

Vibration of a diatomic molecule:

The two atoms vibrate with respect to each other. Amplitude of vibratory motion is very small. Internuclear potential can be expanded about the equilibrium bond distance r_e

$$U(r) = U(r_e) + (r-r_e) \left(\frac{dU}{dr} \right)_{r=r_e} + \frac{1}{2} (r-r_e)^2 \left(\frac{d^2U}{dr^2} \right)_{r=r_e} + \dots$$

$$U(r) = U(r_e) + 0 + \frac{1}{2} (r-r_e)^2 k + \dots$$

At r_e potential 2 is minimum

$$U(r) = U(r_e) + \frac{1}{2} kx^2$$

higher order terms neglected for small amplitudes of motion.

harmonic oscillator approximation

where x = displacement w.r.t equilibrium separation

solve Schrodinger's eq with this Hamiltonian

Allowed energy levels

$$E_{vib} = \frac{1}{2} \hbar \omega (n + \frac{1}{2})$$

$$n=0, 1, 2, \dots \quad \omega_n = \text{constant}$$

$\frac{1}{2} \hbar \omega \Rightarrow$ zero-point energy, even at 0K, some energy present to keep oscillator stable.

$$\text{where } \omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

$\mu \Rightarrow$ reduced mass.

one \rightarrow for each mode of vibration.

3M-6 modes for molecule with M atoms

(3M-3rotational modes - 3translational modes)

Difference between energy levels $E_{n+1} - E_n = \hbar \omega$

Molecules can change vibrational state by absorbing light

if molecule has a change in dipole moment during vibration

only $\Delta n = \pm 1$ allowed by absorption of light.

$$\text{Frequency of light absorbed/emitted} = \frac{E_{n+1} - E_n}{h} = \nu$$

In IR region

for typical values of m_1, m_2, r_e for molecules

per vibrational mode

Just one line in spectrum at frequency ν . From spectroscopy ν can be measured. Just as in case of rotational spectra, \bar{B} can be measured.

Vibrational partition function:

$$q_{\text{vib}}(T) = \sum_n e^{-\beta \epsilon_n} = e^{-\beta h\nu/2} \sum_{n=0}^{\infty} e^{-\beta h\nu n}$$

$$q_{\text{vib}}(T) = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}} \quad (\text{Note } e^{-\beta h\nu} < 1)$$

no need for integration

But if we approach this classically, energy levels are almost continuously spaced if spacing relative to energy is very small

$$\frac{\Delta \epsilon}{\epsilon} = \frac{h\nu}{(n+\frac{1}{2})h\nu} \approx \frac{1}{n} \rightarrow \text{This quantity is very small when } n \rightarrow \infty$$

Now $(n+\frac{1}{2})h\nu = \epsilon_n$

↳ average value is kT as we have seen

$$\therefore \text{Typical value of } n \approx \frac{\epsilon_n}{h\nu} = \frac{kT}{h\nu}$$

\therefore When $kT \gg h\nu$, energies can be assumed to be continuously distributed.

$$T \gg \frac{h\nu}{k}$$

defined by a characteristic vibrational temperature θ_v

$$\therefore \text{When } T \gg \theta_v, \quad q_{\text{vib}}(T) = \sum_{n=0}^{\infty} e^{-\theta_v/T} \left(n+\frac{1}{2}\right) dn$$

$$= e^{-\theta_v/2T} \sum_{n=0}^{\infty} e^{-n\theta_v/T} dn$$

$$\approx 1 = -\frac{T}{\theta_v} (e^{-\infty} - e^0) = \frac{T}{\theta_v} \text{ or } \frac{kT}{h_2}$$

New from exact summation result.

$$q_{\text{vib}}(T) = \frac{e^{-\theta_v/2T}}{1 - e^{-\theta_v/T}} = \frac{1}{(e^{+\theta_v/2T} - e^{-\theta_v/2T})}$$

When $T \gg \theta_v$

$$q_{\text{vib}}(T) \approx \frac{1}{\left(1 + \frac{\theta_v}{2T}\right) - \left(-\frac{\theta_v}{2T}\right)} = \frac{T}{\theta_v} \text{ or } \frac{kT}{h_2}$$

large quantum numbers

same as classical result obtained from integration

Thus, quantum model tends to classical model at high T \Rightarrow correspondence principle.

