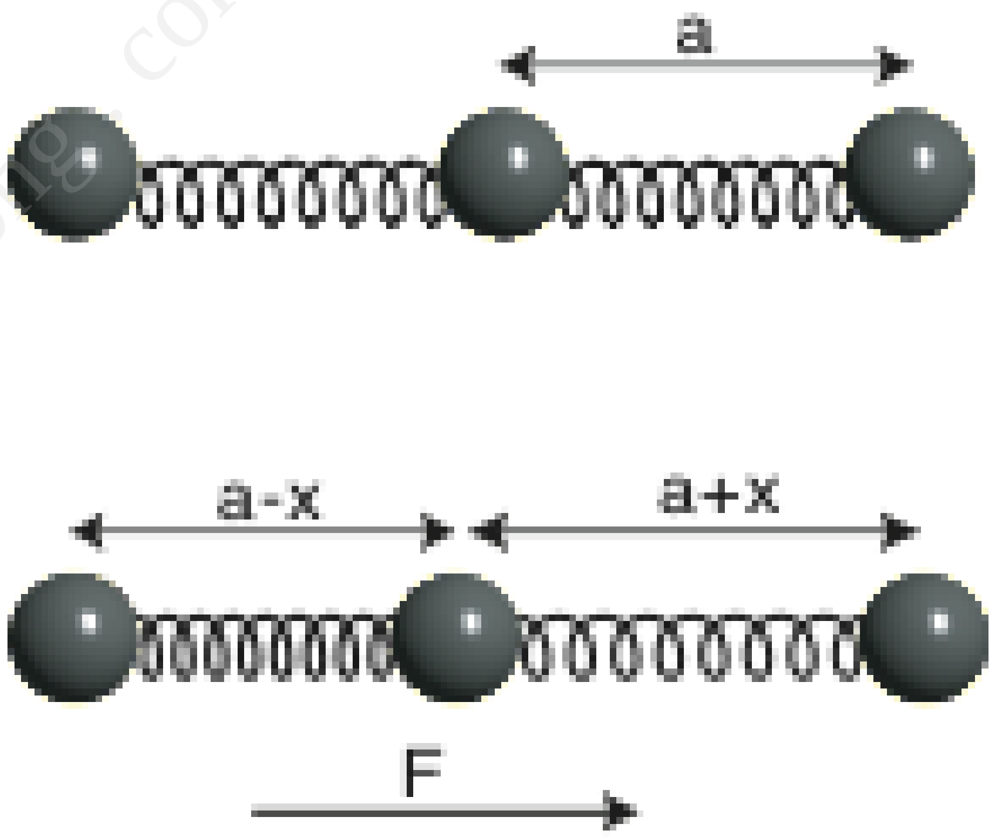
Thermal properties

at the end of this lecture you should understand….

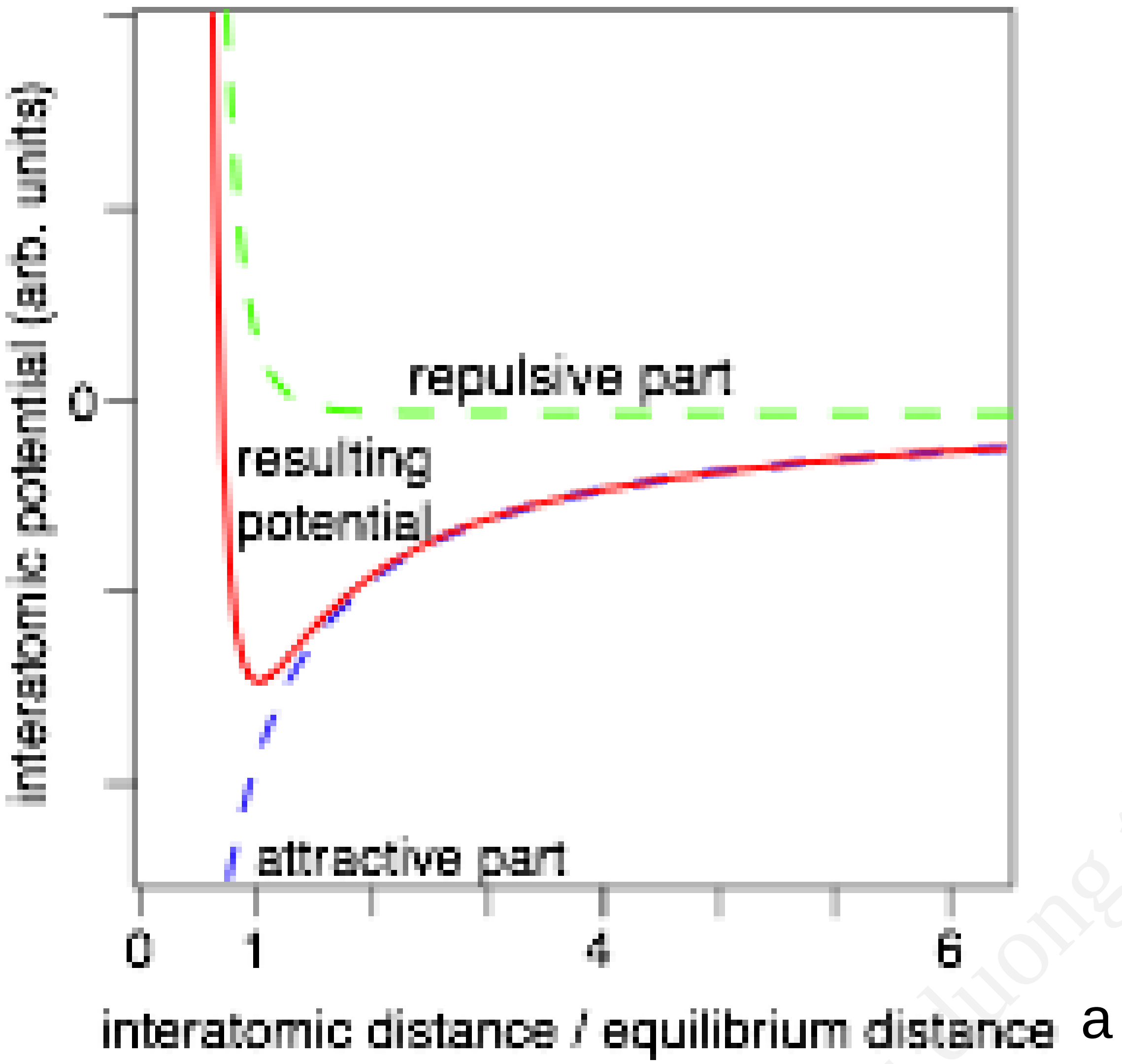
- Lattice vibrations: harmonic oscillator, infinite and finite chains of atoms
- The first Brillouin zone
- Heat capacity of the lattice: Einstein and Debye models
- Thermal conductivity
- Thermal expansion
- Allotropic phase transitions
- Melting

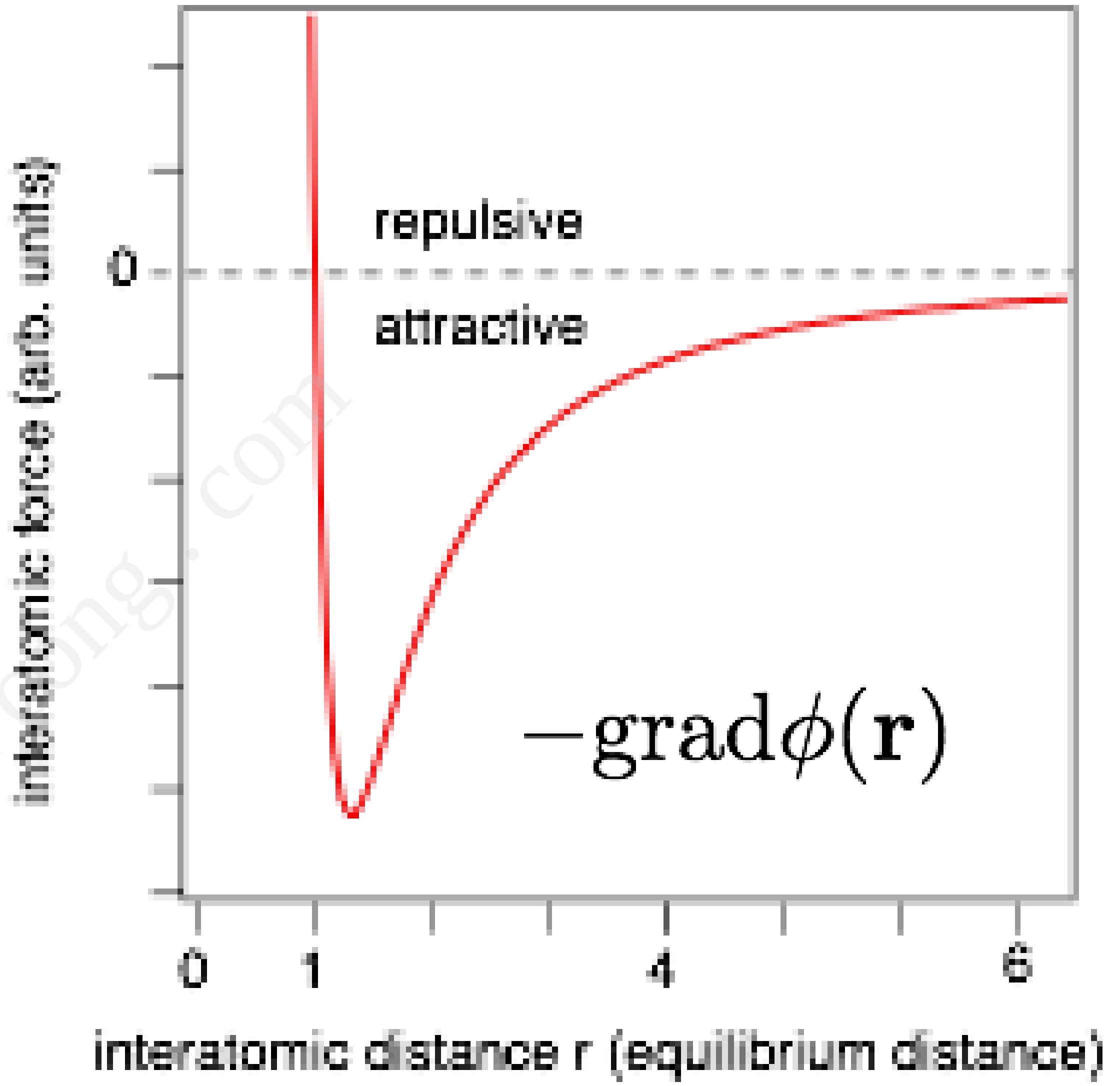
Thermal vibration of the atoms

- What is the frequency and amplitude of the atomic vibrations?
- Consider the strongly simplified case of only one oscillator.
- What is the spring constant?



Lattice vibrations





$-\mathrm{grad}\phi(\mathbf{r})$

$$\phi(x) = \phi(a) + \frac{d\phi(a)}{dx}(x-a) + \frac{1}{2}\frac{d^2\phi(a)}{dx^2}(x-a)^2 + \frac{1}{6}\frac{d^3\phi(a)}{dx^3}(x-a)^3 + \ldots$$

$$F(x-a) \approx -\frac{d^2\phi(a)}{dx^2}(x-a) = -\gamma(x-a)$$

A simple harmonic oscillator

equation of motion

$$M\frac{d^2x}{dt^2} = -\gamma x,$$

solution

$$x(t) = A\cos(\omega t + \delta)$$

angular frequency of the harmonic vibration

$$\omega = \sqrt{\frac{\gamma}{M}}.$$

- Strong force constants and light masses give rise to high frequencies.

Estimate of vibrational amplitudes

Classical treatment using the equipartition theorem.

$$E = \frac{1}{2}Mv^2 + \frac{1}{2}\gamma x^2$$

This must be equal to k_BT. When the kinetic energy is zero

$$\frac{1}{2}\gamma x_{\max}^2 = k_B T$$

$$x_{\max} = \left(\frac{2k_B T}{\gamma}\right)^{1/2}$$

and this is usually only a few percent of the interatomic spacing.

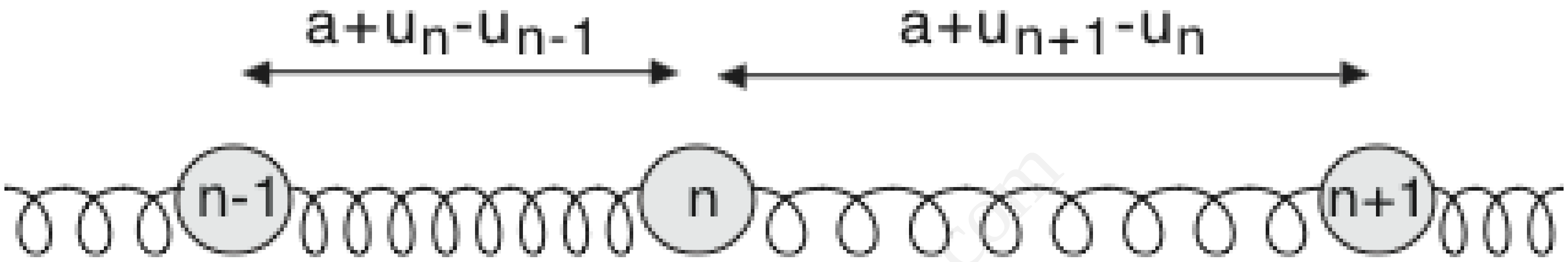
More sophisticated models (but still all in 1D)

- An infinite chain with one atom per unit cell
- An infinite chain with two atoms per unit cell
- A finite chain of atoms

what are the allowed vibrational frequencies ω?

The infinite one-dimensional chain

equ. distance a



equ. of motion
atom n

$$M\frac{d^2u_n}{dt^2} = -\gamma(u_n - u_{n-1}) + \gamma(u_{n+1} - u_n)$$

$$M\frac{d^2u_n}{dt^2} = -\gamma[2u_n - u_{n-1} - u_{n+1}]$$

ansatz

position on chain

$$u_n(t) = ue^{i(kan-\omega t)}$$

wave number

inserting this gives

$$-M\omega^2ue^{i(kan-\omega t)} = -\gamma ue^{i(kan-\omega t)}[2 - e^{-ika} - e^{ika}] = -2\gamma(1-\cos ka)ue^{i(kan-\omega t)}$$

$$-M\omega^2 u e^{i(kan-\omega t)} = -2\gamma(1-\cos ka) u e^{i(kan-\omega t)}$$

$$-M\omega^2 = -2\gamma(1-\cos ka)$$ (works for *any* amplitude *u*)

this can only be solved when

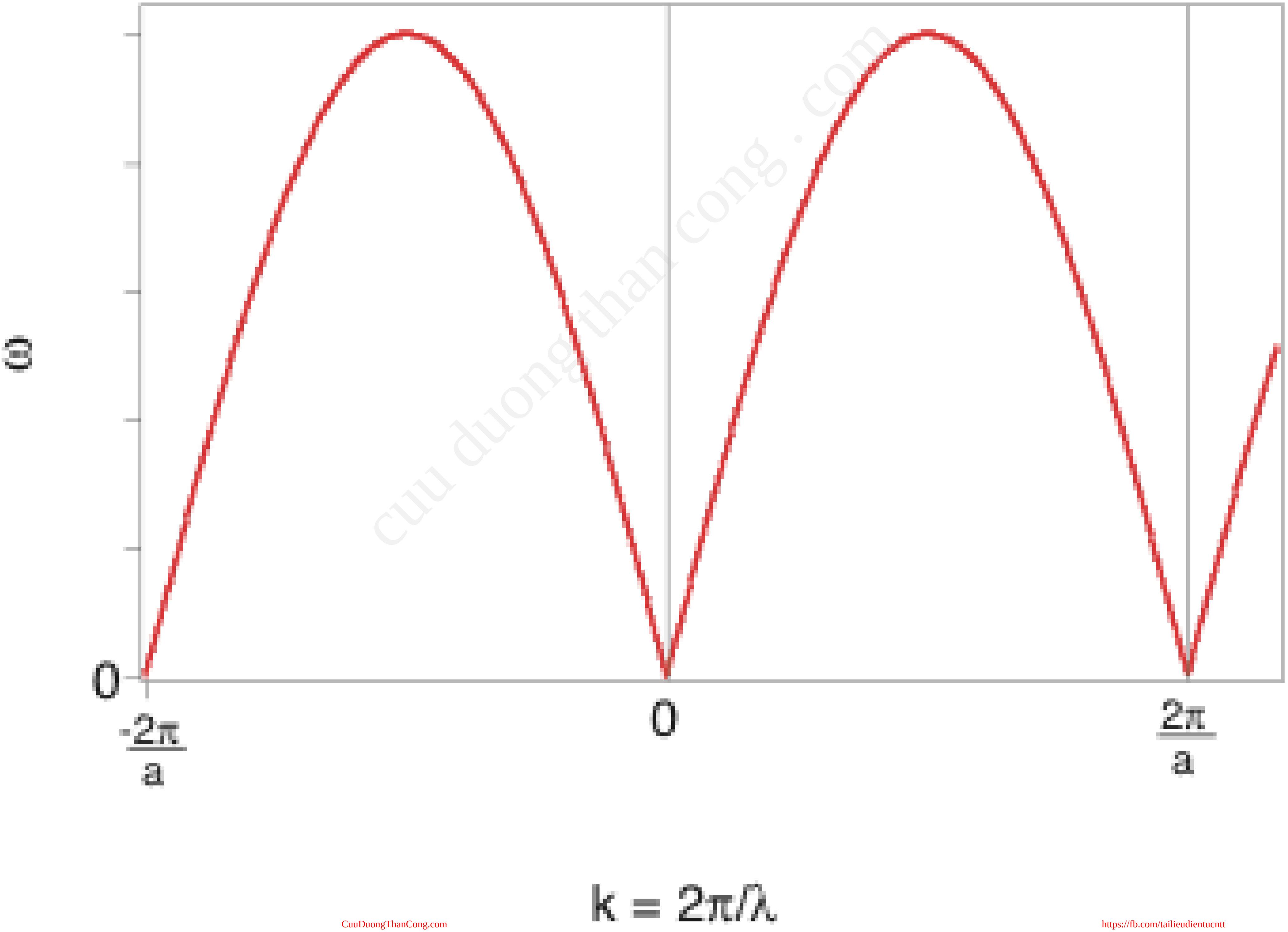
$$\omega(k) = \sqrt{\frac{2\gamma(1-coska)}{M}} = 2\sqrt{\frac{\gamma}{M}}\left|sin\frac{ka}{2}\right|$$

using that $\cos\alpha = \cos^2\frac{\alpha}{2} - \sin^2\frac{\alpha}{2} = 1 - 2\sin^2\frac{\alpha}{2}$

in general we have that ω depends on k.
ω(k) is called the dispersion relation

solution $u_n(t) = ue^{i(kan-\omega t)}$

dispersion relation $\omega(k) = 2\sqrt{\frac{\gamma}{M}}|\sin\frac{ka}{2}|$



phase velocity and group velocity

general 1D wave $A(x,t) = A_0 e^{i(kx-\omega(k)t)}$

or here even $A(x,t) = A_0 \cos(kx - \omega(k)t)$

in general we have that ω depends on k.
ω(k) is called the dispersion relation

we define

the phase velocity $$v_p = \frac{\omega}{k}$$

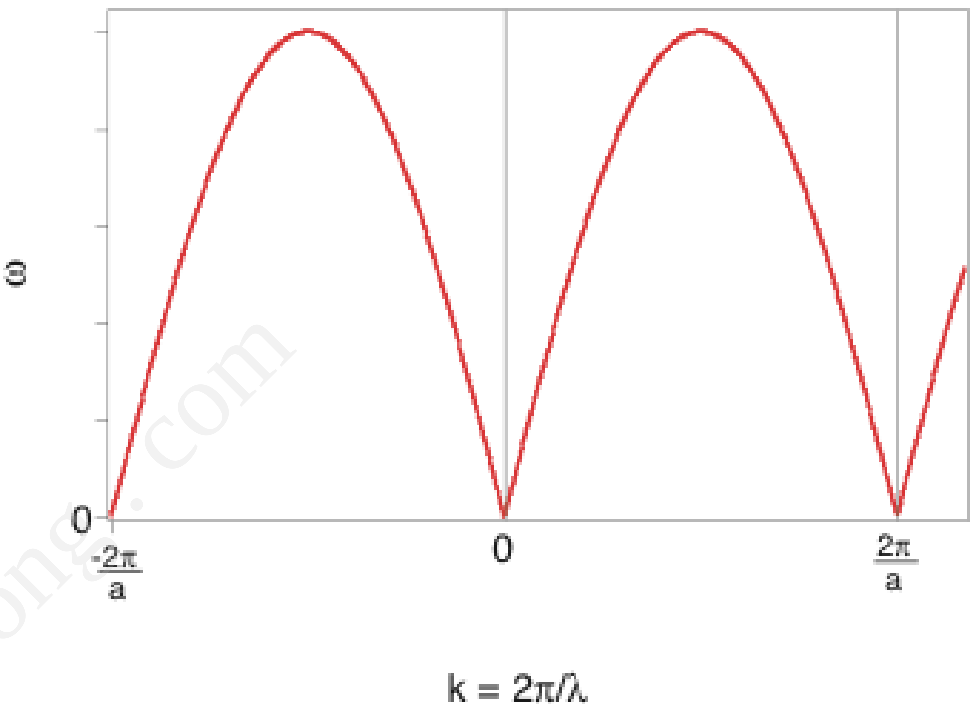
the group velocity $$v_g = \frac{\partial \omega}{\partial k}$$

the two are the same for $\omega(k) = ck$

examples of dispersion relations

vibrations in a 1D chain

$$\omega(k) = 2\sqrt{\frac{\gamma}{M}}\left|\sin\frac{ka}{2}\right|$$

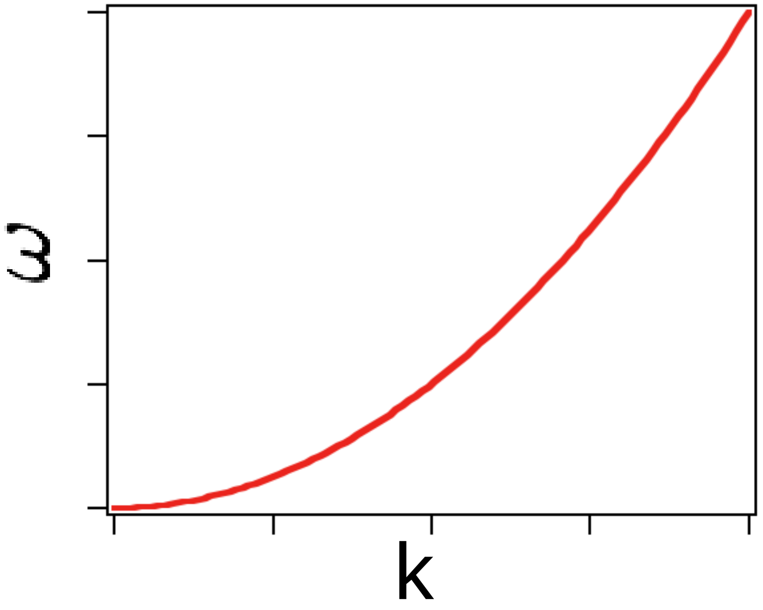


a quantum mechanical particle

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

$$\omega(k) = \frac{\hbar k^2}{2m}$$

$$v_g = \frac{\partial\omega(k)}{\partial k} = \frac{\hbar k}{m} = \frac{p}{m}$$



examples of dispersion relations

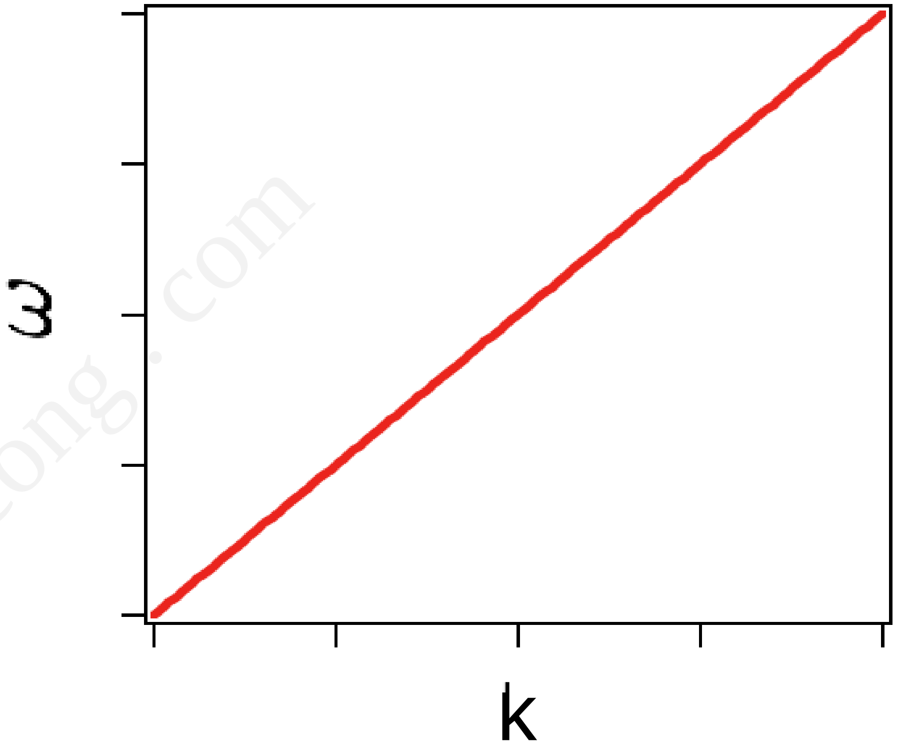
light in vaccum

$$\nu\lambda = c$$

$$2\pi\nu\frac{\lambda}{2\pi} = c$$

$$\omega\frac{1}{k} = c$$

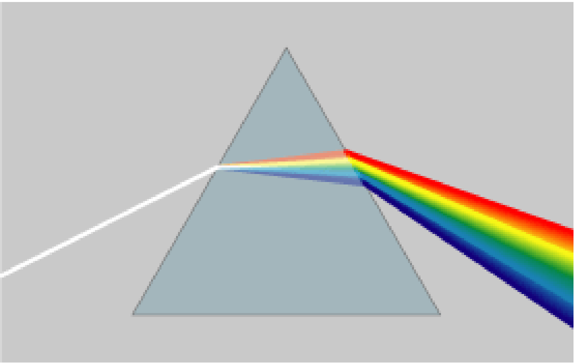
$$\omega(k) = kc$$



in vacuum the dispersion relation of light is *linear*. Light travels with *c* independent of the frequency.

