl: \( (\overline{u^2})^{1/2} = 0.1 \text{ Å} \).

Classical description of atomic motion works even at \( T=0 \)

\( \text{NB}: \) Quantum crystals: Solid H and solid He.

\[ (\overline{u^2})^{1/2} \sim a \]

Atoms tunnel from one equilibrium position to another.

Can zero-point motion be observed?

a) Zero-point motion of atoms in diatomic molecules
Excited state

Ground state

\[ \Delta E \]

\[ \Delta E \]

Light isotope

Transition between excited vibrational model of ground and excited state.

\[ E_e = \Delta E + \hbar \omega_e^* \left( n^* + \frac{1}{2} \right) - \hbar \omega_e \left( n + \frac{1}{2} \right) \]

\[ E_h = \Delta E + \hbar \omega_h^* \left( n^* + \frac{1}{2} \right) - \hbar \omega_h \left( n + \frac{1}{2} \right) \]

\[ E_e = \Delta E + \hbar \omega_e^* n^* - \hbar \omega_e n + \frac{\hbar \omega_e - \hbar \omega_e^*}{2} \]

\[ n^* = n = 0 \]

\[ E_e = \Delta E + \frac{\hbar \omega_e - \hbar \omega_e^*}{2} \]

\[ E_h = \Delta E + \frac{\hbar \omega_h^* - \hbar \omega_h}{2} \]

\[ E_e - E_h = \frac{\hbar \omega_e - \hbar \omega_e^*}{2} - \frac{\hbar \omega_h^* - \hbar \omega_h}{2} \]

Experiment: \( BO \) and \( BO \) molecules

Mulliken Nature 114, 340 (1924)

Jenkins and Mokellar Phys. Rev. 442, 464 (1932)
<table>
<thead>
<tr>
<th>Transition</th>
<th>observed difference (cm⁻¹)</th>
<th>no zero-point motion</th>
<th>with zero-point motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 → 0</td>
<td>-8.6</td>
<td>-9.08</td>
<td>0</td>
</tr>
<tr>
<td>1 → 0</td>
<td>26.7</td>
<td>26.29</td>
<td>35.9</td>
</tr>
<tr>
<td>2 → 0</td>
<td>60.8</td>
<td>60.36</td>
<td>70.09</td>
</tr>
<tr>
<td>3 → 0</td>
<td>93.6</td>
<td>93.14</td>
<td>103.20</td>
</tr>
</tbody>
</table>

**Debye-Waller factor**

**Structure factor for X-ray scattering**

\[
\langle S \rangle = \left\langle \sum_{R_n} e^{i \frac{\mathbf{q} \cdot \mathbf{R}_n}{\hbar}} \right\rangle = \sum_{R_n} e^{i \frac{\mathbf{q} \cdot \mathbf{R}_n + \mathbf{u}}{\hbar}} = S_0 \left\langle \sum_{R_n} e^{i \frac{\mathbf{q} \cdot \mathbf{u}}{\hbar}} \right\rangle
\]

over motion of atom

\[
\left\langle \sum_{R_n} e^{i \frac{\mathbf{q} \cdot \mathbf{u}_n}{\hbar}} \right\rangle = 1 + i \sum_n \left\langle \mathbf{q} \cdot \mathbf{u}_n \right\rangle - \frac{1}{2} \sum_n \left\langle \left( \mathbf{q} \cdot \mathbf{u}_n \right)^2 \right\rangle + \ldots
\]

\[
\left\langle \left( \mathbf{q} \cdot \mathbf{u}_n \right)^2 \right\rangle = \frac{1}{\rho} \sum_{m=1}^{110} \left( \mathbf{q} \cdot \mathbf{e}_m \right)^2 \int \frac{d^3k}{(2\pi)^3} \frac{1}{\cos (\mathbf{k} \cdot \mathbf{R})} \left( N_0 + \frac{1}{2} \right)
\]

at high T

\[
\langle S \rangle = S_0 e^{-\frac{A\mathcal{T}}{k_0}}
\]

However, \( A\mathcal{T} \ll 1 \) for \( T \ll T_{mol} \) and thus Bragg peaks remain sharp.

Even at \( T = 0 \), zero-point motion smear Bragg peaks!
James, Waller, and Hartree, Proc. R. Soc. London A 125 334 (1928) 
next to Dirac’s paper “On the Quantum Theory of Electron”
Non-existence of 2D and 1D crystals

In D-dimensions, \( g(\omega) = a_D \frac{c_D}{\omega D} \); as \( a_2 = \frac{1}{2\pi^2} \)

\[
\overline{u^2} = D \frac{1}{\rho} \int_0^\infty d\omega \ \frac{c_D}{\omega} \left( \frac{1}{e^{\frac{\omega}{k_B T}} - 1} + \frac{1}{2} \right) \quad a_2 = \frac{1}{2\pi}
\]

at \( \omega \to 0 \), the integrand behaves as

\[
\int_0^D d\omega \ \frac{c_D}{\omega} = \int_0^{D-3} d\omega \ \omega = 1 \quad \text{log divergence in 2D}
\]

Therefore, one cannot assume that the crystal is infinite: phonon modes with long wavelengths are quantized by reflections at the sample boundaries.

If, for example, a sample is in contact with a very hard material, so that displacements on boundaries are quenched, quantization conditions lead to

\[
c^2 = \left( N_x \frac{S}{L_x} \right)^2 + \left( N_y \frac{S}{L_y} \right)^2 + \left( N_z \frac{S}{L_z} \right)^2
\]

\( N_x, N_y, N_z \) to integers (we assume isotropic spectrum).

Then, \( c_{\text{min}} \sim \frac{S}{L} \), where \( L \) is a typical size

and the integral has a finite low limit

\[
\frac{c_D}{\omega_{\text{min}}} \sim \left\{ \begin{array}{ll}
\frac{1}{\omega_{\text{min}}} - \omega_{D}^{-1} & , D = 1 \propto \frac{1}{L} \\
\omega_{\text{min}} & , D = 2 \propto \frac{1}{\sqrt{L}}
\end{array} \right.
\]
Therefore, in a macroscopic crystal, the rms displacement exceeds the lattice constant, and the crystalline order is destroyed. This is a particular example of the Mermin-Wagner theorem which states no long-range order is possible in $D \leq 2$.

In fact, the crystalline order is destroyed even stronger by bending modes. For example, in 2D the DOS of the bending mode is constant, therefore, the integral

$$\int_{\omega_{\min}}^{\omega_{\max}} d\omega \frac{g(\omega)}{\omega}$$

diverges as

$$\int_{\omega_{\min}}^{\omega_{\max}} d\omega \omega^{-1} \propto \ln \omega_{\max},$$

as opposed to the logarithmic divergence due to acoustic modes.

Notice, however, that the prefactor of the divergent term is proportional to $T$. Therefore, at $T=0$ this divergence is eliminated. Zero-point part of $\bar{u}^2$ is less divergent

$$\bar{u}^2_0 = \frac{D-4}{2P} \int d\omega \frac{g(\omega)}{\omega}$$

For acoustic modes, $g(\omega) \propto \omega^{D-2}$ and

$$\bar{u}^2_0 \propto \int d\omega \omega^{D-2} \propto \begin{cases} \ln \omega \mapsto \ln \omega_{\max} & D=2,3 \\ \omega \mapsto \omega_{\max} & D=1. \end{cases}$$
Therefore, quantum fluctuations do not destroy the crystalline order in $D=2$ but the do in $D=1$.

Again, with respect to bending modes, both 1D and 2D systems are unstable.