high relative to characteristic temperature $\theta_v \Rightarrow$ which depends on mass of the atoms and bond strength. Light atoms & tighter bonds have higher or \Rightarrow more quantum mechanical at given temperature

typically
0(1000 K)
for typical molecules

$$E_V = -\left(\frac{\partial \ln Q}{\partial \beta}\right)_N = -\left(\frac{\partial \ln q^N}{\partial \beta}\right)_N = -N \frac{\partial \ln q}{\partial \beta}$$

$$= +N \frac{\partial \ln(e^{\theta_V/2T} - e^{-\theta_V/2T})}{\partial \beta}$$

$$= N \frac{1}{e^{\theta_V/2T} - e^{-\theta_V/2T}} (e^{\theta_V/2T} + e^{-\theta_V/2T}) \cdot \frac{\theta_V}{2} \frac{\partial(1/T)}{\partial \beta}$$

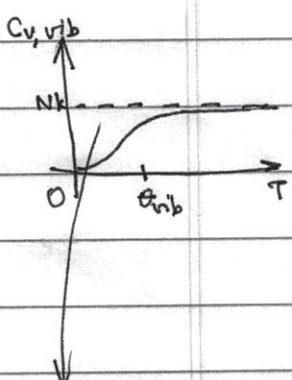
$$= N \left(\frac{e^{\theta_V/2T} + e^{-\theta_V/2T}}{e^{\theta_V/2T} - e^{-\theta_V/2T}} \right) \cdot \frac{\theta_V \cdot k}{2}$$

$$= Nk \frac{\theta_V}{2} \left(1 + \frac{2e^{-\theta_V/2T}}{e^{\theta_V/2T} - e^{-\theta_V/2T}} \right)$$

$$E_V = Nk \left(\frac{\theta_V}{2} + \frac{\theta_V}{e^{\theta_V/T} - 1} \right)$$

zero-point energy contribution \downarrow depends on θ_V and hence on the molecule \rightarrow (bond length & masses)

$$c_V = \left(\frac{\partial E_V}{\partial T} \right)_N = Nk \left(0 + \frac{\theta_V(-1)}{(e^{\theta_V/T}-1)^2} e^{\theta_V/T} \cdot \theta_V \left(\frac{-1}{T^2} \right) \right)$$



$$c_V = Nk \left(\frac{\theta_V}{T} \right)^2 \frac{e^{\theta_V/T}}{(e^{\theta_V/T}-1)^2}$$

$T \gg \theta_V$ i.e. $\theta_V/T \approx 0$

$$c_V = Nk$$

$$E_V \approx Nk \left(\frac{\theta_V}{1+\theta_V/T-1} + \frac{\theta_V}{2} \right)$$

large deviations between
QM and classical expression
for c_V at low temp.

QM result matches experimental
data.

$$E_V = NkT + \frac{Nk\theta_V}{2} \approx NkT$$

$\because T \gg \theta_V$

per vibrational mode

fraction of molecules in an excited vibrational state

$$f_n = e^{-\beta h\nu(n+\frac{1}{2})}$$

$$f_{n>0} = \sum_{n=1}^{\infty} e^{-\beta h\nu(n+\frac{1}{2})} = \frac{1}{q_{\text{vib}}} (q_{\text{vib}} - e^{-\beta h\nu})$$

$$= 1 - f_0 = 1 - (1 - e^{-\beta h\nu}) = e^{-\beta h\nu} = e^{-\alpha V/T}$$

When $\alpha_v \gg T$

$f_{n>0} = 0$, not any significant number of molecules in any of the excited states combined.
Almost all molecules in ground state.

A crystal of N atoms \Rightarrow Treatment of vibrations \Rightarrow

N -atom system has $3N$ ^{normal} co-ordinates or degrees of freedom. Of these 3 are rotational and other 3 are translational.

Thus there are $3N-6 \approx 3N$ (for large N) degrees of freedom.