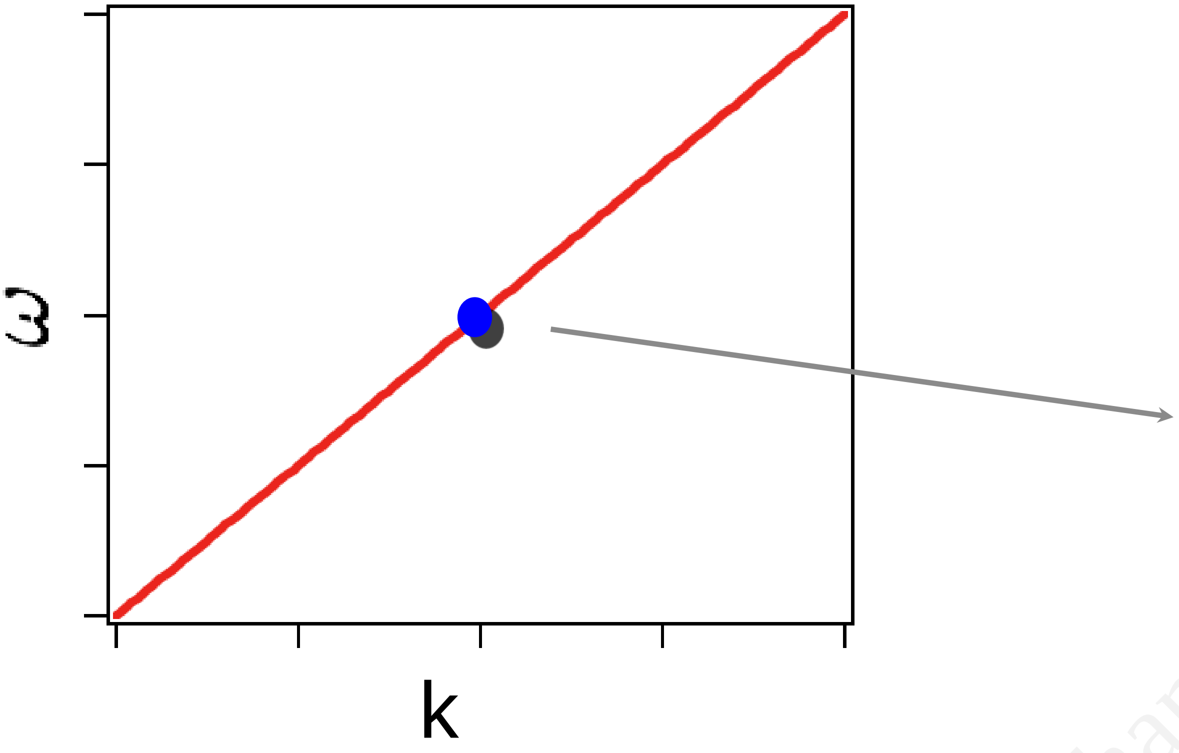
light in matter

$$\omega(k) = kc(\omega)$$



linear dispersion (acoustic phonons, photons)

one partial wave $v_p = \frac{\omega}{k}$

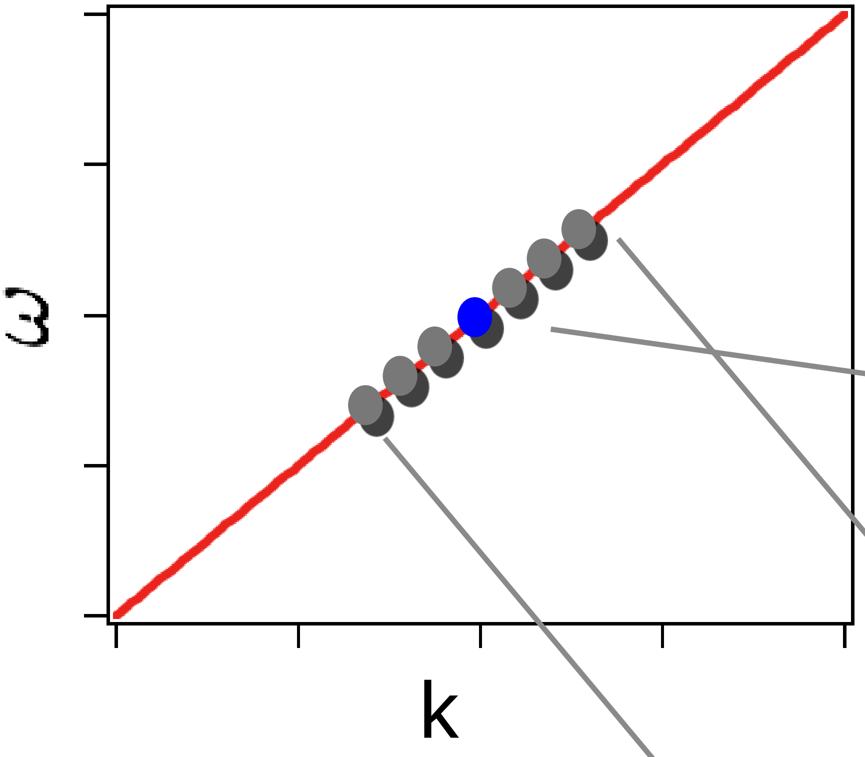


amplitude

distance

linear dispersion (acoustic phonons, photons)

one partial wave $v_p = \frac{\omega}{k}$



amplitude

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

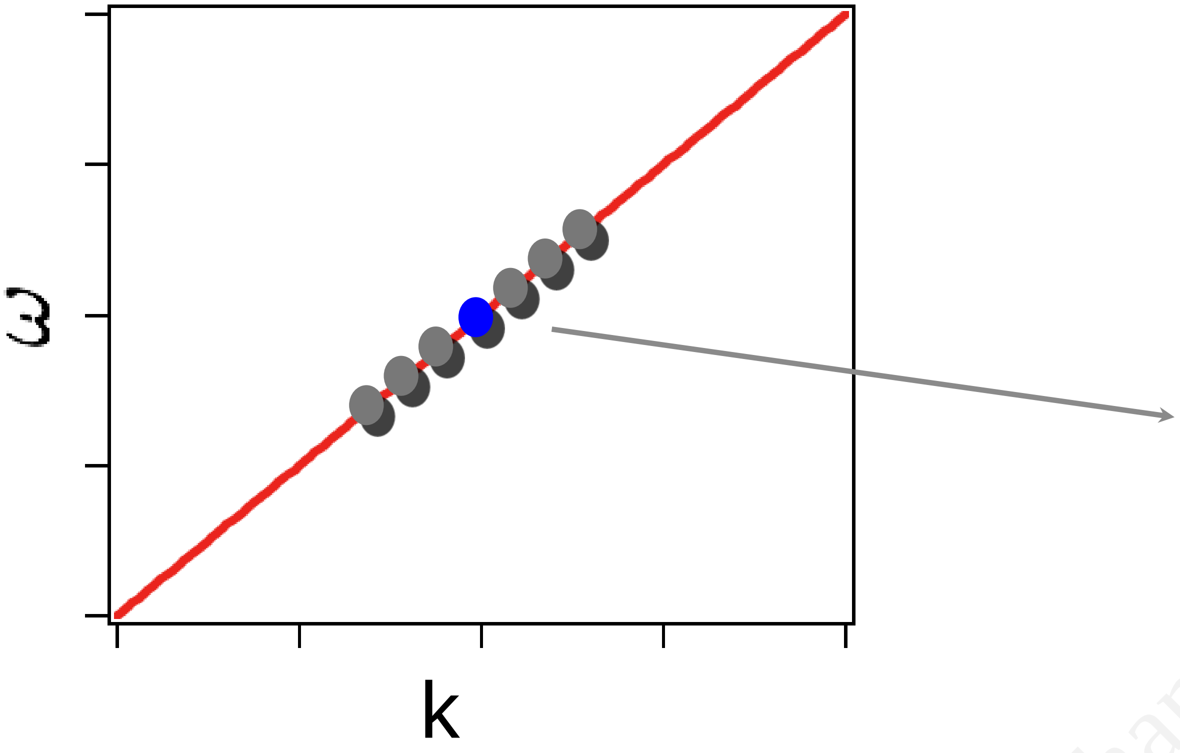
7 partial waves

partial wave #

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

linear dispersion (acoustic phonons, photons)



one partial wave $v_p = \frac{\omega}{k}$

amplitude

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Video decompressor
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distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

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distance

7 partial waves

partial wave #

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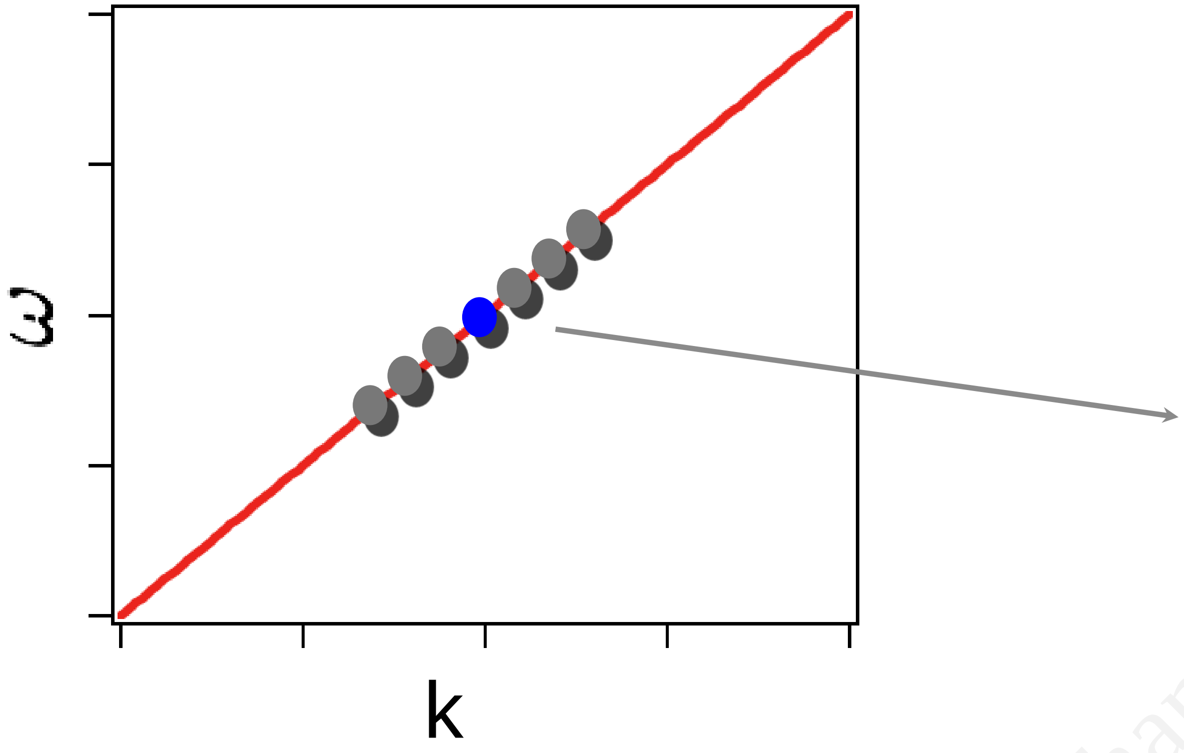
distance

linear dispersion (acoustic phonons, photons)



one partial wave $v_p = \frac{\omega}{k}$

amplitude

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distance

- phase and group velocities are the same
- the wave packet does not change when travelling

sum of partial waves (package)

amplitude

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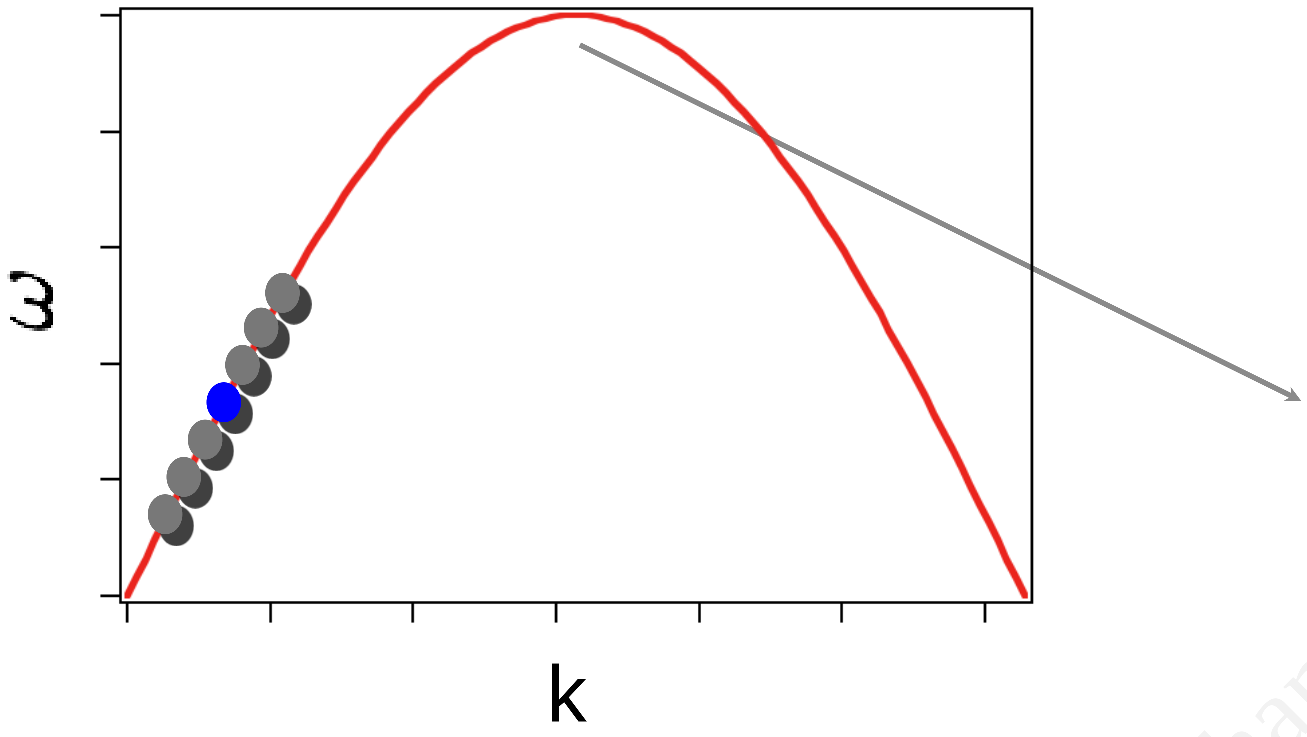
distance

sine-like dispersion



one partial wave $v_p = \frac{\omega}{k}$

amplitude

distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

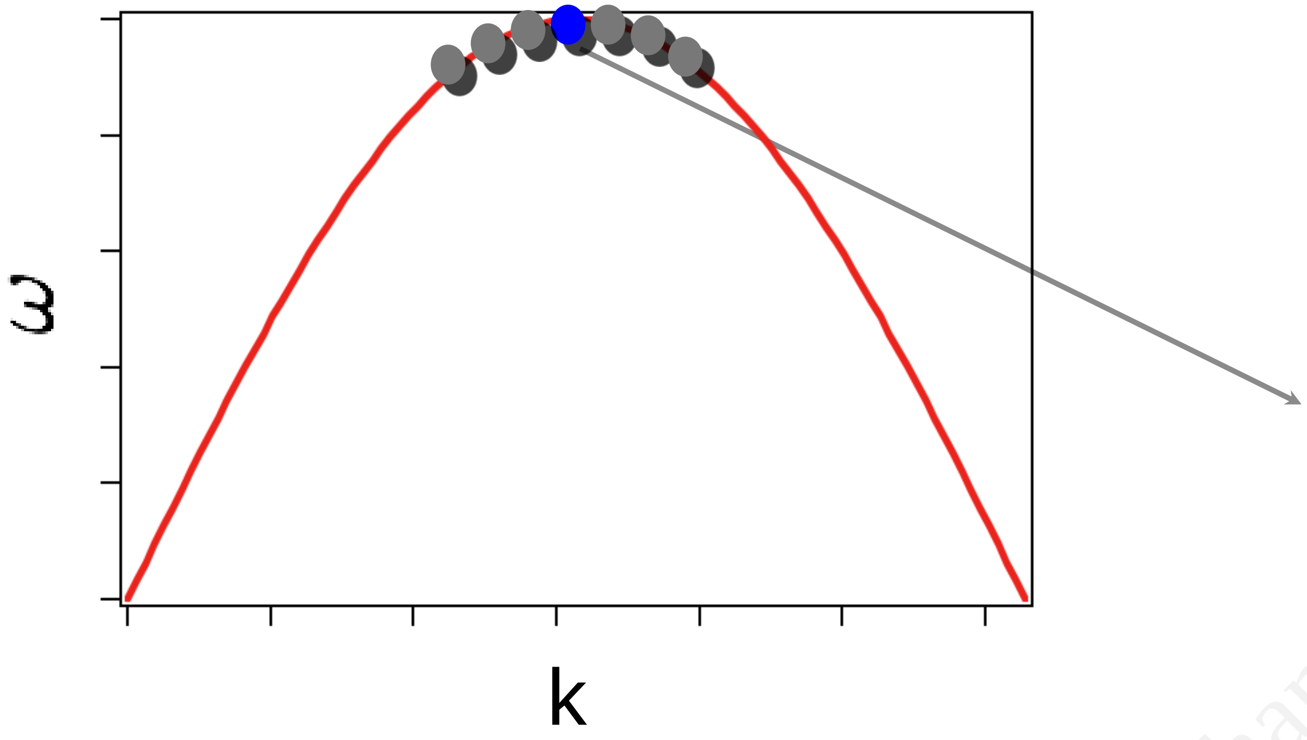
distance

7 partial waves

partial wave #

distance

sine-like dispersion



one partial wave $v_p = \frac{\omega}{k}$

amplitude

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distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

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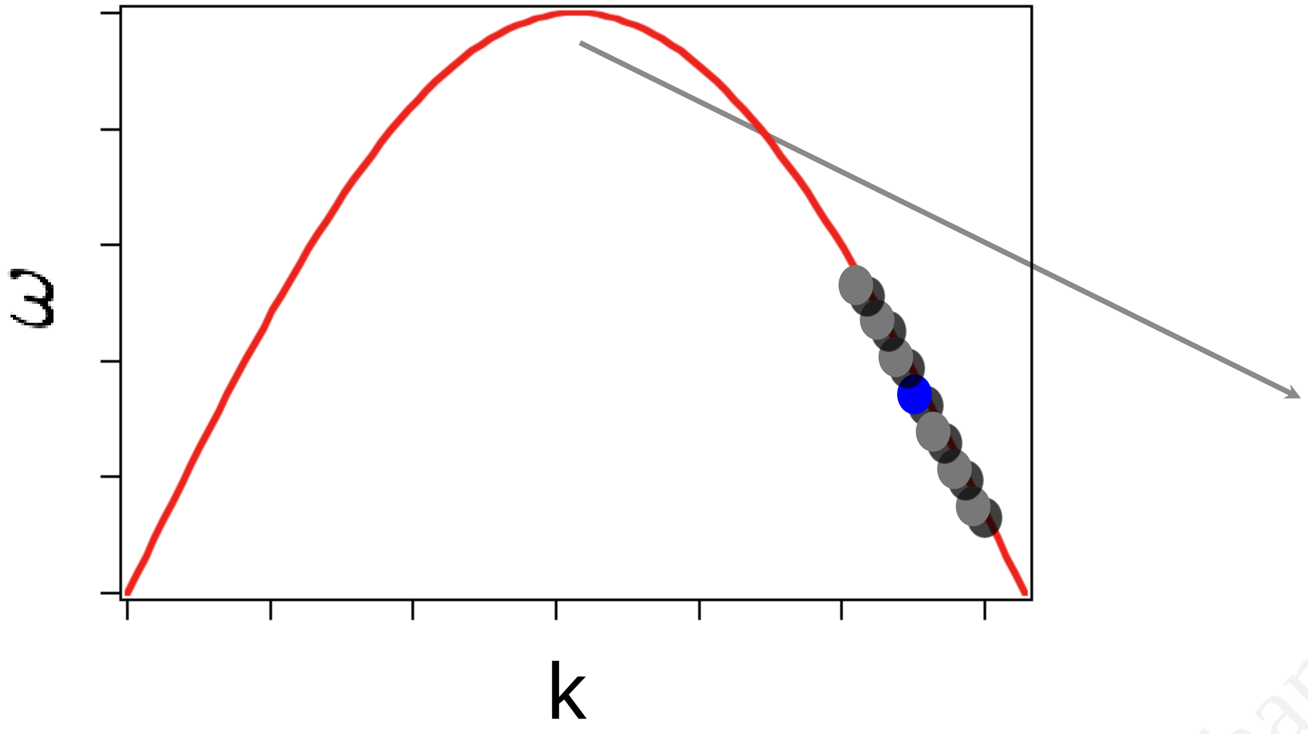
sine-like dispersion



one partial wave $v_p = \frac{\omega}{k}$

amplitude

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distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

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distance

7 partial waves

partial wave #

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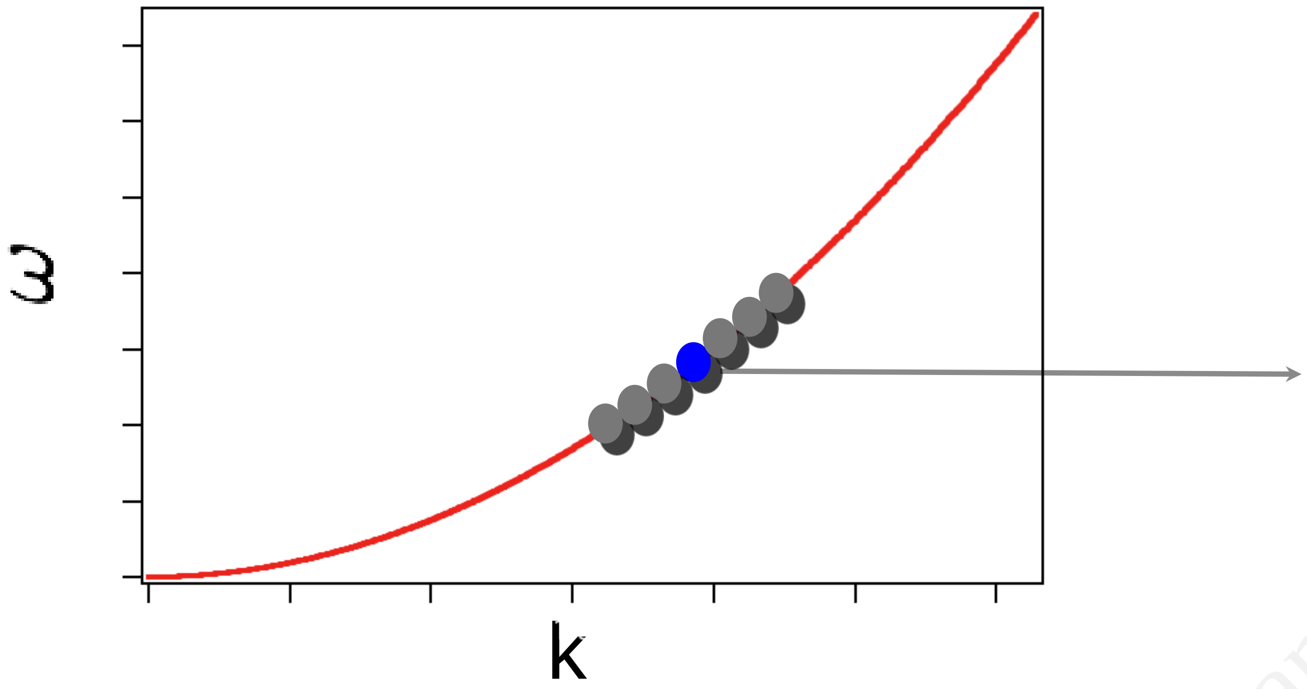
distance

k^2 dispersion



one partial wave $v_p = \frac{\omega}{k}$

amplitude

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

QuickTime™ and a
Video decompressor
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distance

7 partial waves

partial wave #

QuickTime™ and a
Video decompressor
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distance

solution

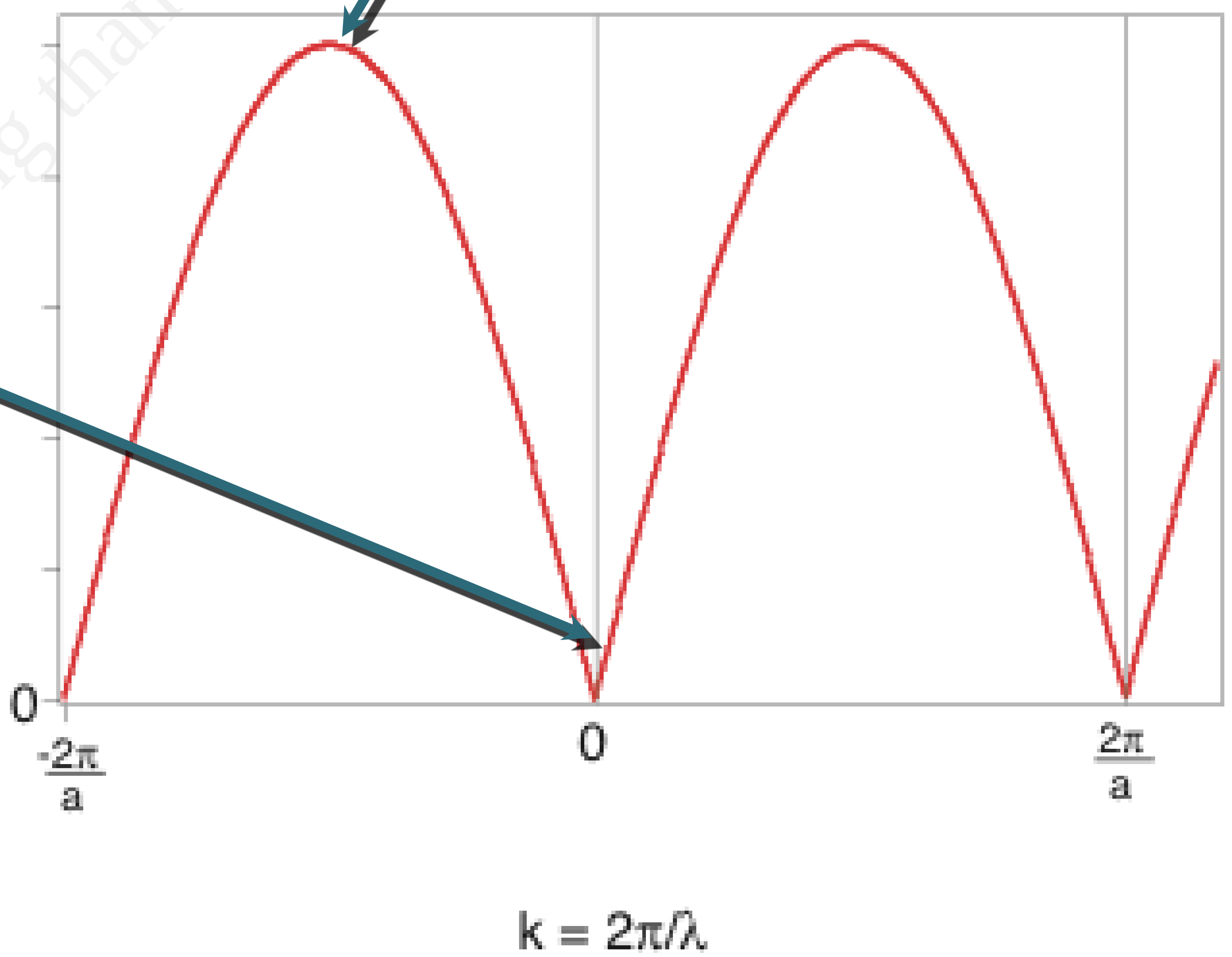
$$u_n(t) = ue^{i(kan-\omega t)}$$

dispersion relation

$$\omega(k) = 2\sqrt{\frac{\gamma}{M}}\left|\sin\frac{ka}{2}\right|$$

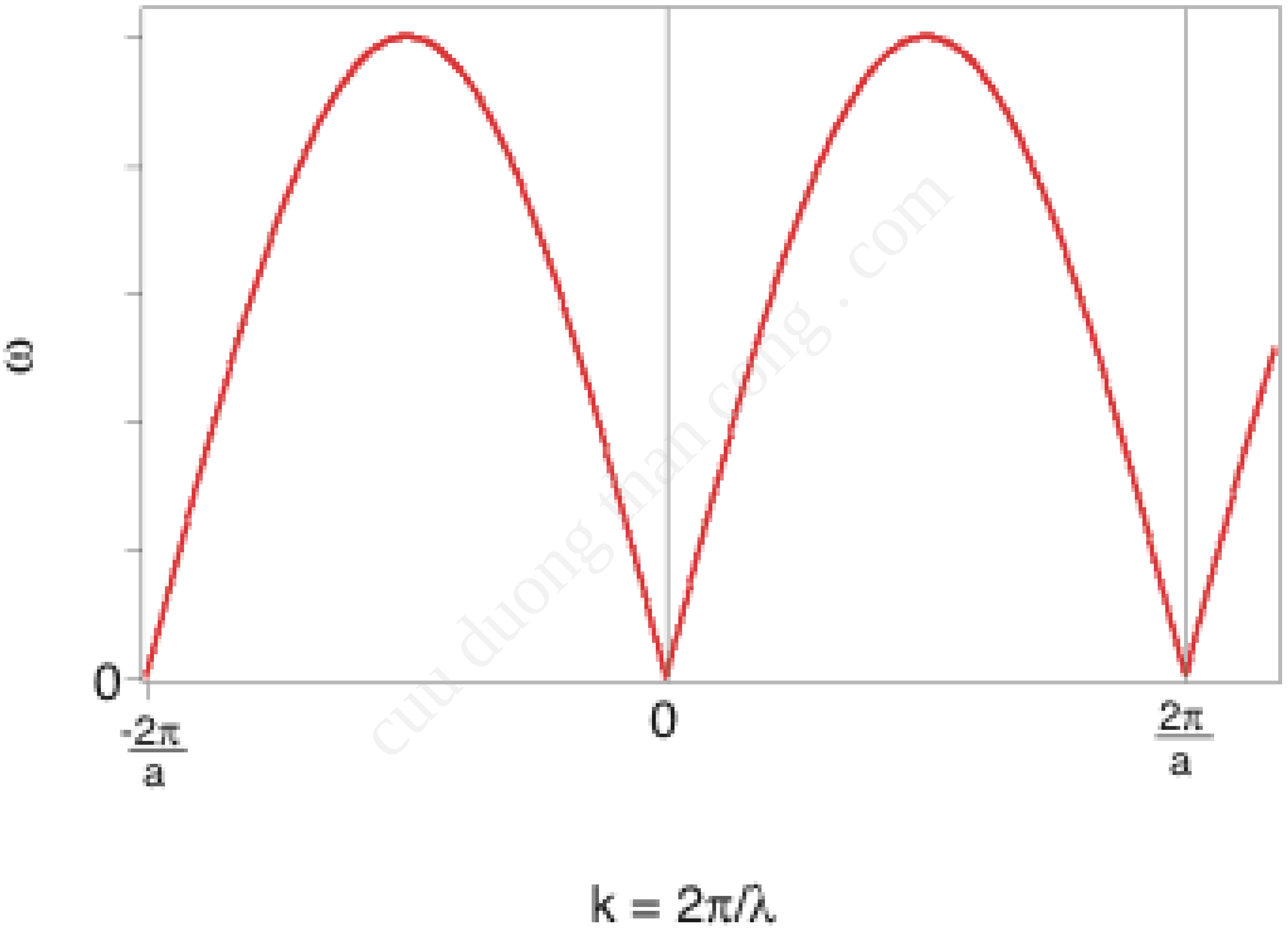
standing wave

sound wave

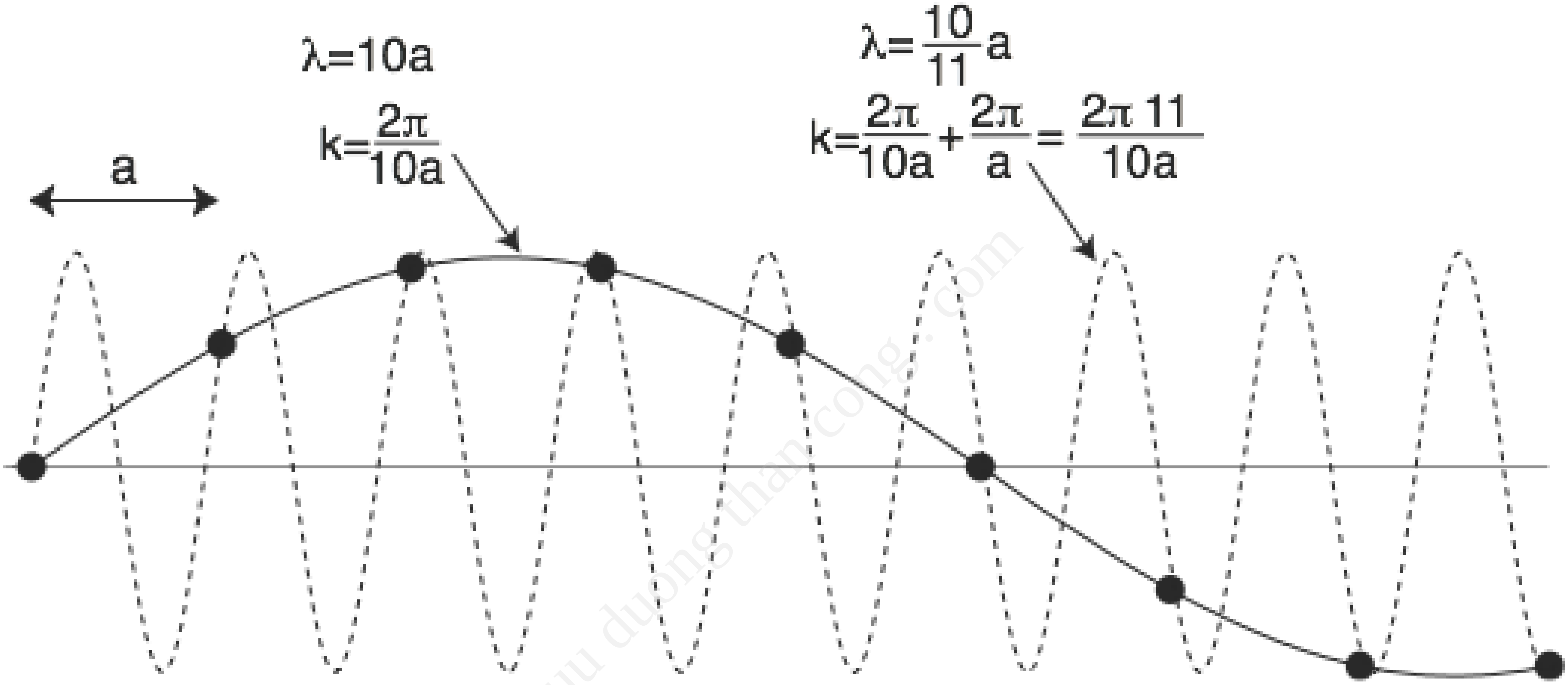


$$\omega = \sqrt{\frac{\gamma}{M}}ak = \nu k$$

$$\omega(k) = 2\sqrt{\frac{\gamma}{M}}\left|\sin\frac{ka}{2}\right|$$

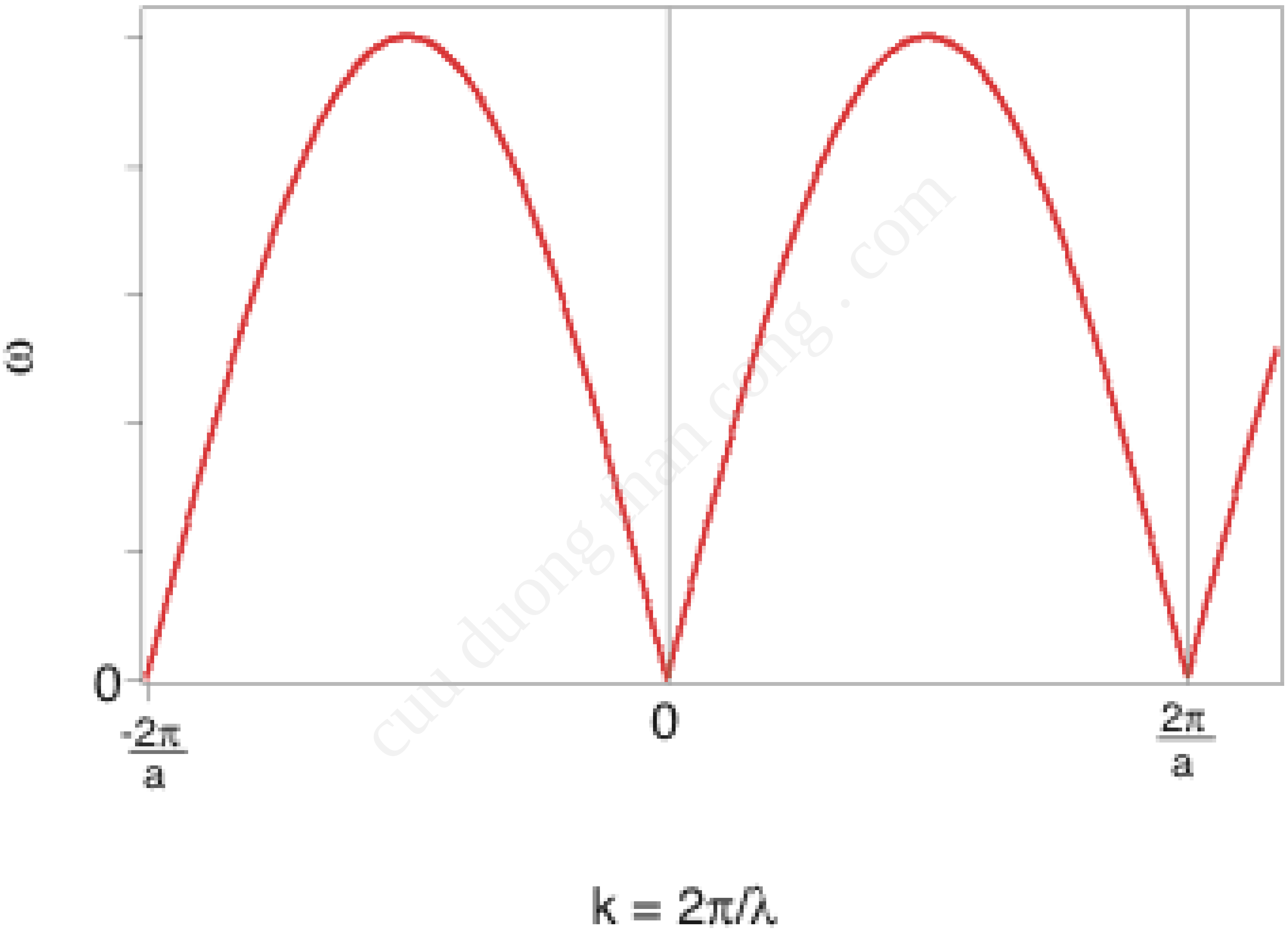


- The dispersion relation is periodic and the periodicity is one reciprocal lattice vector!

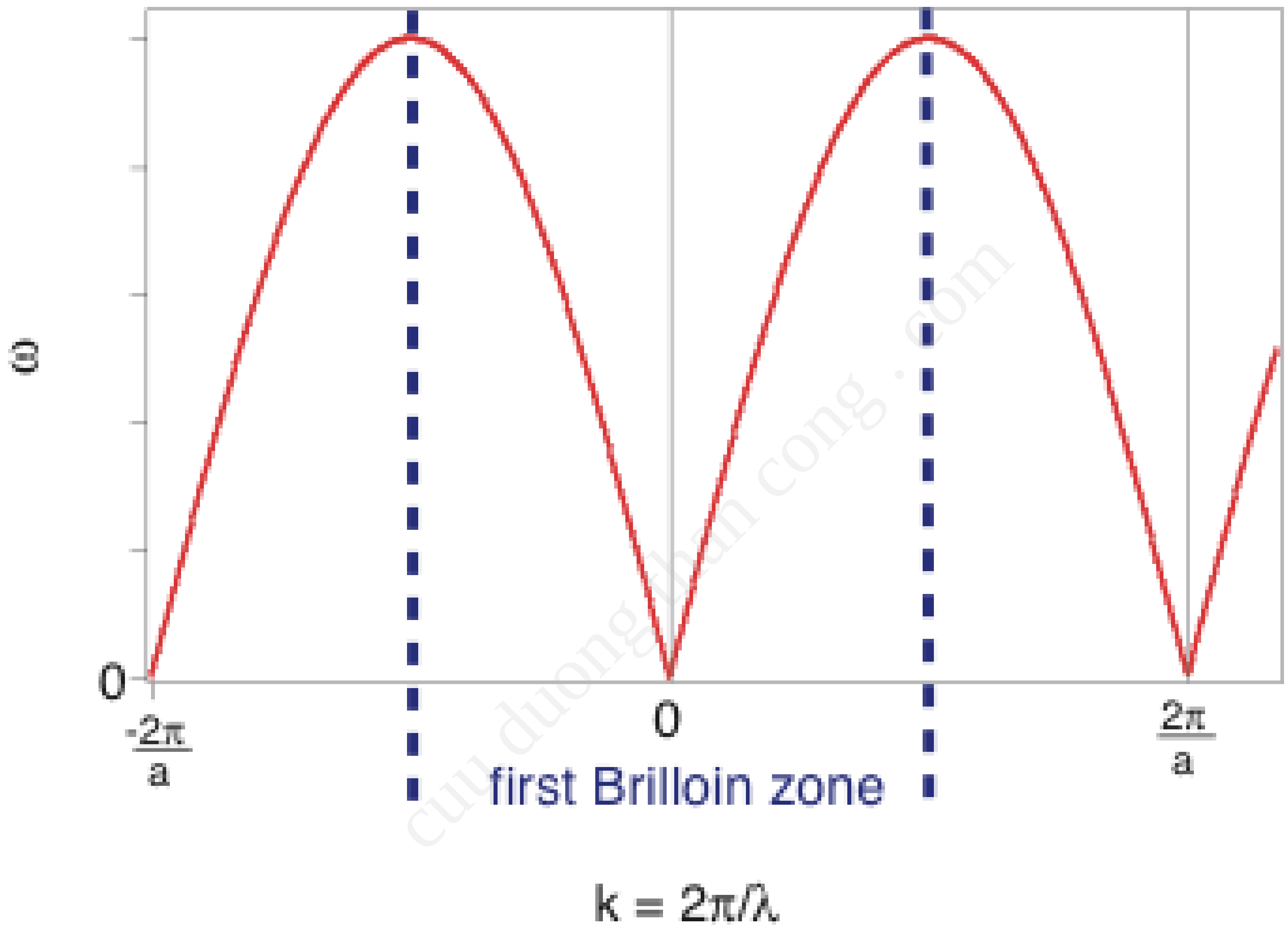


- Changing k by one reciprocal lattice vector gives exactly the same movement of the atoms.