$\{n_j\}$ is set of occupation numbers for different vibrational states

$$\text{Total energy } E(\{n_j\}) = \sum_{j=1}^{3N} h\nu_j (n_j + \frac{1}{2})$$

$$= E_0 + \sum_{j=1}^{3N} h\nu_j n_j$$

zero-point energy contribution

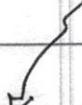
$\frac{h\nu_j}{2}$ per degree of freedom

can be seen as energy of a system of independent particles, which occupy states $1, 2, \dots, 3N$ with energies $h\nu_1, h\nu_2, \dots$ with n_1, n_2, \dots particles in states respectively

These are "virtual" (energy-only-carrying) particles or quasi-particles known as phonons. There is no restriction on the numbers n_j i.e. $n_j = 0, 1, \dots, 3N$. These particles are bosonic. We can,

use Bose-Einstein statistics

$$\therefore \bar{n}_j = \frac{\lambda e^{-\beta \epsilon_j}}{1 - \lambda e^{-\beta \epsilon_j}} \quad \text{where } \lambda = e^{\frac{h\nu_j}{kT}} \text{ or } e^{\frac{h\nu_j}{kT}}$$


solid with different modes of vibration (due to coupling between atoms) is treated as an ideal gas of phonons.

Now phonons are virtual particles. You can have as many as you need to utilize the available vibrational energy in the system.

Number of phonons not conserved \Rightarrow can be created/annihilated as per available vibrational energy

$$\therefore n_p \rightleftharpoons m_p \quad \text{possible where:}$$

Condition for equilibrium $\mu_p(n-m)=0$

$$\therefore n \neq m \text{ in general } \mu_p = 0, \lambda = 1$$

\therefore An ideal gas of phonons (virtual particles) has zero chemical potential.

$$\therefore \bar{n}_j = \frac{e^{-\beta \epsilon_j}}{1 - e^{-\beta \epsilon_j}} = \frac{1}{e^{\beta \epsilon_j} - 1}$$

$$\bar{E} = \sum_{j=1}^{3N} \bar{n}_j h\nu_j + E_0 \quad \text{#} = E_0 + \sum_{j=1}^{3N} \frac{h\nu_j}{e^{\beta \nu_j} - 1}$$

This summation depends on knowing how ν_j 's are distributed

$$c_v = \left(\frac{\partial \bar{E}}{\partial T} \right)_{N,V} = 0 + k \sum_{j=1}^{3N} \left(\frac{h\nu_j}{kT} \right)^2 \frac{e^{\hbar\nu_j/kT}}{(e^{\hbar\nu_j/kT} - 1)^2}$$

Einstein's theory of solids.

Solid comprised of $3N$ independent oscillators $\Rightarrow 1$ per direction per atom. i.e. each atom vibrates about its mean position independent of other atoms.

The frequency of vibration ν is same for each vibrating atom. $\hookrightarrow \nu \Rightarrow$ Einstein frequency

Only discrete packets of energy $h\nu$ are allowed to each oscillator. (Quantum mechanics).

Insight was a precursor to development of QM.

We know that for an oscillator of frequency ν

$$q = \frac{e^{-\beta h\nu/2}}{1 - e^{-\beta h\nu}}$$

$$\therefore Q = q^{3N}$$

No correction for indistinguishability since each atom can be identified by its position

$$\bar{E} = -\frac{\partial \ln Q}{\partial \beta} = -3N \frac{\partial \ln \left(\frac{1}{e^{\beta h\nu/2} - e^{-\beta h\nu/2}} \right)}{\partial \beta}$$

$$= 3N \frac{e^{\beta h\nu/2} + e^{-\beta h\nu/2}}{e^{\beta h\nu/2} - e^{-\beta h\nu/2}} \cdot \frac{h\nu}{2}$$

$$= 3N \left(\frac{h\nu}{2} + \frac{h\nu}{e^{\beta h\nu} - 1} \right)$$

zero-point
energy

$$C_V = \left(\frac{\partial E}{\partial T}\right)_{N,V} = 3N \left(0 + \frac{h\nu}{(e^{\beta h\nu} - 1)^2} e^{\beta h\nu} \cdot h\nu \frac{\partial \beta}{\partial T} - 1\right)$$

$$= 3N \frac{(h\nu)^2 e^{\beta h\nu}}{(e^{\beta h\nu} - 1)^2} \cdot \frac{1}{T^2 k}$$

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

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

ν is hypothetical frequency of vibration given to each atom

$\frac{h\nu}{k}$ is known as the Einstein temperature T_E

"Einstein frequency"

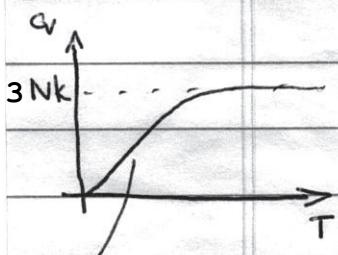
$$\text{At } T \gg \frac{h\nu}{k}$$

$$C_V \rightarrow 3Nk$$

($3k$ per atom or $3R$ per mole)