$$\omega(k) = 2\sqrt{\frac{\gamma}{M}}\left|\sin\frac{ka}{2}\right|$$

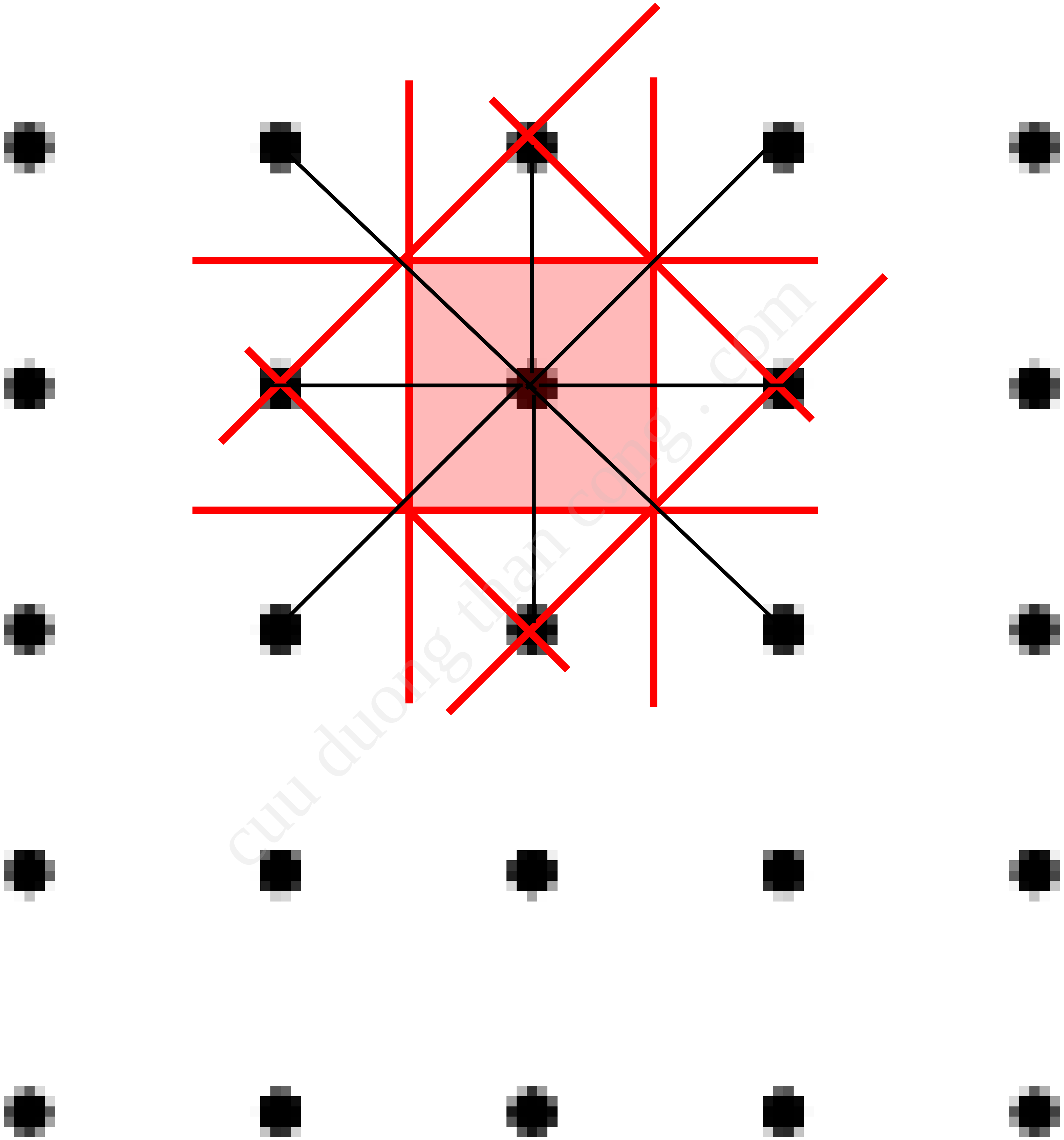


The first Brillouin zone

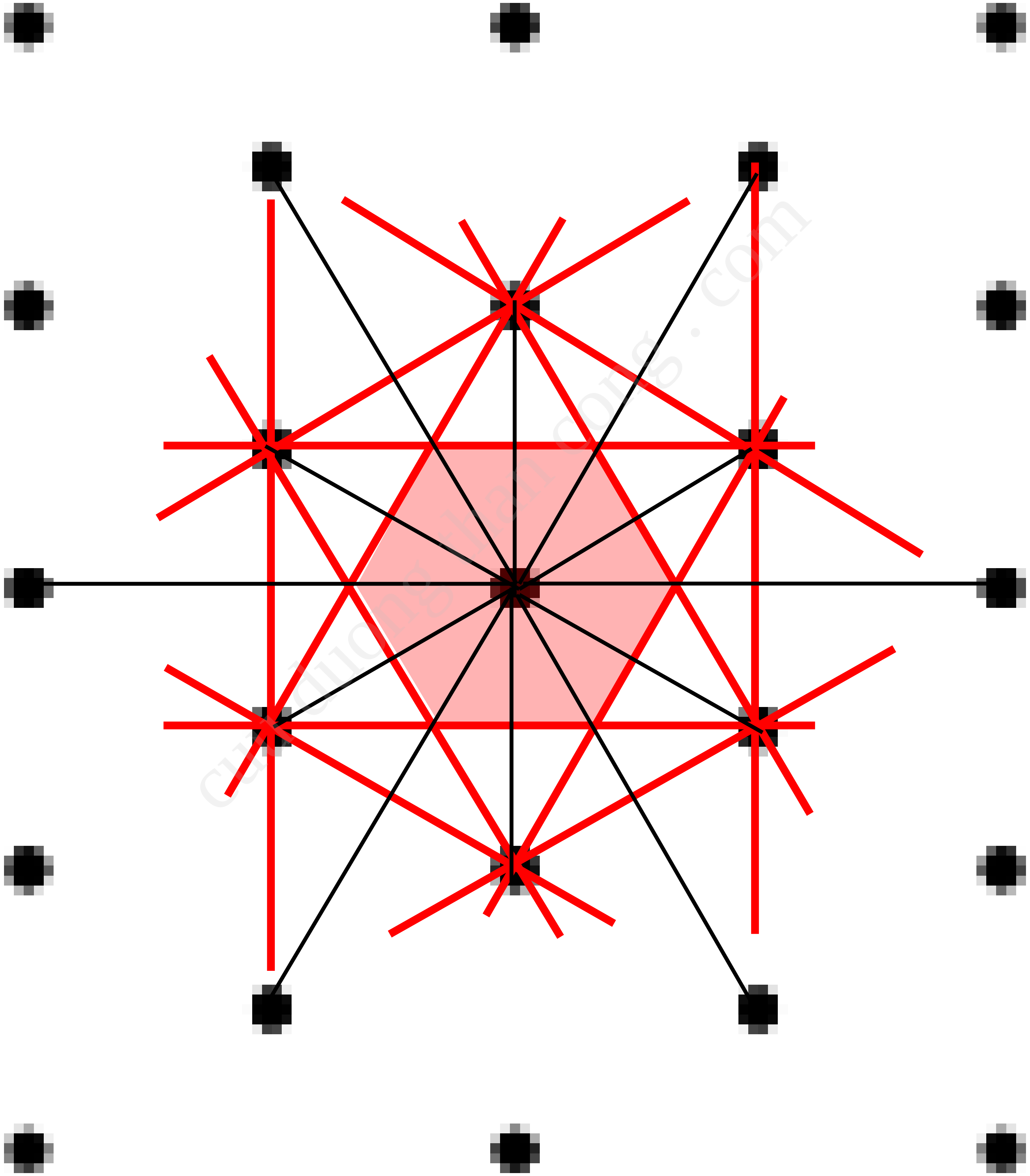


The first Brillouin zone is the region of reciprocal space which is closer to one reciprocal lattice point than to any other (Wigner-Seitz cell in reciprocal space).

The first Brillouin zone



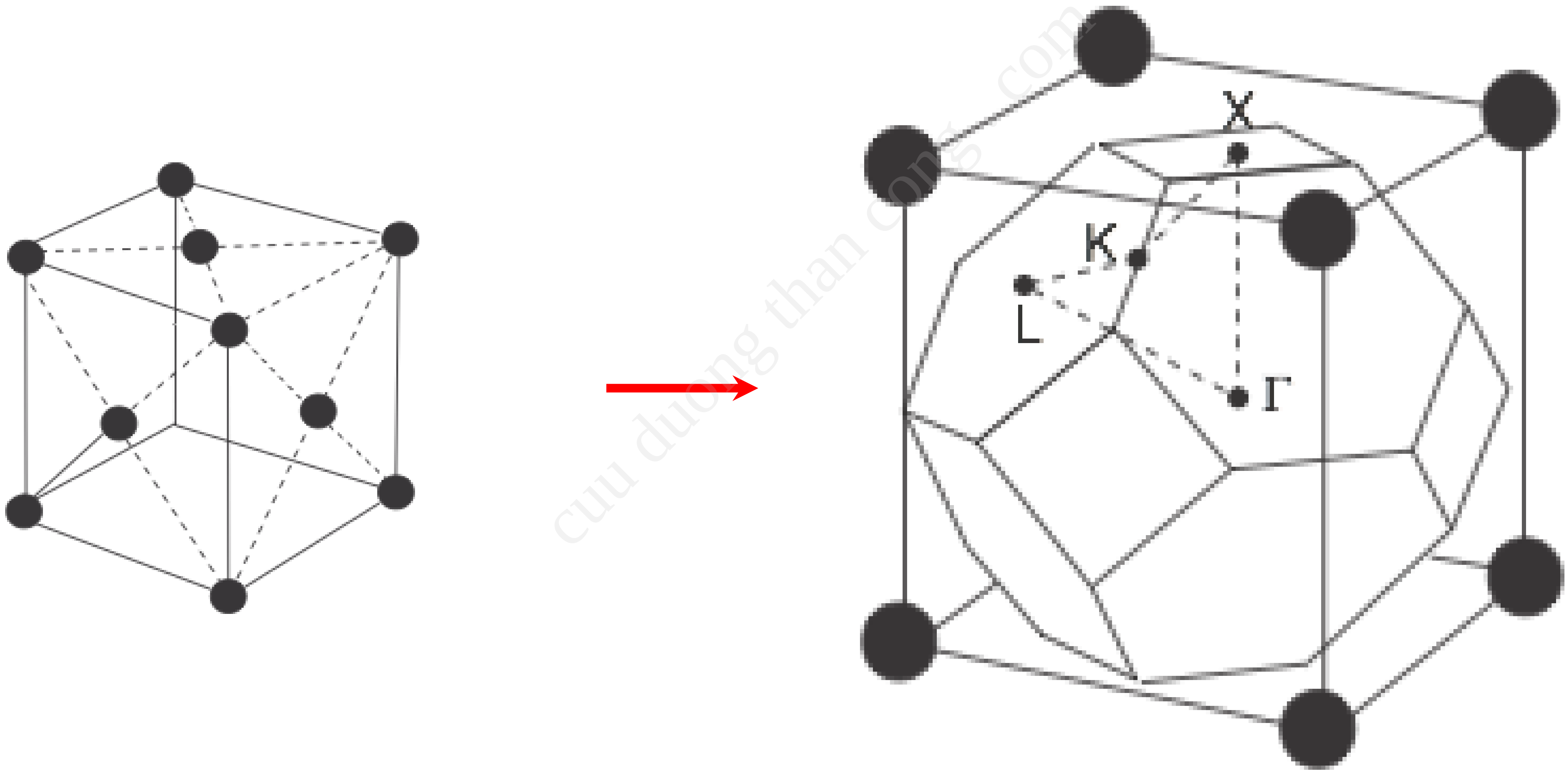
The first Brillouin zone



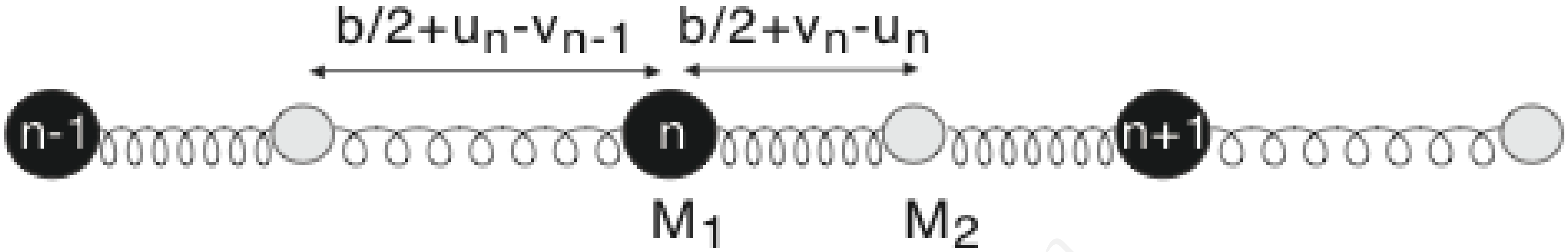
The first Brillouin zone

real
space

reciprocal
space



Two atoms per unit cell



equations of motion

$$M_1 \frac{d^2 u_n}{dt^2} = -\gamma[2u_n - v_{n-1} - v_n] \qquad M_2 \frac{d^2 v_n}{dt^2} = -\gamma[2v_n - u_n - u_{n+1}]$$

ansatz

$$u_n(t) = u e^{i(kbn - \omega t)} \qquad v_n(t) = v e^{i(kbn - \omega t)}$$

two linear equations, two unknowns

$$-\omega^2 M_1 u = \gamma v(1 + e^{-ikb}) - 2\gamma u \qquad -\omega^2 M_2 v = \gamma u(e^{ikb} + 1) - 2\gamma v.$$

(system of homogeneous linear equations)

Two atoms per unit cell

$$-\omega^2 M_1 u = \gamma v(1+e^{-ikb}) - 2\gamma u \qquad -\omega^2 M_2 v = \gamma u(e^{ikb}+1) - 2\gamma v.$$

$$(2\gamma - \omega^2 M_1)u - \gamma(1+e^{-ikb})v = 0$$
$$-\gamma(e^{ikb}+1)u + (2\gamma - \omega^2 M_2)v = 0$$

this has only a (non-trivial) solution when

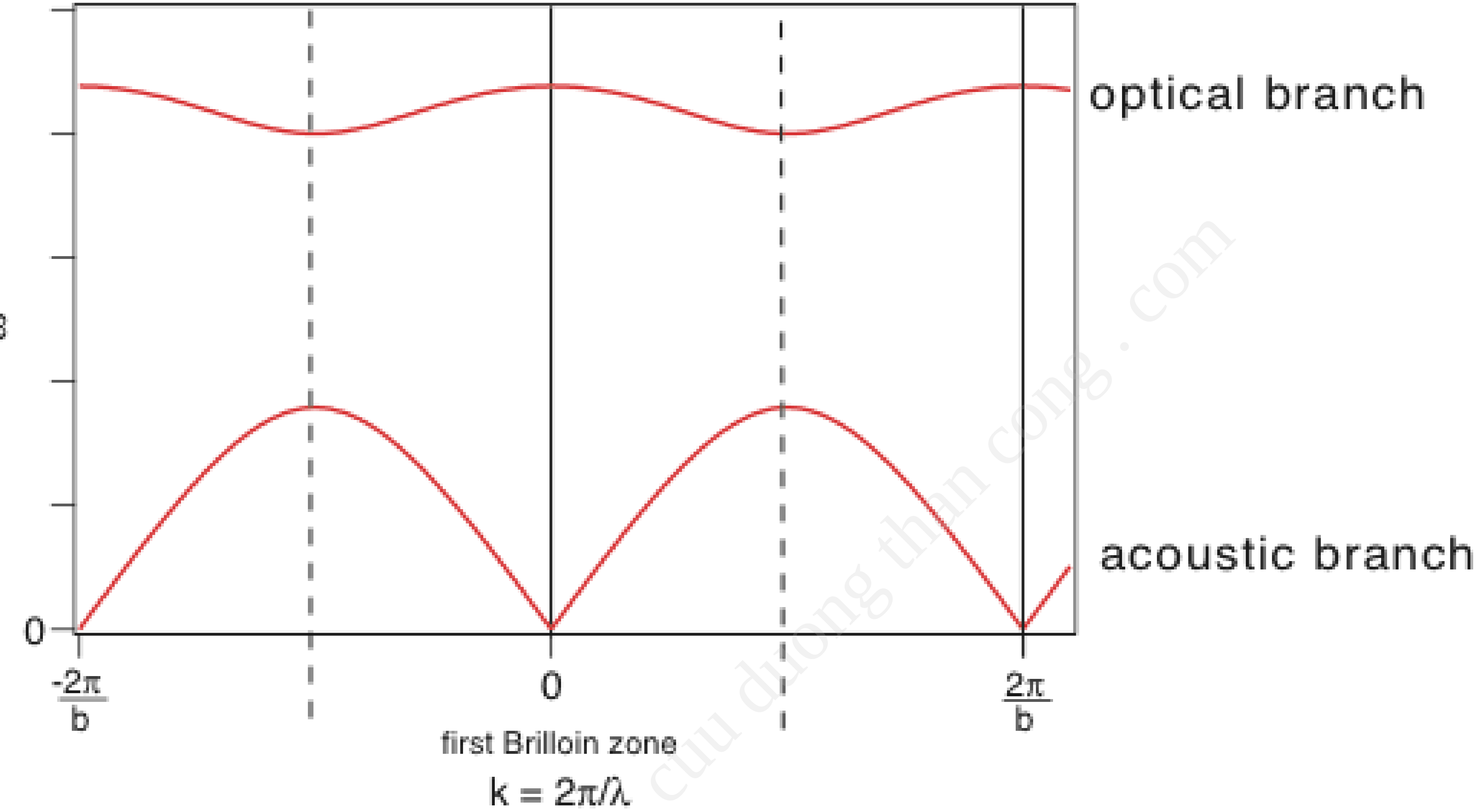
coefficient matrix →

$$\begin{vmatrix} 2\gamma - \omega^2 M_1 & -\gamma(e^{-ikb}+1) \\ -\gamma(1+e^{ikb}) & 2\gamma - \omega^2 M_2 \end{vmatrix} = 0$$

two solutions for every value of k

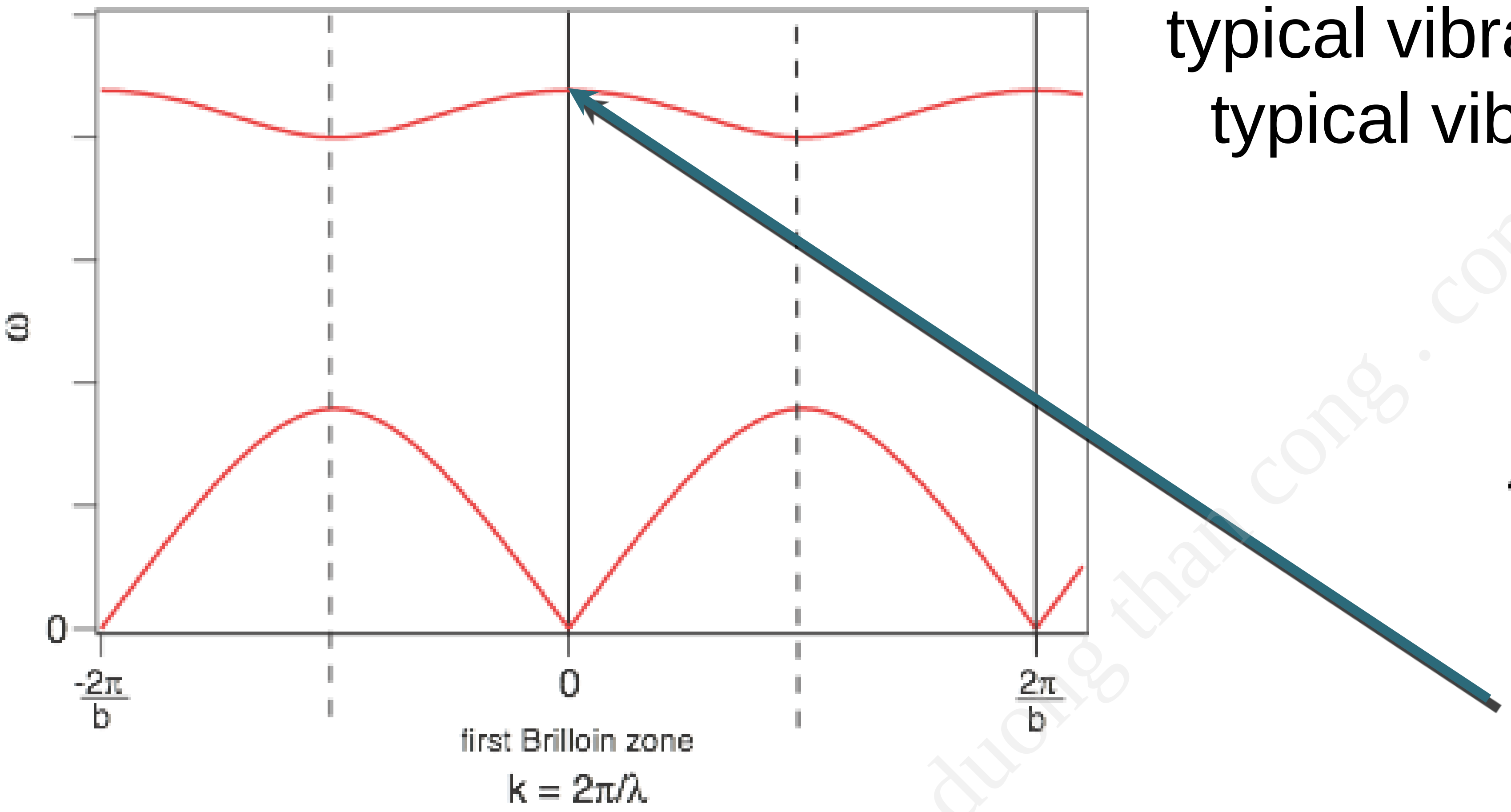
$$\omega^2 = \gamma\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \gamma\left[\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1 M_2}\sin^2\frac{kb}{2}\right]^{1/2}$$

Two atoms per unit cell



$$\omega^2 = \gamma\left(\frac{1}{M_1}+\frac{1}{M_2}\right) \pm \gamma\left[\left(\frac{1}{M_1}+\frac{1}{M_2}\right)^2 - \frac{4}{M_1M_2}\sin^2\frac{kb}{2}\right]^{1/2}$$

Why "optical branch"?



typical vibrational frequency ~ 10^{12} Hz
typical vibrational energy ~ 10 meV

light:

$$\lambda = \frac{2\pi c}{\omega} \approx 10^{-4} \text{ m}$$

$$k = \frac{2\pi}{\lambda} \approx 6\text{x}10^{4} \text{ m}^{-1}$$

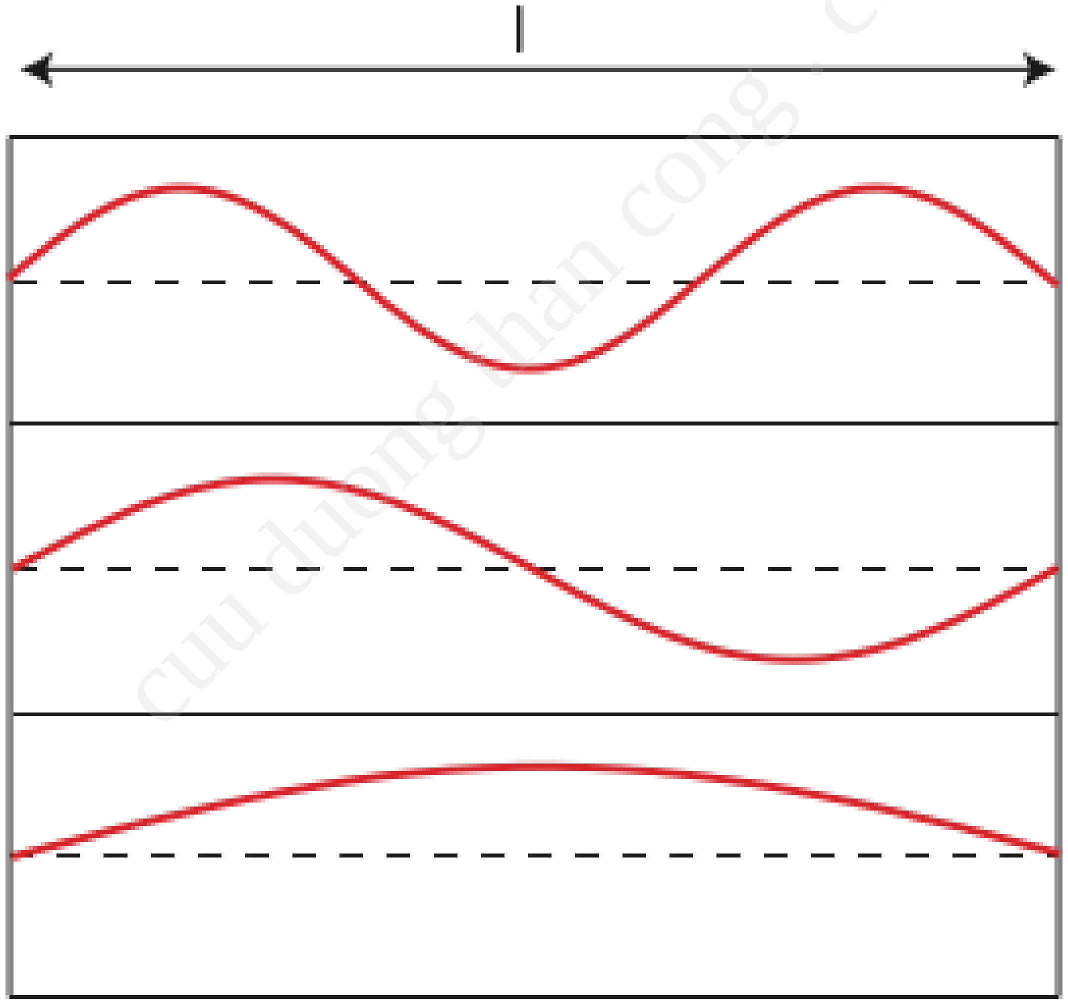
$$\frac{2\pi}{b} \approx 6\text{x}10^{10} \text{ m}^{-1}$$

light E-field the same over very long distance

A long chain of finite, but macroscopic length

What are the boundary conditions?
What do we do about the ends of the chain?

length l, fix the end atoms.



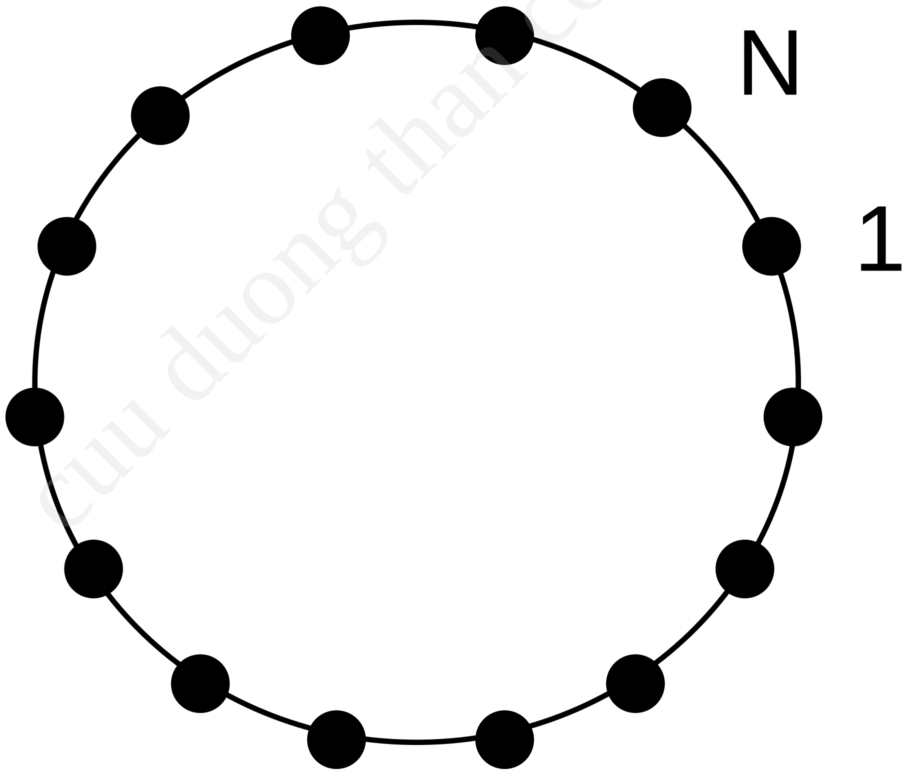
This gives only standing waves.

Periodic boundary conditions

Max Born and Theodore von Karman (1912)

chain with N atoms:

$$u_{N+n}(t) = u_n(t)$$

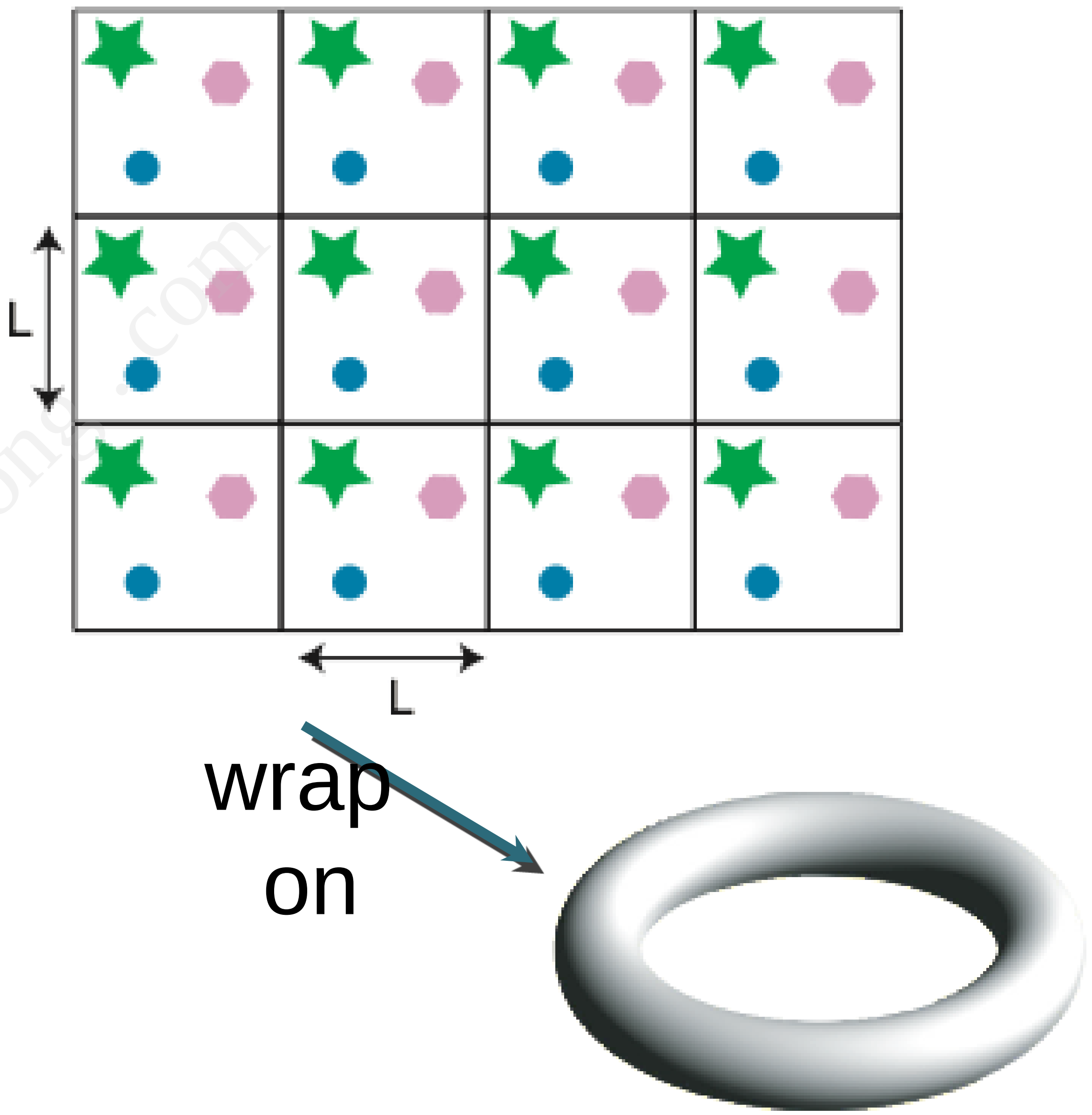


A finite chain with no end!

Periodic boundary conditions

Max Born and Theodore von Karman (1912)

- We want to get rid of the surface restrictions, i.e. we want a solid which is finite in size but has no surfaces (!).
- If we move by one crystal size L, we have to get the same.



wrap on

$$u(x,y,z) = u(x+L,y,z) = u(x,y+L,z) = u(x,y,z+L)$$

The surface was invented by the devil - Wolfgang Pauli

Periodic boundary conditions

Max Born and Theodore von Karman (1912)

chain with N atoms:

$$u_{N+n}(t) = u_n(t)$$

wave must be the same when going N sites further

$$e^{ikan} = e^{ika(N+n)}$$

$$e^{ikNa} = 1$$

This restricts the possible k values

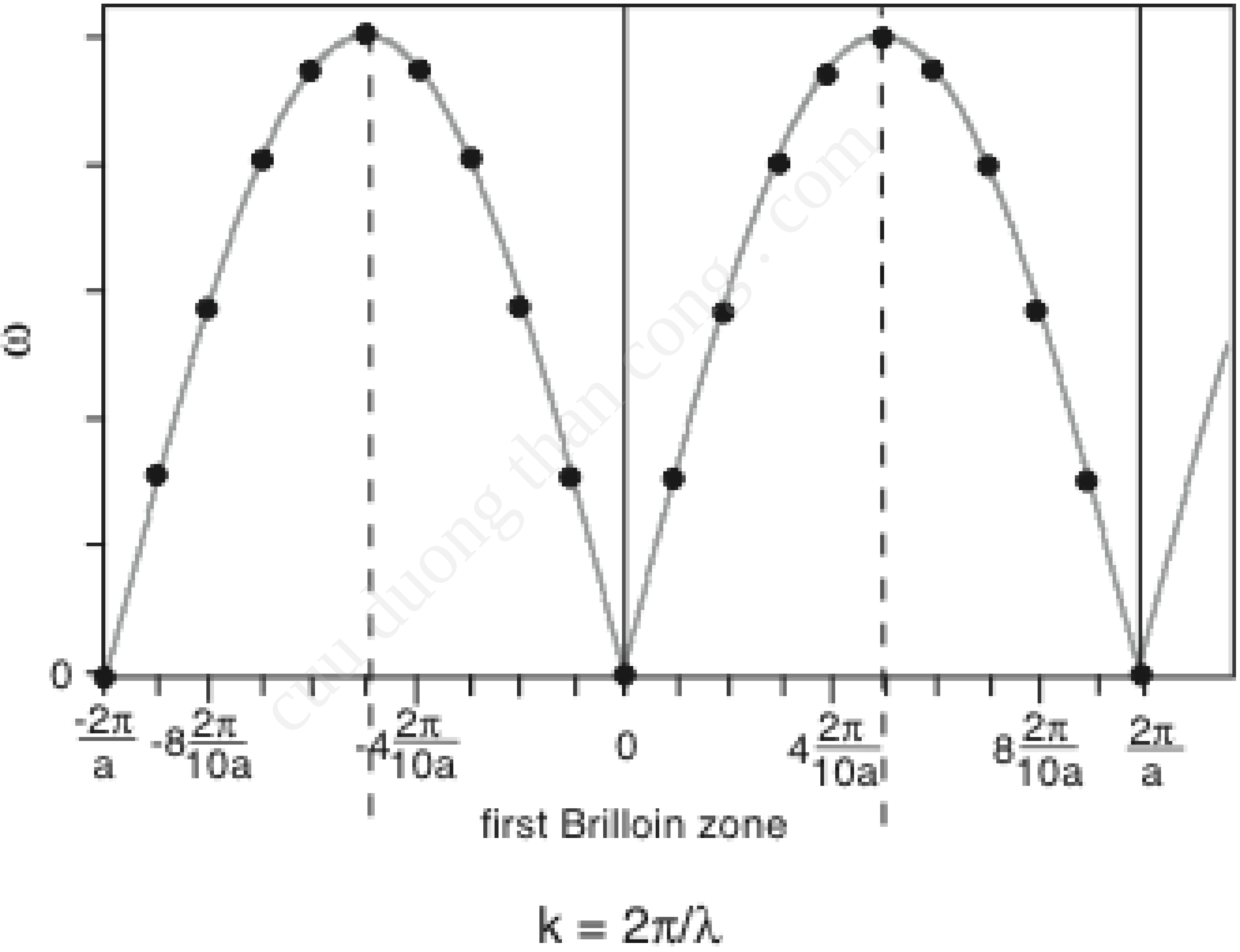
$$kNa = 2\pi m$$

$$k = \frac{2\pi}{aN} m$$

So there are N possible different vibrations (m=0....N-1)

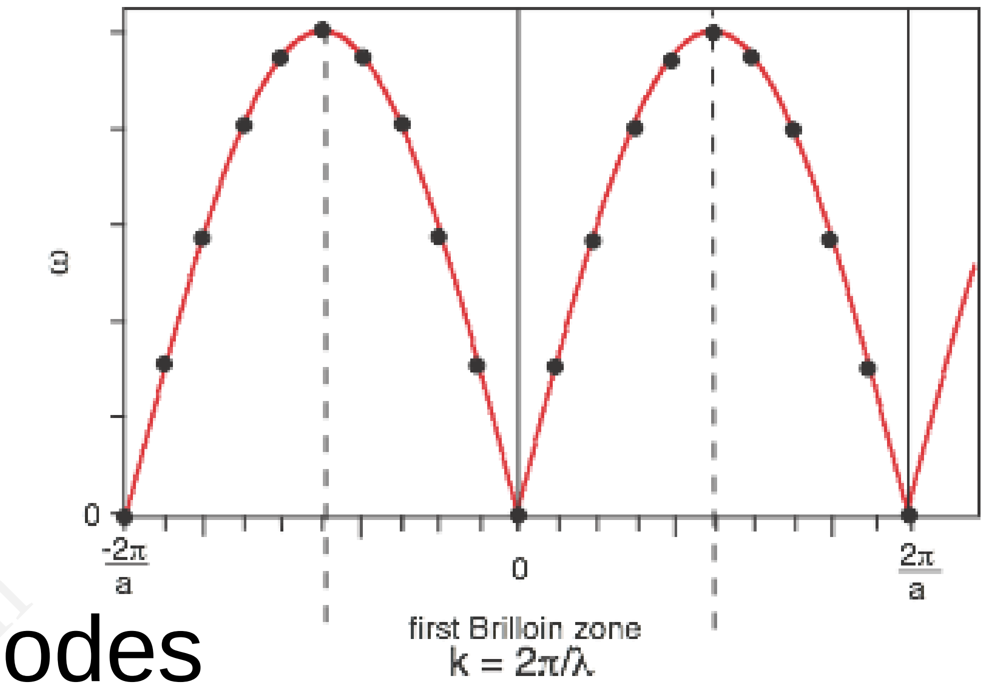
Finite chain with 10 unit cells and one atom per unit cell

$$k = \frac{2\pi}{aN} m$$



- N atoms give N so-called normal modes of vibration.
- For long but finite chains, the points are very dense.

counting normal modes.....



boundary conditions $$k = \frac{2\pi}{aN} m$$

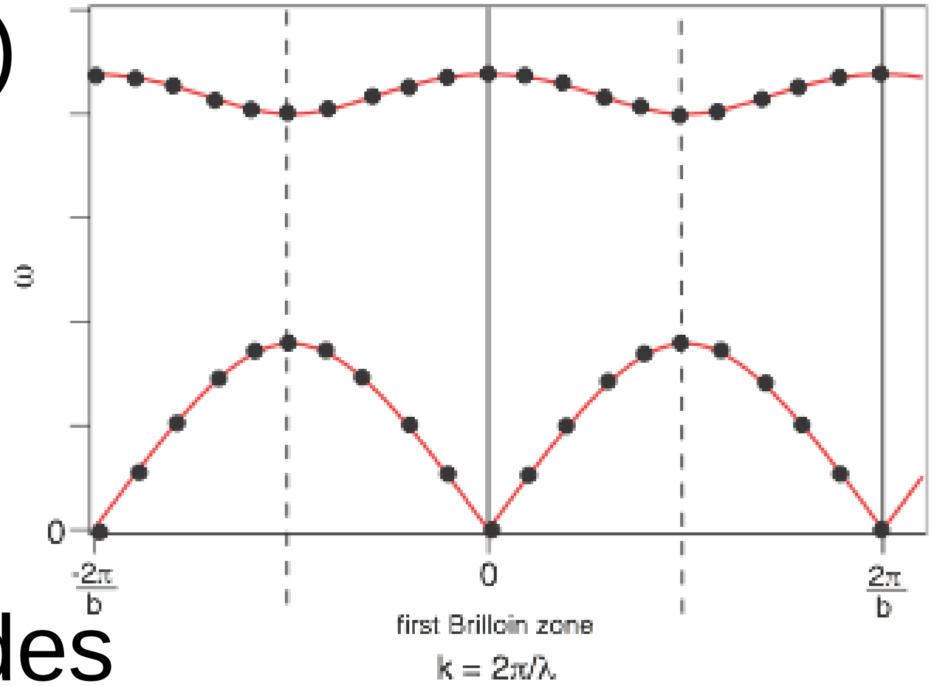
chain with 1 atom / unit cell and
N unit cells

\# k-points

N x 1 modes

\# eigenvalues per k-point

(since we have N degrees of freedom)



chain with 2 atom / unit cell and
N unit cells

\# k-points

N x 2 modes

\# eigenvalues per k-point

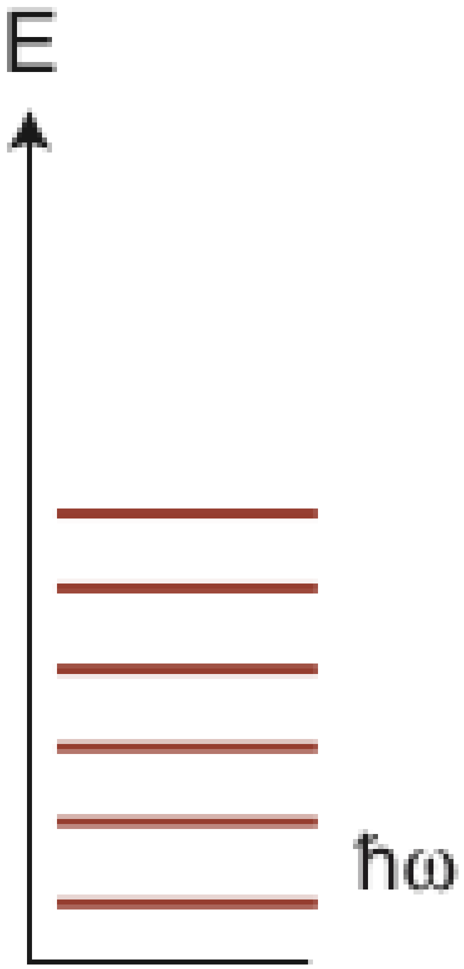
(since we have 2xN degrees of freedom)

Quantised vibrations

- We have the vibrational frequencies and can treat the solid as quantum mechanical oscillators of these frequencies.
- We shall call these quantized oscillations “phonons”.

One harmonic oscillator: quantum model

The energy levels are quantized



$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$\omega = \sqrt{\frac{\gamma}{M}},$$

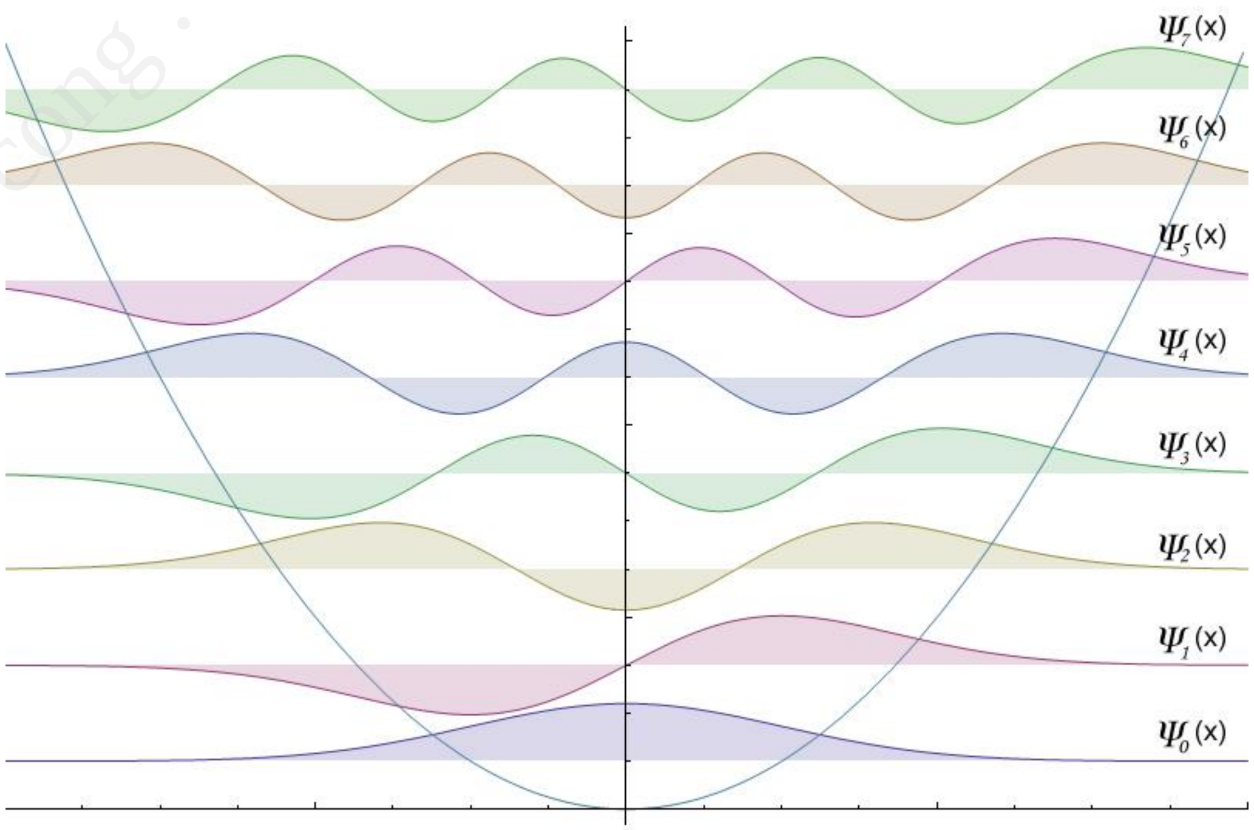
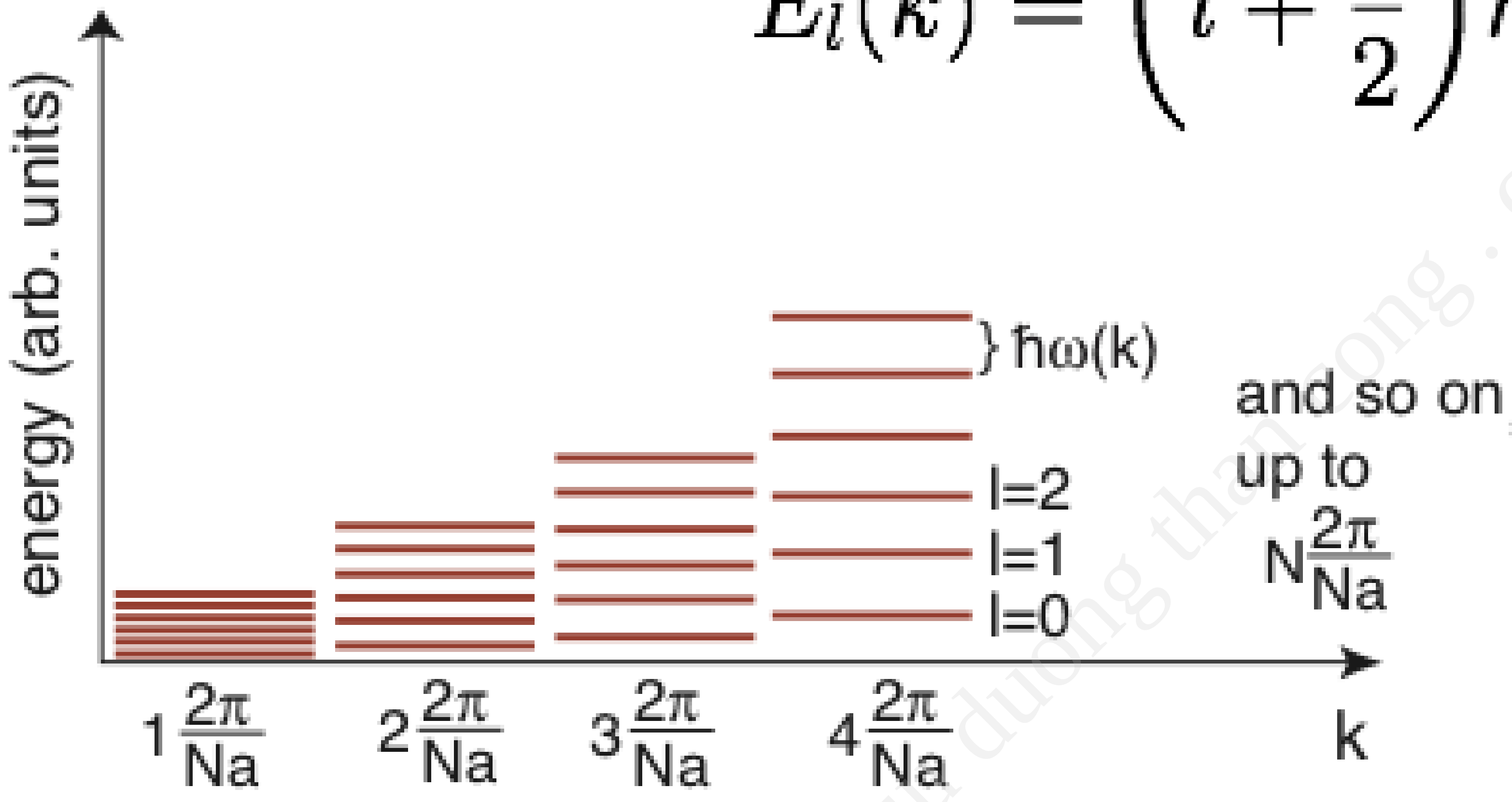
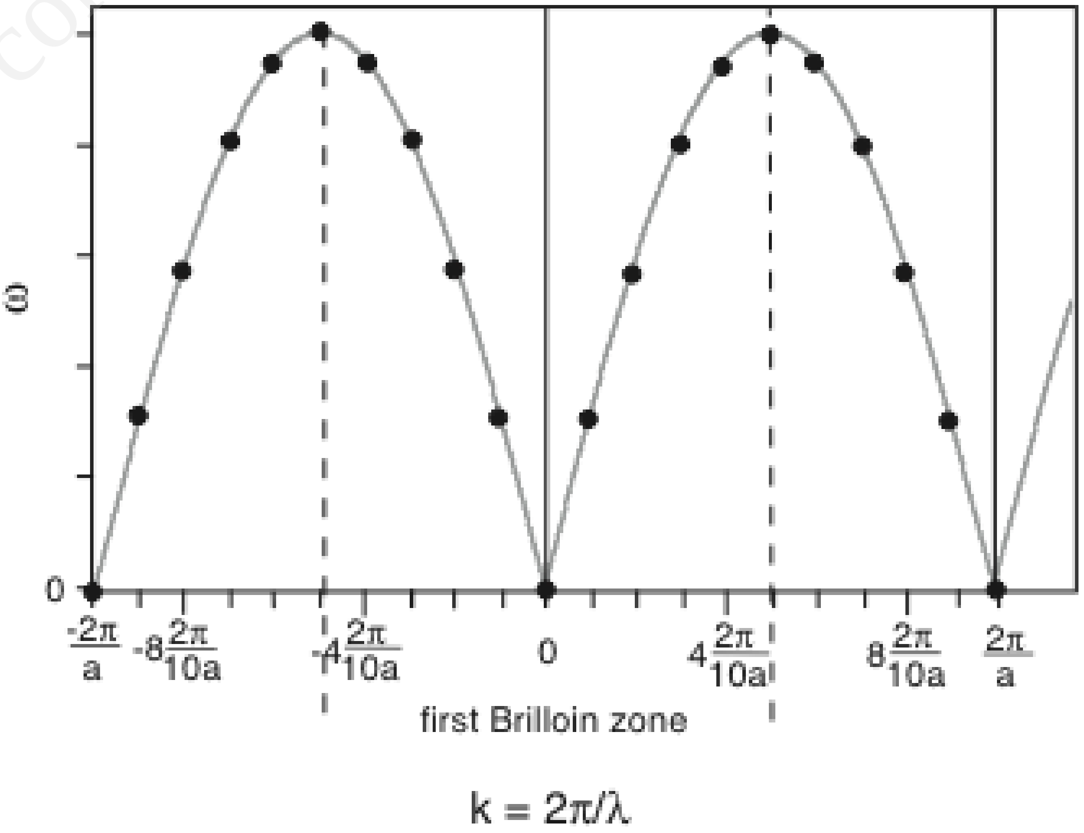


image source: wikimedia, author AllenMcC.