But $T \sim T_E$ or much lower then the exponential factors become important $\Rightarrow C_V$ deviates from $3Nk$ value. & has a temperature dependence

At very low temperatures



$$C_V \approx 3Nk \frac{\left(\frac{h\nu}{kT}\right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left(e^{\frac{h\nu}{kT}} - 1\right)^2}}{\left(\frac{h\nu}{kT}\right)^2} = 3Nk \left(\frac{h\nu}{kT}\right)^2 e^{-\frac{h\nu}{kT}}$$

As $T \rightarrow 0$, $C_V \rightarrow 0$. The approach is exponential in Einstein's model. In reality $C_V \propto T^3$.

something freezes out vibrational excitations (thermal) at low temperature, quantization!

This is due to crude approximation that all normal modes have the same frequency.

$h\nu_i$ long wavelength modes \rightarrow lower frequency \rightarrow spacing between these is smaller. Much more difficult to freeze out. These able to make a significant contribution to the

heat capacity even at very low temperatures.

More exact model by Peter Debye \Rightarrow modes that matter at low temperatures are long wavelength modes. These are not sensitive to discrete nature of solid \Rightarrow positions of atoms : their wavelengths greatly exceed interatomic spacings. Solid can be treated as an isotropic continuous medium to account for all these modes.

Phonons are quanta of lattice vibrations or sound waves
 (Photons " " " electromagnetic vibrations or light waves)

Phonons have a wave-vector \mathbf{k} which describes the momentum of the quasi-particle. Note this momentum is conserved in collisions. There are various types of collisions.

Phonon-electron : electrical resistance.

Phonon-photon : Brillouin scattering

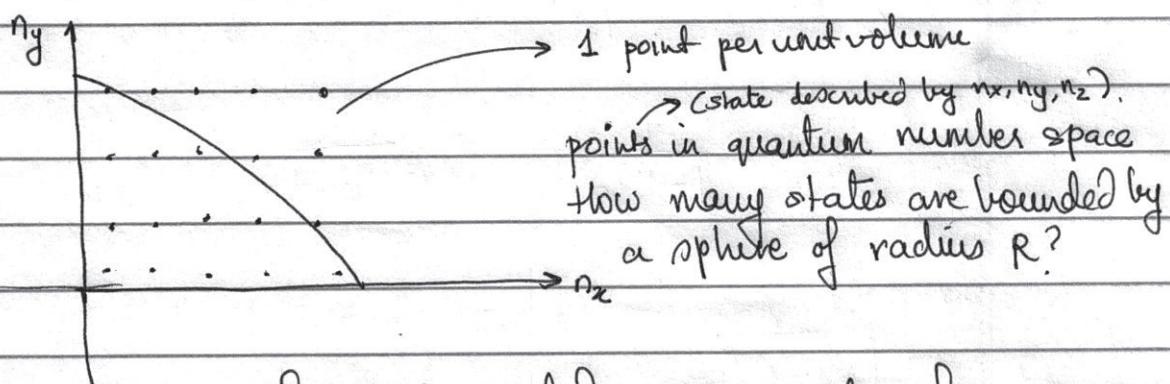
Phonon-neutron scattering

In a crystal which is a cube of length L , say. allowed values of wave-vector require fitting a standing wave. Similar to particle in a box $\frac{n\lambda}{2} = L \quad \therefore k = 2\pi/\lambda \Rightarrow$

$$\therefore \mathbf{k} = \frac{n\pi}{L} \quad \text{i.e. } k_x = \frac{n_x\pi}{L}, \quad k_y = \frac{n_y\pi}{L}, \quad k_z = \frac{n_z\pi}{L}$$

In three dimensions $k^2 = \left(\frac{\pi}{L}\right)^2 (n_x^2 + n_y^2 + n_z^2)$ ^{n_x, n_y, n_z} = positive integers
 k is magnitude of wave-vector

How many standing waves with wave-number between k and $k+dk$



Only positive quadrant is needed, the number of states (each with a distinct n_x, n_y, n_z) = $\frac{\pi R^3}{6} \times \frac{1}{\text{no. of points per unit volume}}$

$$\text{Now } R^2 = n_x^2 + n_y^2 + n_z^2 = \frac{L^2 k^2}{\pi^2}$$

~~Medium can in principle do = as wave propagation
longitudinal waves perpendicular to direction of~~

$$\phi(k) = \frac{\pi}{6} \left(\frac{Lk}{\pi}\right)^3 = \frac{L^3 k^3 \pi^4}{6 \pi^3} = \frac{V k^3}{6 \pi^2}$$

Number of standing waves with wave-vector of magnitude less than k .