long chain: quantum model

$$E_l(k) = \left(l + \frac{1}{2}\right)\hbar\omega(k)$$



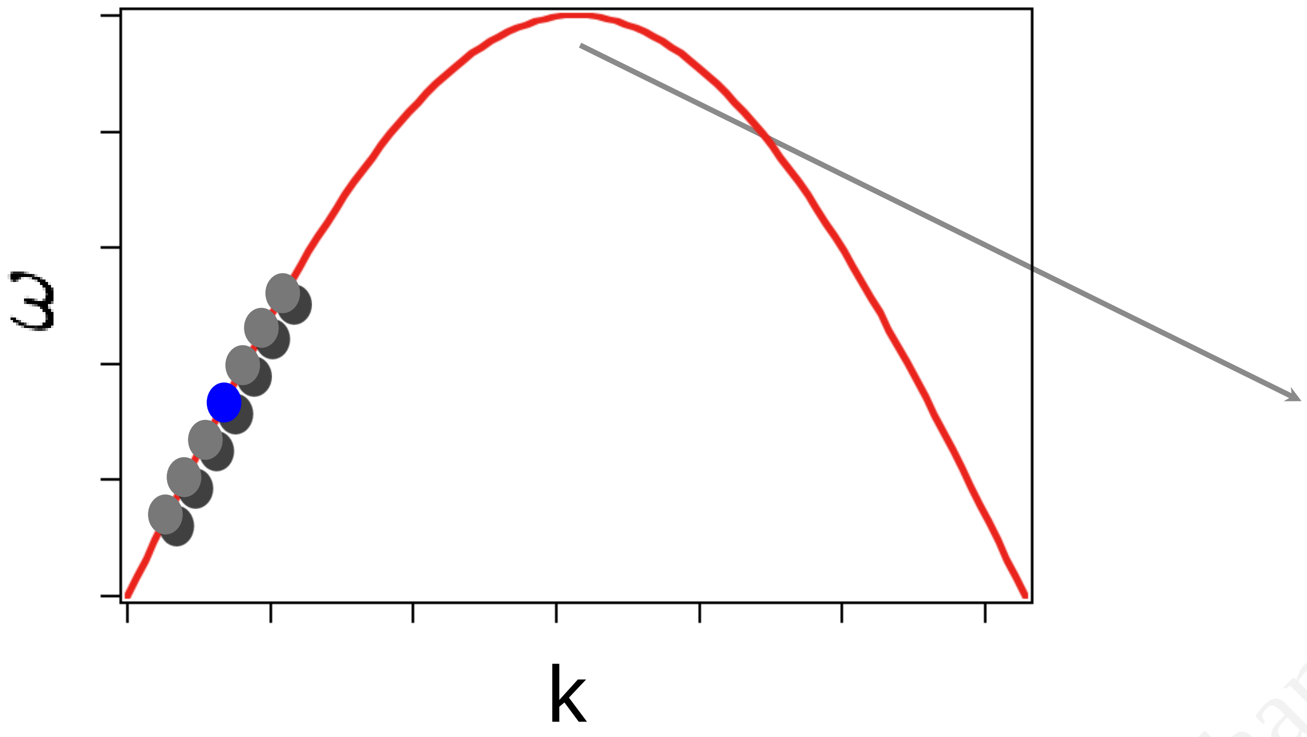


- The excitations of these oscillators are called phonons.
- The dispersion is often called a phonon dispersion curve.

Phonons <-> Photons

- Strong analogy: both bosonic excitations
- Both described by quantum mechanical harmonic oscillators
- Wave-particle duality

sine-like dispersion



one partial wave $v_p = \frac{\omega}{k}$

amplitude

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

sum of partial waves (package)

$$v_g = \frac{\partial \omega}{\partial k}$$

amplitude

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

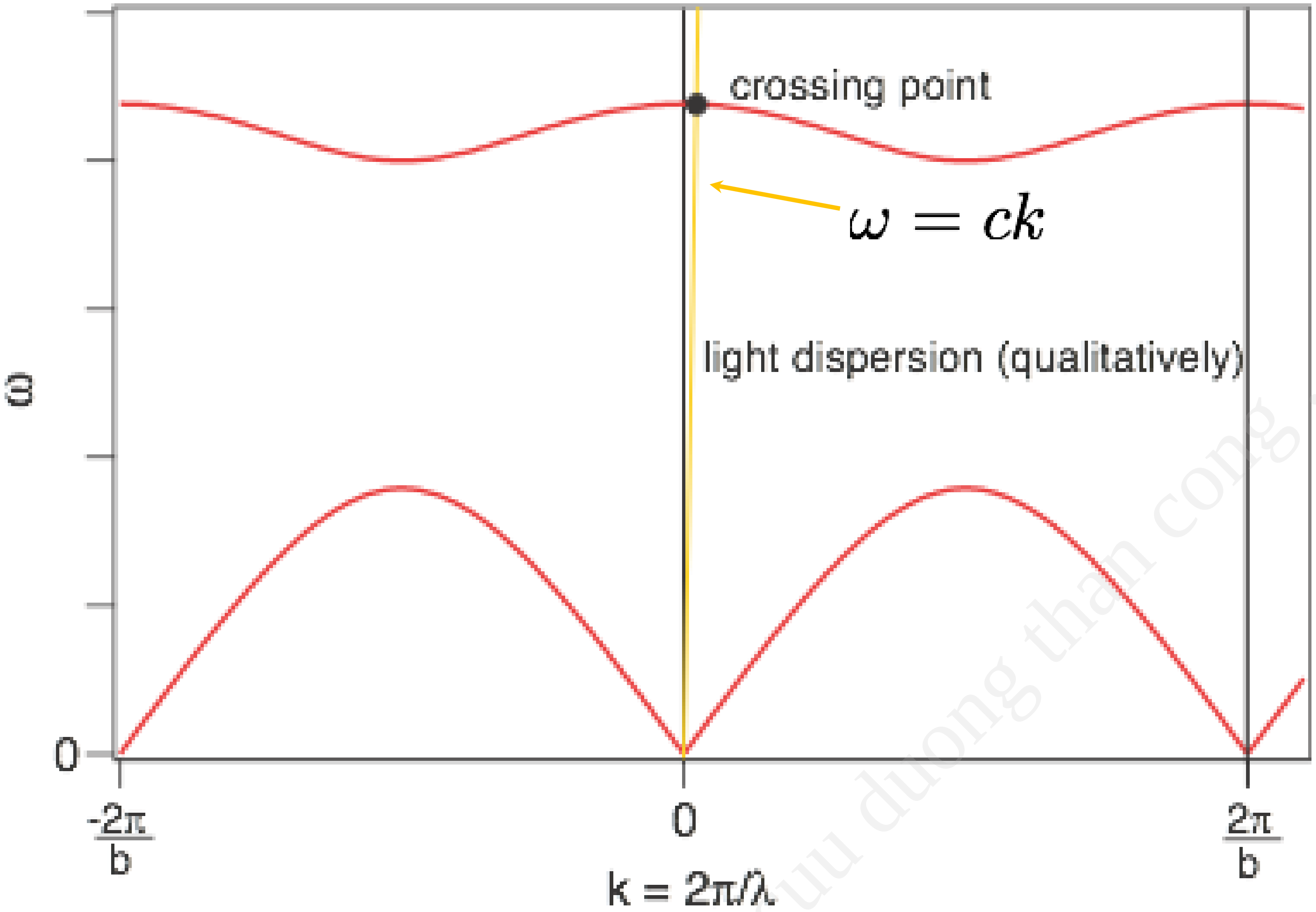
7 partial waves

partial wave #

QuickTime™ and a
Video decompressor
are needed to see this picture.

distance

Excitation of optical vibrations: particle picture



annihilation of photon
creation of phonon

Two conditions:

$$k_{light} = k_{phonon}$$

$$\hbar\omega_{light} = \hbar\omega_{phonon}$$

light E-field the same over very long distance

Three dimensional solids

1D $$k = \frac{2\pi}{aN} n$$

cubic crystal with lattice spacing a and macroscopic side length L and N unit cells in each direction:

$$L = aN$$

3D $$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{aN}(n_x, n_y, n_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L} \frac{n_z 2\pi}{L})$$

many indices (for example in the equations of motion)

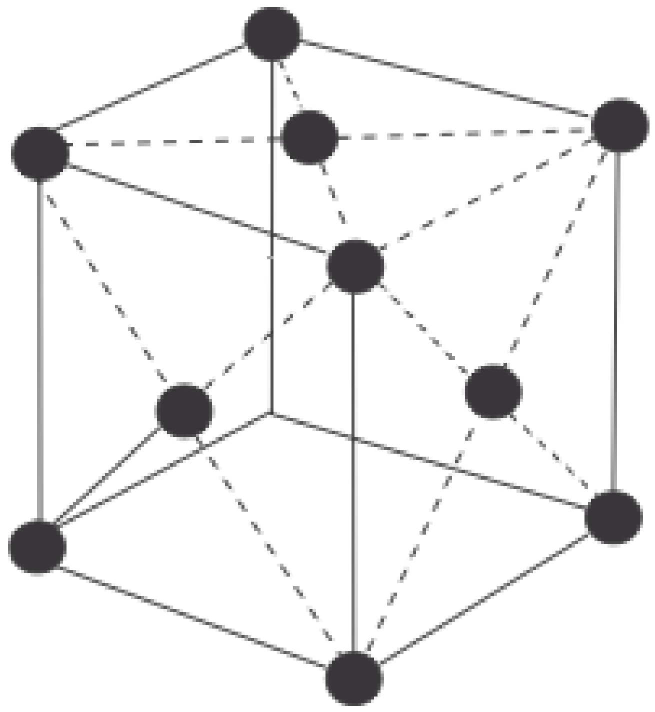
$$M_\alpha \ddot{x}_{\mathrm{n}\alpha i} + \sum_{\mathrm{m}\beta j} \Phi^{\mathrm{m}\beta j}_{\mathrm{n}\alpha i} x_{\mathrm{m}\beta j} = 0$$

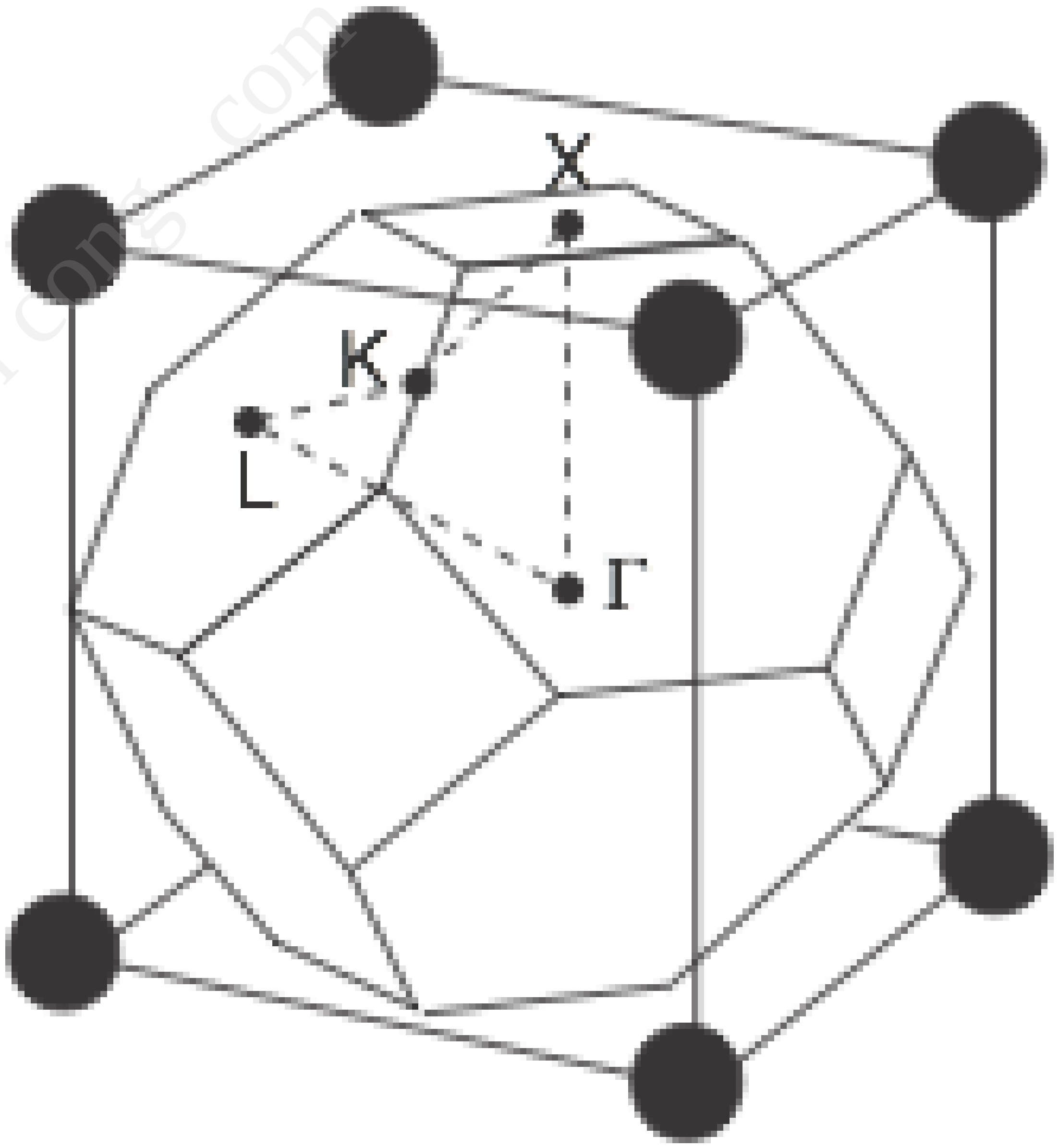
3 x (#atoms / unit cell) x (unit cells) solutions
i.e. 3 x (#atoms / unit cell) solutions for every k-point in the BZ

The first Brillouin zone

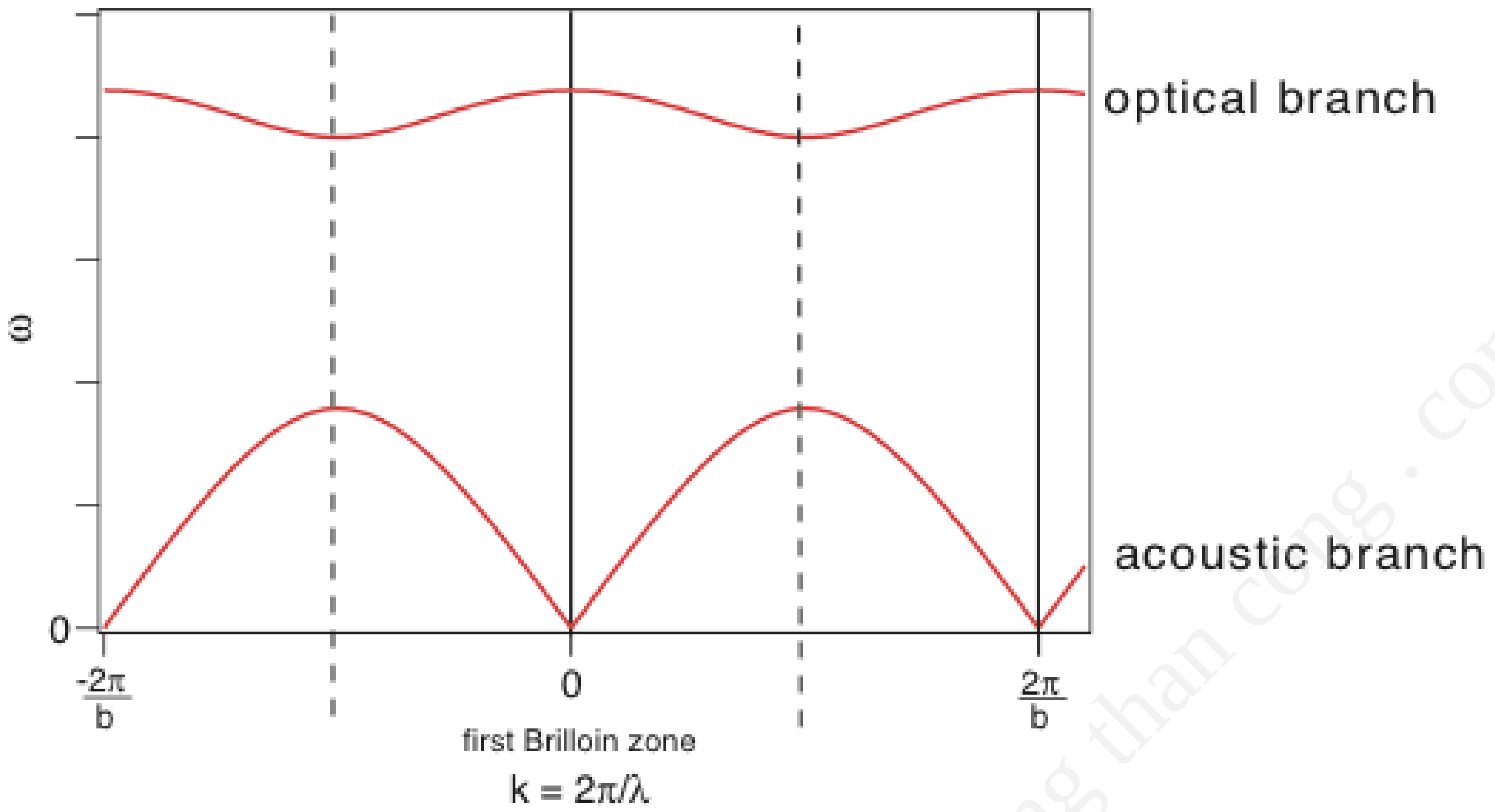
real
space

reciprocal
space





Phonons in 1D



$$\omega_i(k)$$

branch

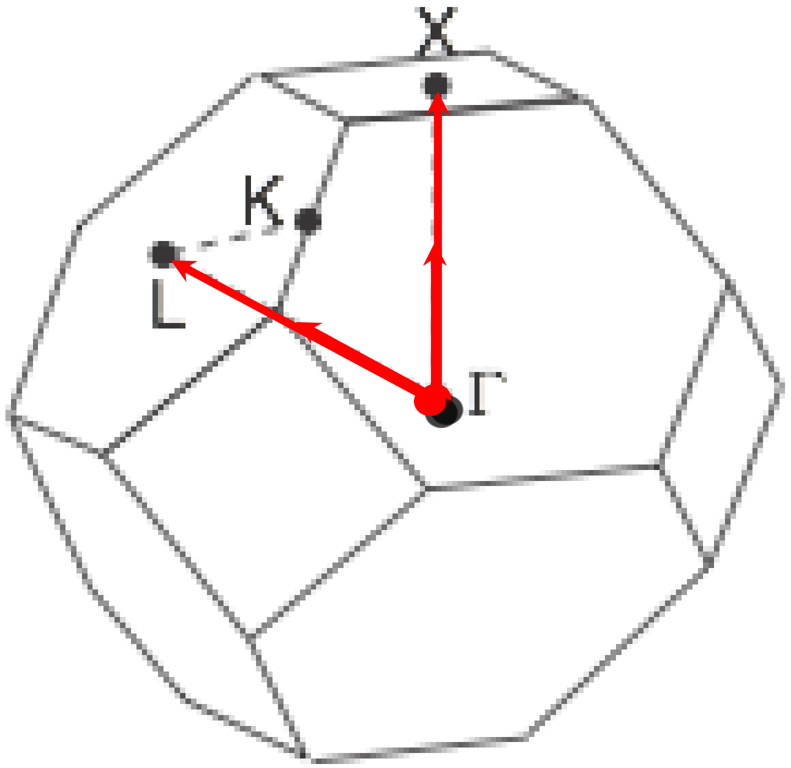
Phonons in 3D

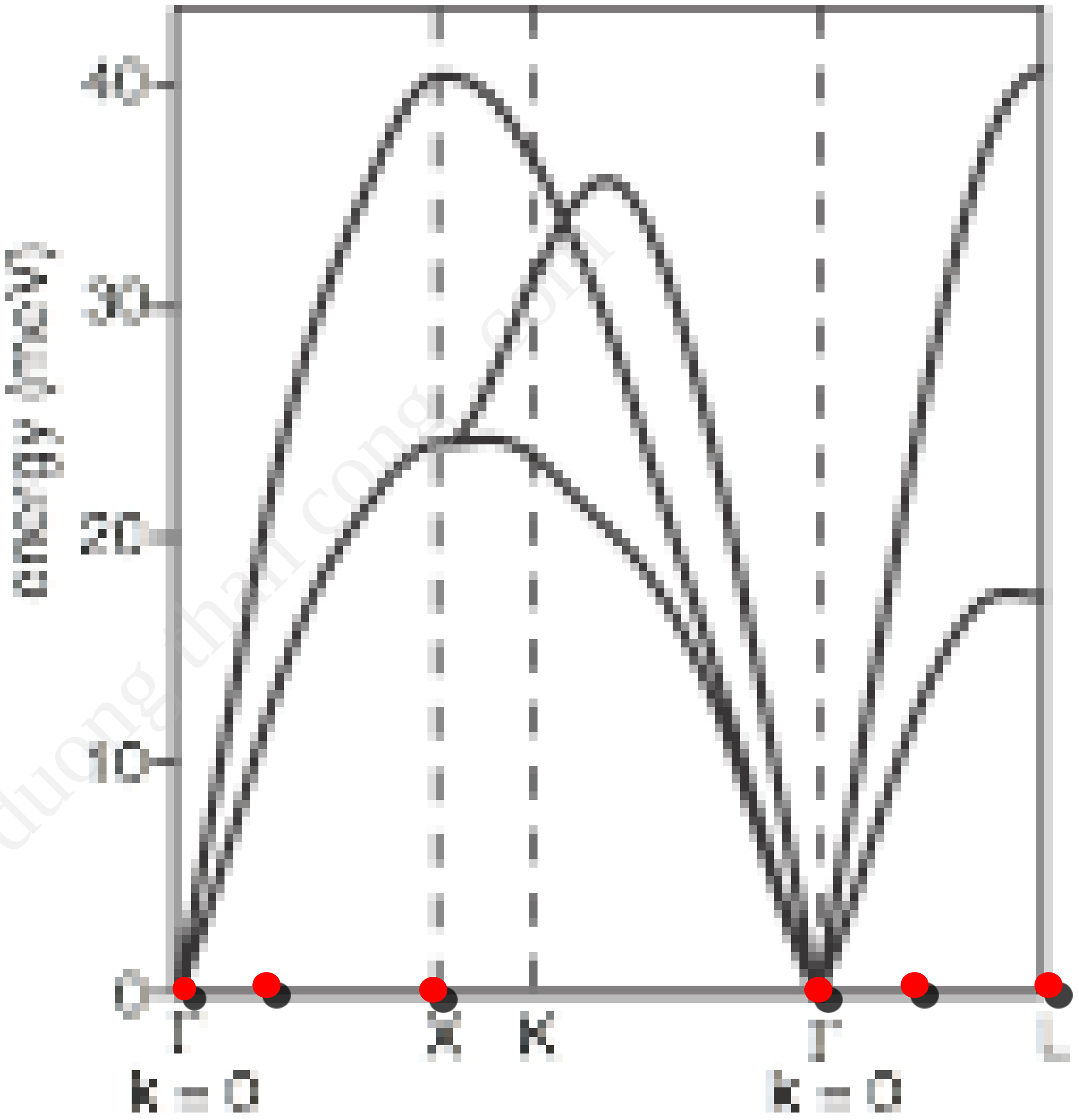
3D wave vector

$$\omega_i(\mathbf{k})$$

branch

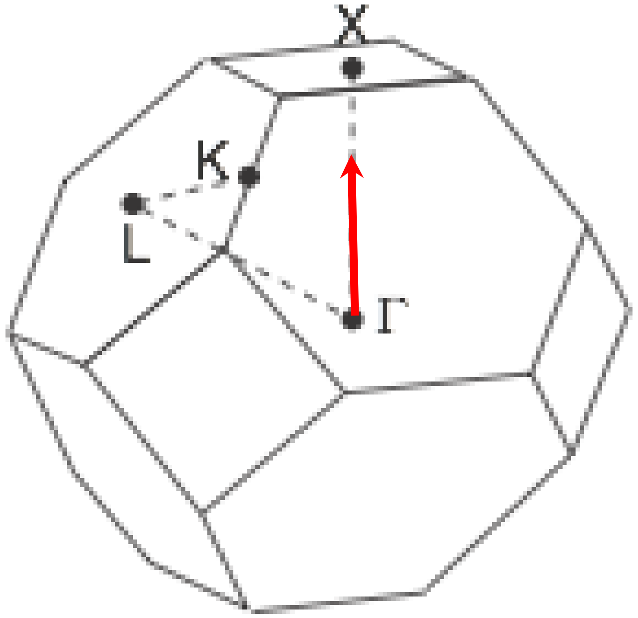
Phonons in 3D crystals: Aluminium

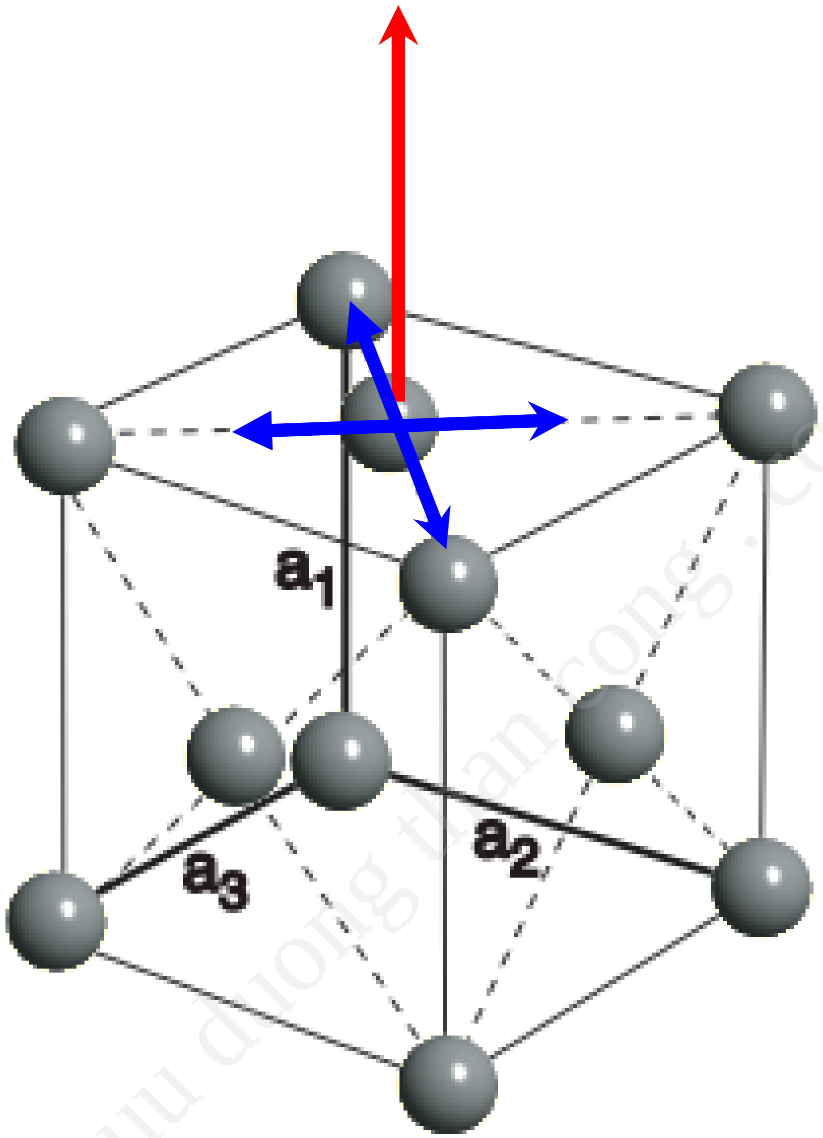


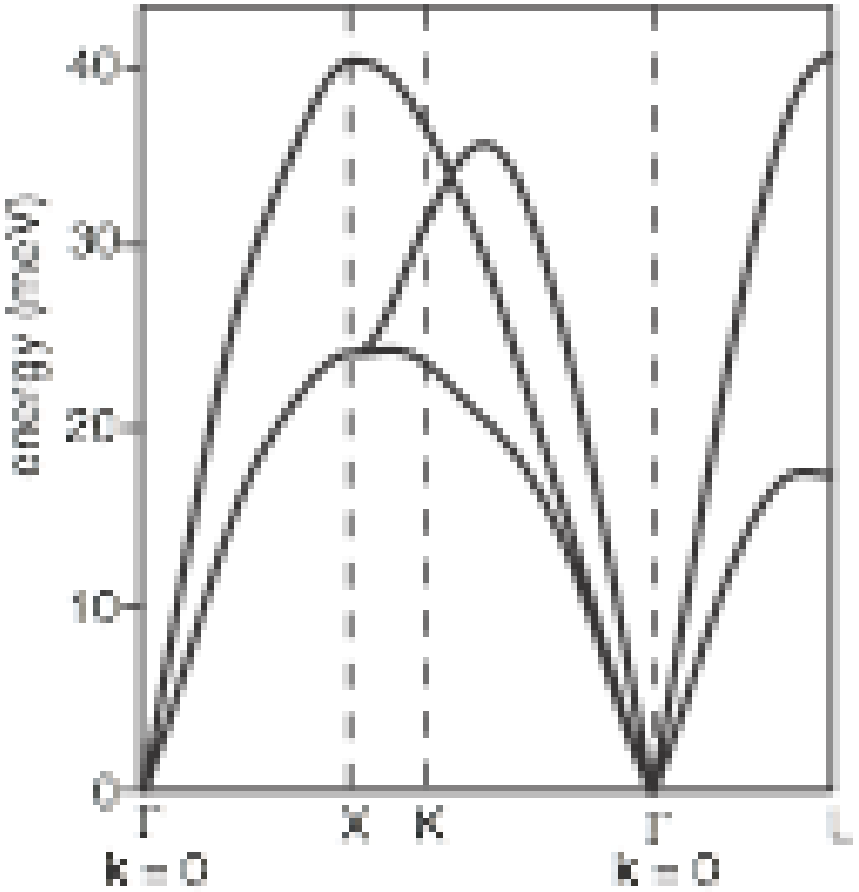


- Results from inelastic x-ray scattering / neutron scattering.

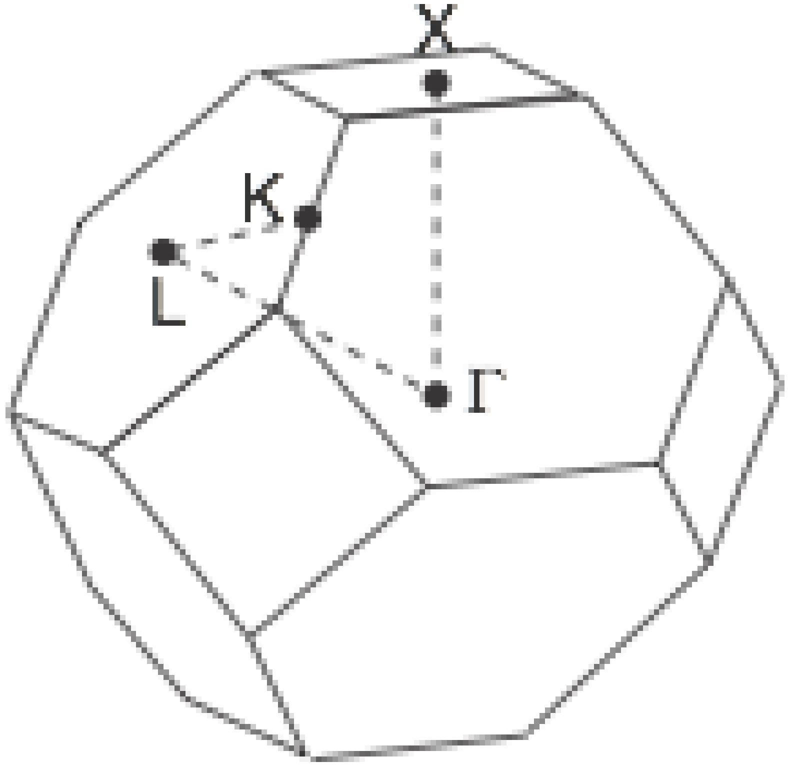
Phonons in 3D crystals: Aluminium

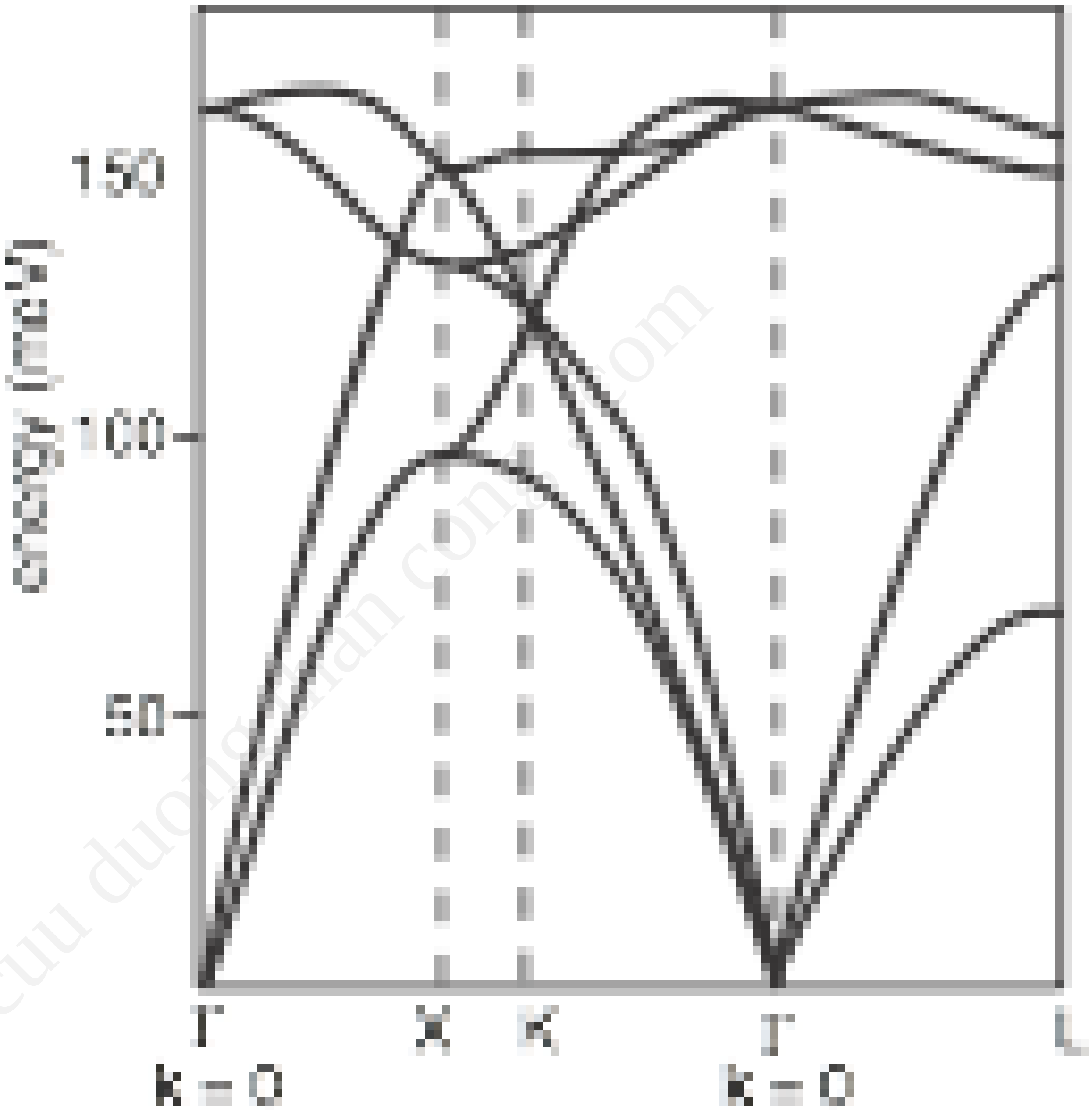






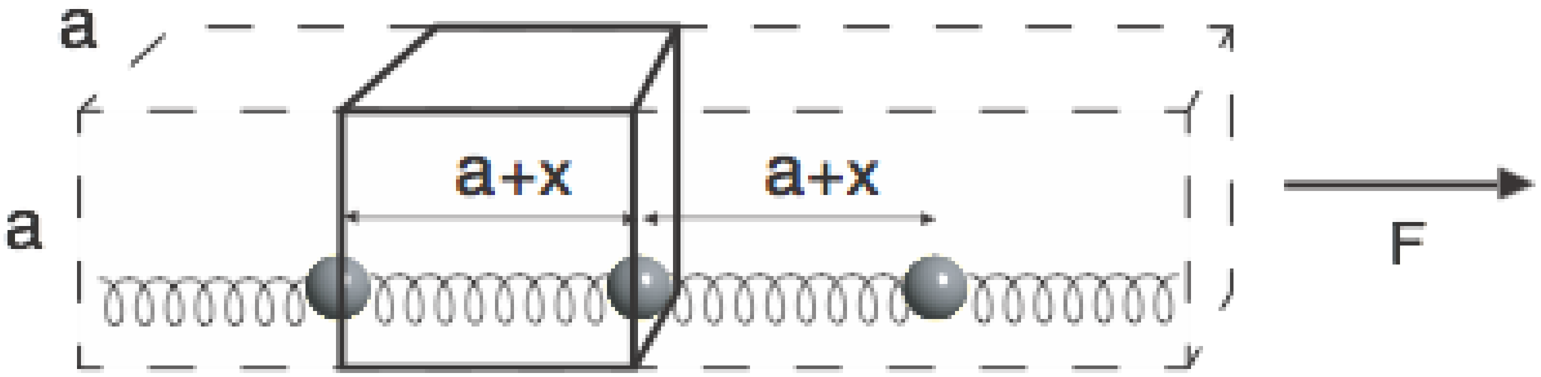
Phonons in 3D crystals: diamond





- Results from inelastic x-ray scattering / neutron scattering.
- Acoustic and optical branches present.

Estimate ϒ from Young's modulus



stress $\sigma = \frac{F}{a^2}$

harmonic oscillator $F = \gamma x$

$$\sigma = \frac{\gamma x}{a^2} \qquad \epsilon = \frac{x}{a}$$

$$Y = \frac{\sigma}{\epsilon} = \frac{\gamma x}{a^2}\frac{a}{x} = \frac{\gamma}{a}$$

$$\boxed{\gamma = Ya}$$

Estimate ϒ from Young's modulus

$$\boxed{\gamma = Ya}$$

example with numbers:

$Y=500\times10^{9}\ \mathrm{Nm}^{-2}$
$a=10^{-10}\ \mathrm{m}$

$\gamma = 50\ \mathrm{Nm}^{-1}$

and look again at the classical result for the amplitude (at 300 K)

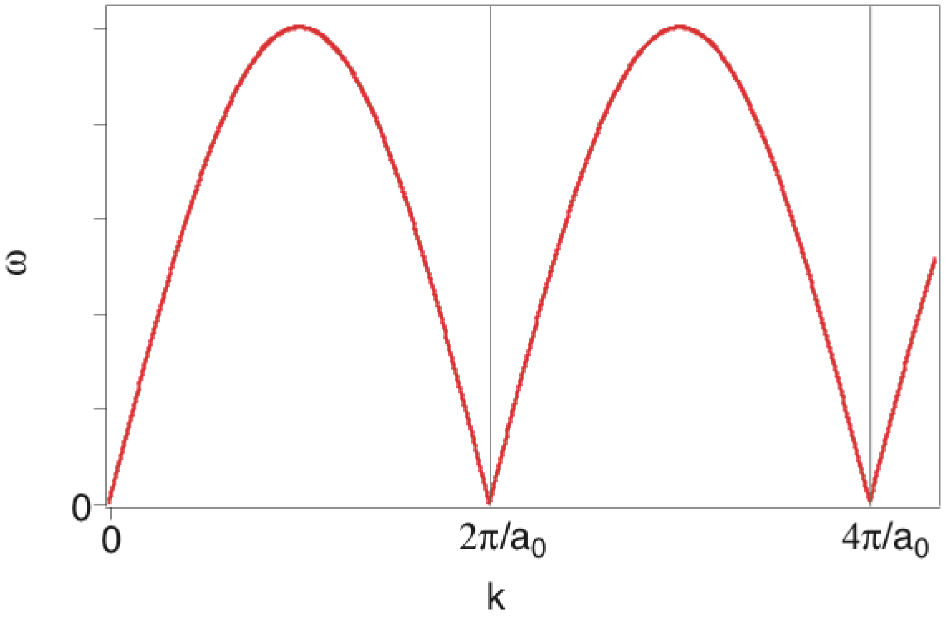
$$x_{\max} = \left(\frac{2k_BT}{\gamma}\right)^{1/2} \approx 1.3\times10^{-11}\mathrm{m}$$

Estimate ω from Young's modulus

$$\omega = \sqrt{\frac{\gamma}{M}} \qquad \gamma \approx Y a_0$$

	diamond	lead
mass	12 u	207 u
Y	$950*10^9$ Nm^{-2}	$15*10^9$ Nm^{-2}
ω calc	$8*10^{13}$ Hz	$4*10^{12}$ Hz
ω exp	0 to $2*10^{14}$ Hz	0 to $1*10^{13}$ Hz

remember



- reasonable agreement
- most important, again: light elements and strong forces give high frequencies.

Heat capacity of the lattice

General Theories

Thermodynamics

$C_V \to 0$ for $T \to 0$

no numerical value
at finite T

Classical Statistical Mechanics

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R$$

Dulong-Petit law, numerical value
independent of T

Heat capacity: classical statistical mechanics

so for a one classical dimensional harmonic oscillator we have

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}\gamma x^2$$

so the mean energy is $k_B T$. For a three-dimensional oscillator we have 3 $k_B T$. For one mole of ions we get

$$< E >= E = 3N_A k_B T = 3RT$$

and so

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R$$

This is called the Dulong-Petit law.

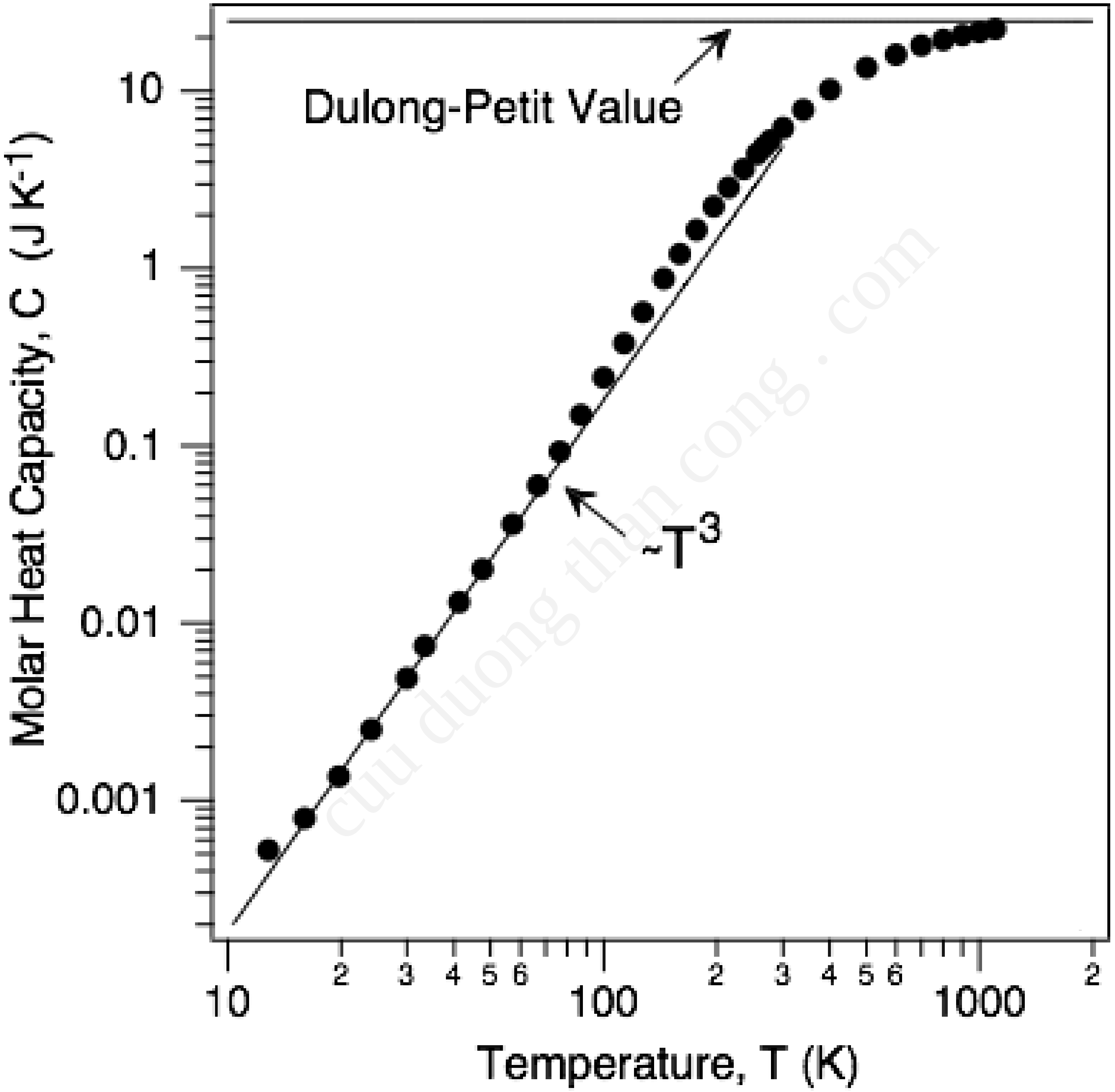
Comparison of the Dulong-Petit law to experiment

	77 K (JK^{-1})	273 K (JK^{-1})
classical value	24.9	24.9
copper	12.5	24.3
aluminium	9.1	23.8
gold	19.1	25.2
lead	23.6	26.7
iron	8.1	24.8
sodium	20.4	27.6
silicon	5.8	21.8

values for one mole of substance

- At high temperatures the Dulong-Petit law works quite well, also for metals.