Number of waves with wave-number between k and $k+dk = \omega(k) dk$

$$\text{where } \omega(k) = \frac{d\phi(k)}{dk} = \frac{3V k^2}{6\pi^2} = \frac{V k^2}{2\pi^2}$$

density of states.

Number of waves between k and $k+dk$ can be converted to number of waves between ν and $\nu+d\nu$ ($g(\nu)d\nu$)

$$\therefore \nu = \frac{vk}{\lambda} = \frac{vk}{2\pi} \quad k = \frac{2\pi\nu}{v}$$

$$\therefore g(\nu)d\nu = \omega(k)dk = V \left(\frac{2\pi\nu}{v} \right)^2 d \left(\frac{2\pi\nu}{v} \right)$$

wave propagating! \Rightarrow These are imp at low T. At high T

quantization is not important. Spin-orbit coupling and other

$$= V \frac{4\nu^2}{2v^2} \cdot \frac{2\pi}{v} d\nu$$

$$= \frac{4V\pi}{163} \nu^2 d\nu$$

But we have to take account of a "degeneracy"

for each k (wave propagating in a particular $d\nu$ with particular momentum).

$$\frac{2\pi V}{3} \nu^2 = 3N \Rightarrow \nu_0 = (3N)^{1/3}$$

Medium can vibrate in same dir[±] as wave propagation (longitudinal waves) or perpendicular to direction of \mathbf{k} (transverse waves).

There are two transverse directions and one longitudinal direction. All three contribute to $g(\nu)$

$$g(\nu) d\nu = \left(\frac{2}{v_L^3} + \frac{1}{v_T^3} \right) 4\pi V \nu^2 d\nu.$$

waves of a given frequency.

In terms of an average velocity v_0 where,

$$\frac{3}{v_0^3} = \frac{2}{v_L^3} + \frac{1}{v_T^3}$$

We can express conveniently

$$g(\nu) d\nu = \frac{12\pi V}{v_0^3} \nu^2 d\nu.$$

This expression is arrived at by treating crystal as a continuum solid (continuous elastic body) and is exact in the limit of low frequencies or long wavelengths, where the atomic nature of the solid is not important (to the wave propagating!). \Rightarrow These modes imp at low T. At high T quantization is not important. Equipartition explains c_v and \bar{E} values.

Now we know it is only possible to have $3N$ modes of vibration or $3N$ frequencies.

\therefore Debye who followed this treatment put ~~a~~ a bound on the maximum frequency ν_0 such that

$$\int_0^{\nu_0} g(\nu) d\nu = 3N$$

depends on
elastic
properties
of solid.

$$\therefore \frac{12\pi V}{v_0^3} \frac{\nu_0^3}{3} = 3N \Rightarrow \nu_0 = \left(\frac{3N}{4\pi V} \right)^{1/3} v_0$$

related to $1/\text{interatomic spacing}$

ν_D is known as a Debye frequency.

Thus the distribution function in terms of Debye frequency ν_D is

$$g(\nu) d\nu = \frac{9N}{\nu_D^3} \nu^2 d\nu \quad 0 \leq \nu \leq \nu_D$$

$$= 0 \quad \nu > \nu_D$$

$g(\nu) d\nu$ can be used in any of the integrals (over ν) to calculate thermodynamic properties of a crystal.

$$C_V = \sum_{\text{modes}} c_V \text{ due to each mode}$$

$$= \sum_{\nu} k \left(\frac{\hbar \nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$c_V = \int_{\nu=0}^{\infty} k g(\nu) d\nu \left(\frac{\hbar \nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

$$c_V = \frac{9Nk}{\nu_D^3} \cdot \frac{\hbar^2}{(kT)^2} \int \frac{\nu^4 e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\nu$$

$$= \frac{9Nk}{\nu_D^3} \cdot \frac{\hbar^2}{(kT)^2} \int \left(\frac{\hbar \nu}{kT} \right)^4 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2} d\left(\frac{\hbar \nu}{kT} \right) \cdot \left(\frac{kT}{\hbar} \right)^5$$

$$= 9Nk \frac{(kT)^3}{(\hbar \nu_D)^3} \int_{x=0}^{\theta_D/T} x^4 \frac{e^x}{(e^x - 1)^2} dx$$

where $\theta_D = \frac{\hbar \nu_D}{k}$ is known as the Debye temperature

$$c_V = 9Nk \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

reproduces T^3 dependence

Numerically evaluated. Depends on θ_D/T

$$c_v = 3Nk D\left(\frac{T}{\theta_D}\right) \quad \text{where } D\left(\frac{T}{\theta_D}\right) = 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

Debye function. \Rightarrow A well-tabulated function of T/θ_D

High temperature limit, θ_D/T is small.

$$\begin{aligned} \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx &\rightarrow \int_0^{\theta_D/T} \frac{x^4 (1 + x + \dots)}{(1 + x + \dots - 1)^2} dx \\ &= \int_0^{\theta_D/T} \frac{x^4}{x^2} dx = \int_0^{\theta_D/T} x^2 dx = \frac{1}{3} \left(\frac{\theta_D}{T}\right)^3 \end{aligned}$$

$$\therefore c_v \rightarrow 3Nk$$

Low temperature limit, $\theta_D/T \rightarrow \infty$

$$\begin{aligned} \therefore D\left(\frac{T}{\theta_D}\right) &\rightarrow 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\infty} \frac{x^4 e^x}{(e^x - 1)^2} dx \\ &\qquad \qquad \qquad \text{an exact integral } 4\pi^4/15 \end{aligned}$$

$$\therefore c_v = \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D}\right)^3$$

$\nwarrow T^3 \text{ dependence}$

Different models for a solid of atoms \Rightarrow

Classical : Equipartition

details of modes do not matter.

$$3N \text{ modes of vibration} \times \frac{\text{energy}}{\text{cv}} \times kT \text{ per mode} = 3NkT$$
$$\times k \text{ per mode} = 3Nk$$

Einstein model :

Solid \Rightarrow Ideal gas of vibrating atoms

N atoms . 3 directions for vibration \Rightarrow $3N$ degrees of freedom.

So, vibrations of individual atoms separated/independent/uncorrelated. \Rightarrow this is far from reality. Crystal vibrations are collective vibrations \Rightarrow involving all atoms in the crystal.

The part Einstein model gets right is the quantization of energies for each "atomic vibration." i.e. Each vibration can be energized only in jumps of $\hbar\nu$.

$$\therefore C_V = C_V, \text{each quantized oscillator} \times 3N$$

\Downarrow
3N independent degrees of freedom

These are centered on atoms.

All these degrees are identical and have a frequency $\nu \Rightarrow$ Einstein frequency, which of course is not a real frequency.

\therefore Atoms vibrate in unison and it is meaningless to describe frequency of vibration for each atom.

deviates at low temperature where the ^{inaccurate} assumptions of model have an effect.

$$C_V = 3Nk \left(\frac{\hbar\nu}{kT} \right)^2 e^{\frac{\hbar\nu}{kT}}$$
$$\therefore \left(\frac{kT}{\hbar\nu} \right) \left(e^{\frac{\hbar\nu}{kT}} - 1 \right)^{-2}$$

Debye model

$3N$ modes



all possible frequencies from
0 to ω_0

These are collective modes of
crystal. Involve all atoms.

They include the inter-atomic
coupling via elastic properties
of the solid.

ω_0 the upper bound in frequency
reflects the inter-atomic spacing.

The highest frequency mode

is "centered" on individual atoms.

Modes cannot have any higher
frequencies.

$$\left(\frac{3N}{4\pi V}\right)^{1/3} \omega_0$$

→ of given frequency
Modes arrived at by quantizing sound
waves within crystal boundaries

Besides each mode can have only discrete amounts of energy.

∴ There are two quantizations, i.e. each type of oscillator has
quantized energy levels (can change amplitude in jumps only).
Since oscillators "confined" within a solid only oscillators of
specific frequency allowed.

$$C_V = \sum_{\text{allowed modes}} k \left(\frac{\hbar \nu}{kT} \right)^2 \frac{e^{\hbar \nu / kT}}{(e^{\hbar \nu / kT} - 1)^2}$$