Heat capacity of diamond



The Einstein model for the heat capacity

The solid's vibrations are represented by independent oscillators

$$E_n = \left(n + \frac{1}{2}\right)\hbar\omega_E$$

the mean energy for all the 3 N_A oscillators in one mole is

$$\langle E\rangle = 3N_A\left(\langle n\rangle + \frac{1}{2}\right)\hbar\omega_E$$

and using the Bose-Einstein distribution

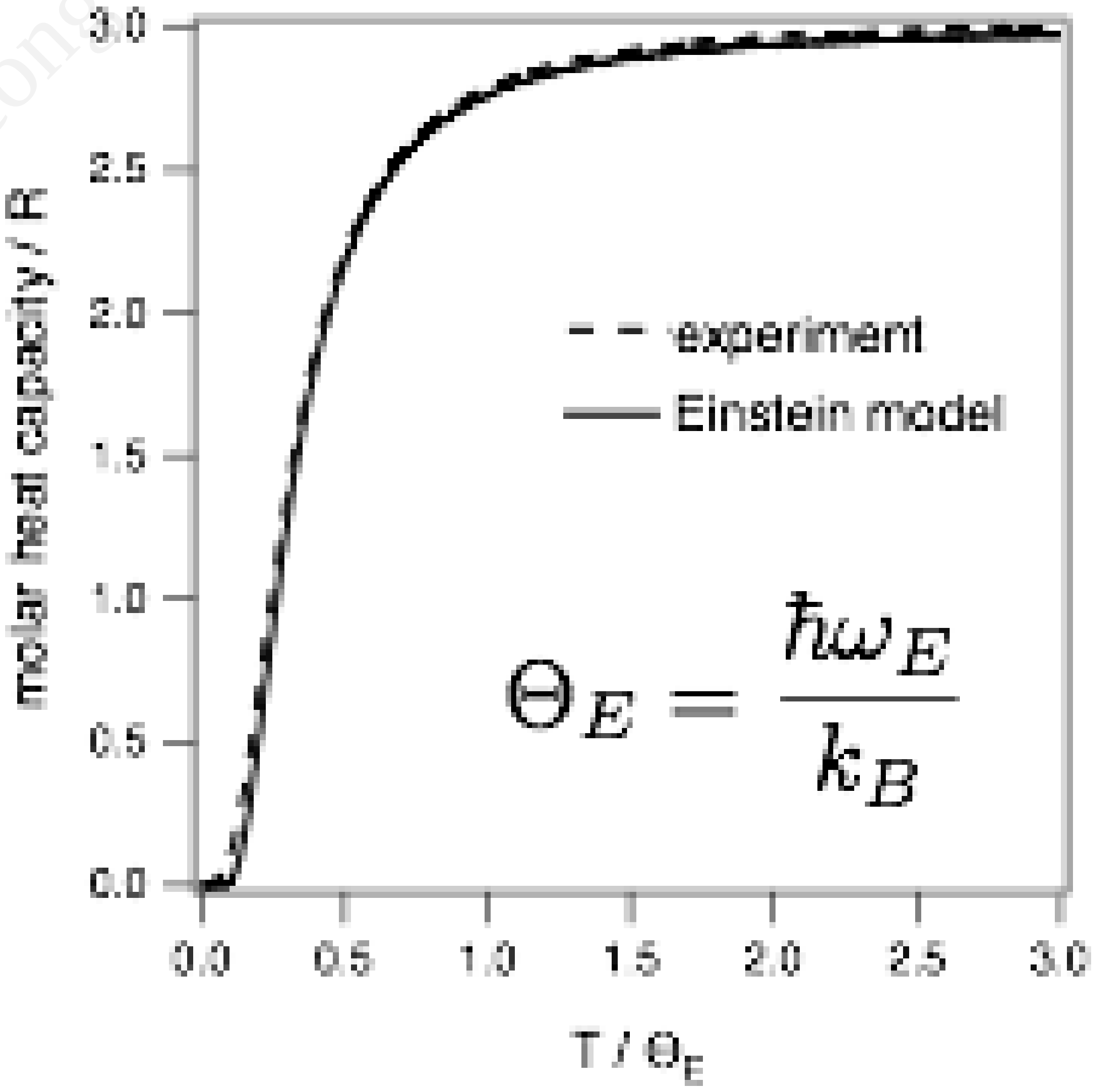
$$\langle n\rangle = \frac{1}{e^{\hbar\omega_E/k_BT} - 1}$$

$$\langle E\rangle = 3N_A\left(\frac{1}{e^{\hbar\omega_E/k_BT} - 1} + \frac{1}{2}\right)\hbar\omega_E$$

The Einstein model for the heat capacity

$$C = 3N_A\left(\frac{\partial\langle E\rangle}{\partial T}\right)_V = 3R\left(\frac{\hbar\omega_E}{k_BT}\right)^2\frac{e^{\hbar\omega_E/k_BT}}{(e^{\hbar\omega_E/k_BT}-1)^2}$$

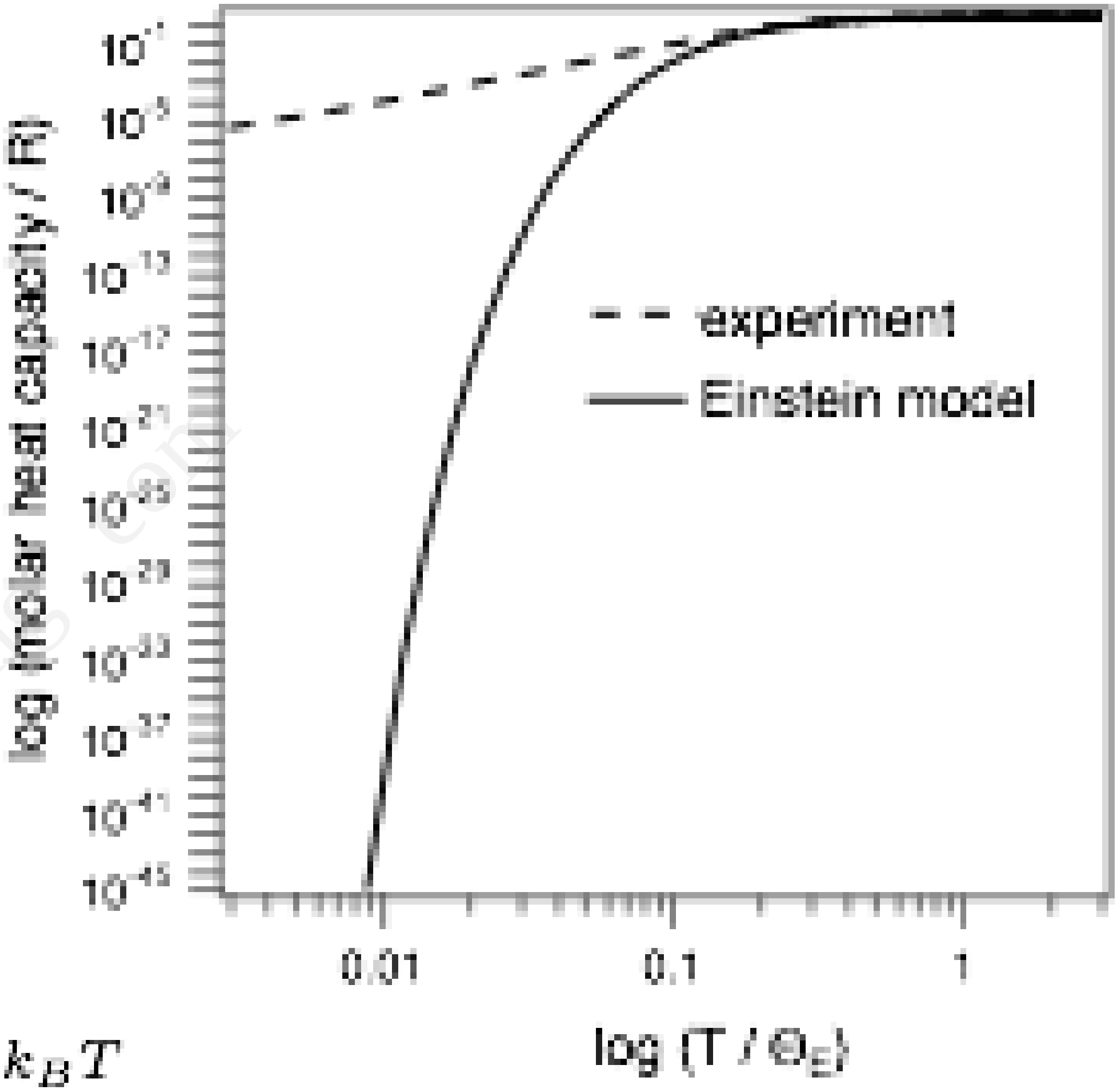
- correct Dulong-Petit value for high temperatures
- zero heat capacity at zero temperature
- The Einstein frequency / temperature is an adjustable parameter.



$$\Theta_E = \frac{\hbar\omega_E}{k_B}$$

The Einstein model: low-temperature heat capacity

- but low temperature behaviour of the experiment not correctly reproduced. T^3 behaviour in experiment, exponential behaviour here



$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3R\left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{\hbar\omega_E/k_B T}-1)^2}$$

$$= 3R\left(\frac{\hbar\omega_E}{k_B T}\right)^2 \frac{e^{\hbar\omega_E/k_B T}}{(e^{2\hbar\omega_E/k_B T}-2e^{\hbar\omega_E/k_B T}+1)}$$

$$= 3R\left(\frac{\hbar\omega_E}{k_B T}\right)^2 e^{-\hbar\omega_E/k_B T}$$

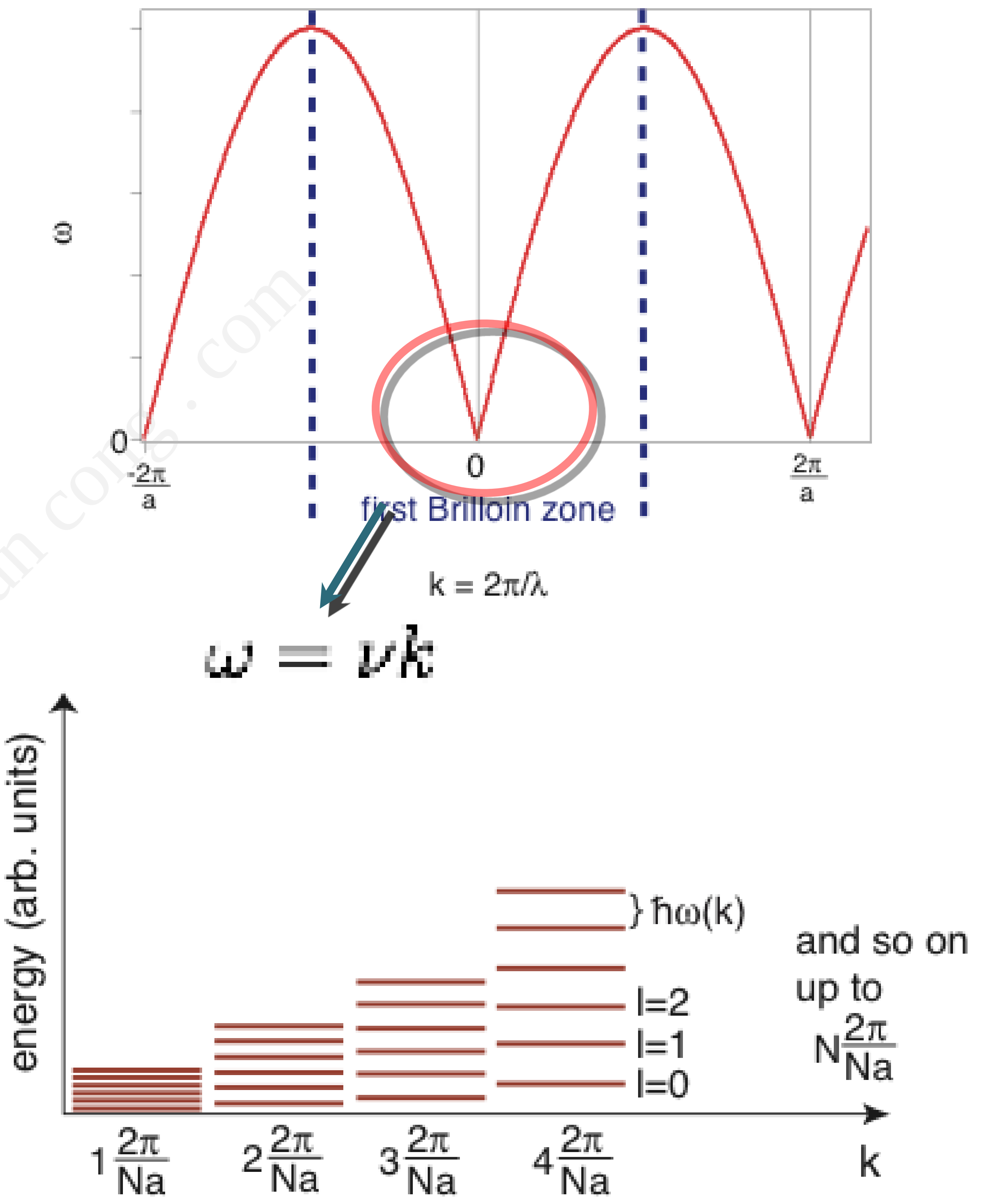
for very low T

Why does the Einstein model work at high T? Why does it fail at low T?

- At high T the small spacing between the energy levels is irrelevant.
- At sufficiently low temperature, the energy level separation is much bigger than $k_B T$.
- Eventually all the oscillators are “frozen” in the ground state. Increasing T a little does not change this, i.e. it does not change the energy.

The Debye model for the heat capacity

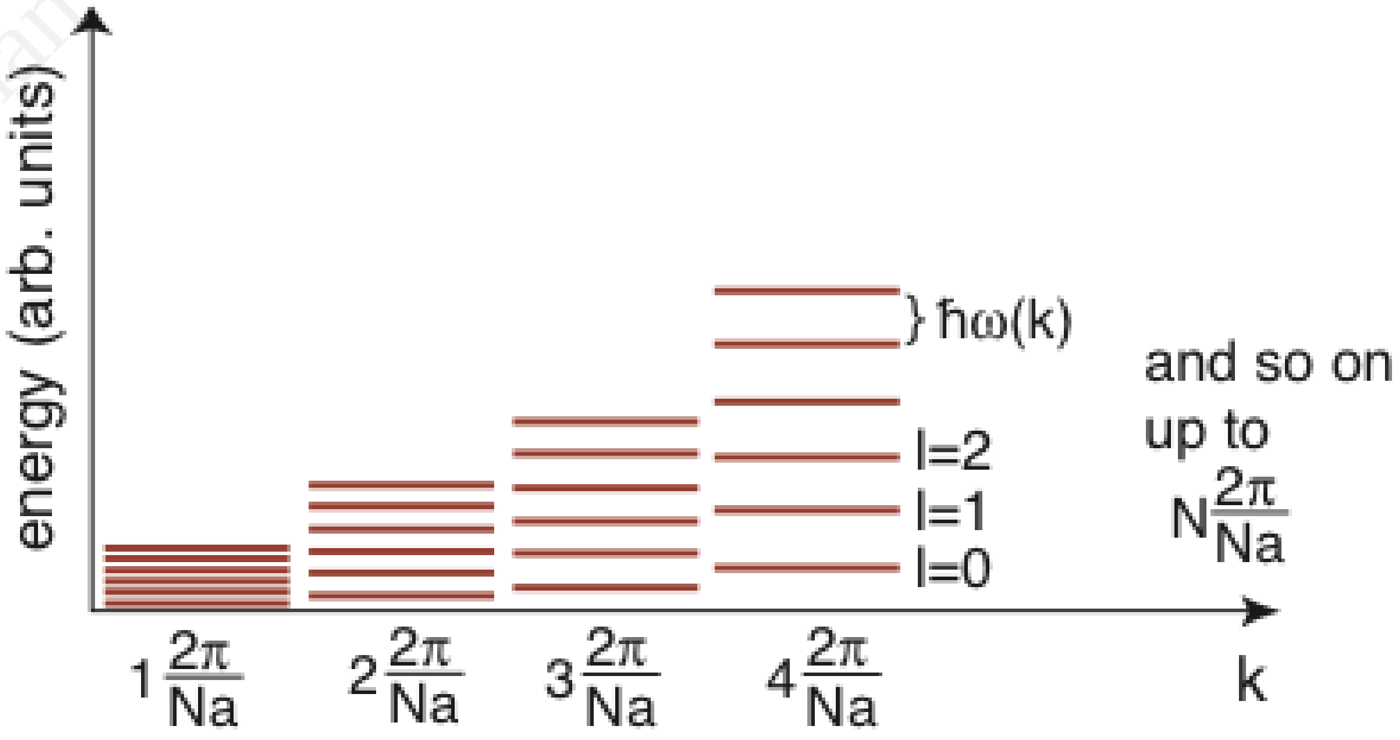
- General idea: use a better, more realistic description of the crystal vibrations, especially for those with low energies.
- These are the acoustic, very long wavelength vibrational models of the crystal.
- The energy separation between the levels is VERY small for low k.



- Now we have many oscillators with different values of ω for different values of k.

$$E_l(k) = \left(l + \frac{1}{2}\right)\hbar\omega(k)$$

$$\omega = vk$$



mean energy for one oscillator

$$\langle E\rangle = \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}$$

mean energy for three dimensional solid (sum over all phonons)

$$\langle E\rangle = 3\sum_i \frac{\hbar\omega_i}{e^{\hbar\omega_i/k_BT}-1}$$

two transverse, one longitudinal wave,all with $\omega = \nu k$

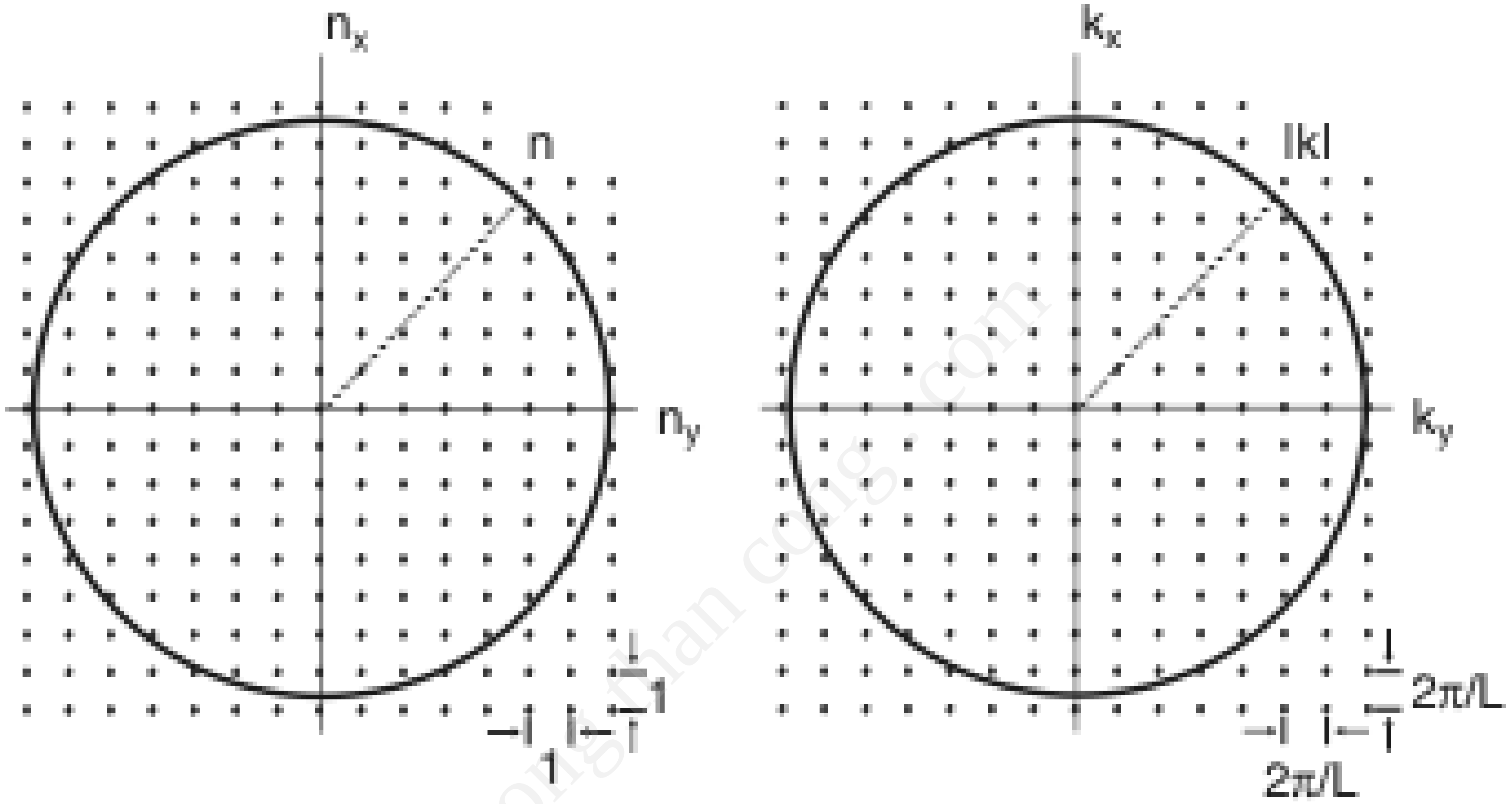
$$\langle E\rangle = 3\int_0^{\omega_D} \frac{g(\omega)\hbar\omega}{e^{\hbar\omega/k_BT}-1}d\omega$$

Problems:
1. What is $g(\omega)$
2. What is ω_D

$$g(\omega) = \frac{dN(\omega)}{d\omega}$$

strategy: $\left.\begin{matrix} N(k) \\ \omega(k)\ \ k(\omega) \end{matrix}\right\} N(\omega)$

Vibrational density of states $g(\omega)$



each state characterised by

$$\mathbf{k} = (k_x, k_y, k_z) = \frac{2\pi}{aN}(n_x, n_y, n_z) = (\frac{n_x 2\pi}{L}, \frac{n_y 2\pi}{L} \frac{n_z 2\pi}{L})$$

total number of states for a maximum n

$$N = \frac{4}{3}\pi n^3;$$

total number of states for a maximum |k|

$$N = \frac{4}{3}\pi\left(\frac{L|\mathbf{k}|}{2\pi}\right)^3$$

total number of
states for a
maximum |k|

$$N = \frac{4}{3}\pi\left(\frac{L|\mathbf{k}|}{2\pi}\right)^3$$

$$\omega(|\mathbf{k}|) = \nu|\mathbf{k}|$$

$$|\mathbf{k}| = \frac{\omega}{\nu}$$

$$N(\omega) = \frac{4}{3}\pi\left(\frac{L\omega}{2\pi\nu}\right)^3 = \frac{V}{6\pi^2\nu^3}\omega^3$$

$$g(\omega)d\omega = \frac{dN}{d\omega}d\omega = \frac{\omega^2 V}{2\pi^2\nu^3}d\omega$$

mean energy for one oscillator

$$\langle E\rangle = \frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}$$

tentative mean energy for
three dimensional solid

$$\langle E\rangle = 3\int \frac{\hbar\omega'}{e^{\hbar\omega'/k_BT}-1}d\omega'$$

two transversal, one longitudinal wave,all with $\omega = \nu k$

$$\langle E\rangle = 3\int_0^{\omega_D} \frac{g(\omega)\hbar\omega}{e^{\hbar\omega/k_BT}-1}d\omega$$

Problems:
1. What is $g(\omega)$
2. What is ω_D

What is the upper integration limit?

$$3N = 3\int_0^{\omega_D} g(\omega)d\omega$$

ω_D Debye angular frequency

$\Theta_D = \hbar\omega_D/k_B$ Debye temperature

(no more vibrational modes than three times atoms in crystal)

$$g(\omega)d\omega = \frac{dN}{d\omega}d\omega = \frac{\omega^2 V}{2\pi^2\nu^3}d\omega$$

$$\omega_D^3 = 6\pi^2\frac{N}{V}\nu^3$$

$$\hbar\omega_D = k_B\Theta_D$$

The Debye model for the heat capacity

so that

$$< E >= 3\int_0^{\omega_D} \frac{g(\omega)\hbar\omega}{e^{\hbar\omega/k_BT}-1}d\omega$$

$$\langle E\rangle = 3\int_0^{\omega_D} \frac{\omega^2 V}{2\pi^2\nu^3}\frac{\hbar\omega}{e^{\hbar\omega/k_BT}-1}d\omega = \frac{3V\hbar}{2\pi^2\nu^3}\int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/k_BT}-1}d\omega$$

substitute $x = \hbar\omega/k_BT$ $\quad x_D = \hbar\omega_D/k_BT$

$$\langle E\rangle = \frac{3Vk_B^4T^4}{2\pi^2\nu^3\hbar^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^3}{e^x-1}dx$$

$$\hbar\omega_D = k_B\Theta_D$$

The Debye model for the heat capacity

$$\langle E\rangle = \frac{3Vk_B^4T^4}{2\pi^2\nu^3\hbar^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^3}{e^x-1}dx$$

$1+x.$

high temperature, $x=\hbar\omega/k_BT$ small

$$\langle E\rangle = 3Nk_BT$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

for one mole

$$\boxed{C_V = 3R}$$

The Debye model for the heat capacity

substitute $x_D = \hbar\omega_D / k_B T$

$$\langle E \rangle = \frac{3Vk_B^4T^4}{2\pi^2\nu^3\hbar^3}\int_0^{x_D}\frac{x^3}{e^x-1}dx = 9Nk_BT\left(\frac{T}{\Theta_D}\right)^3\int_0^{x_D}\frac{x^3}{e^x-1}dx$$

low temperature, $x = \hbar\omega / k_B T$ large

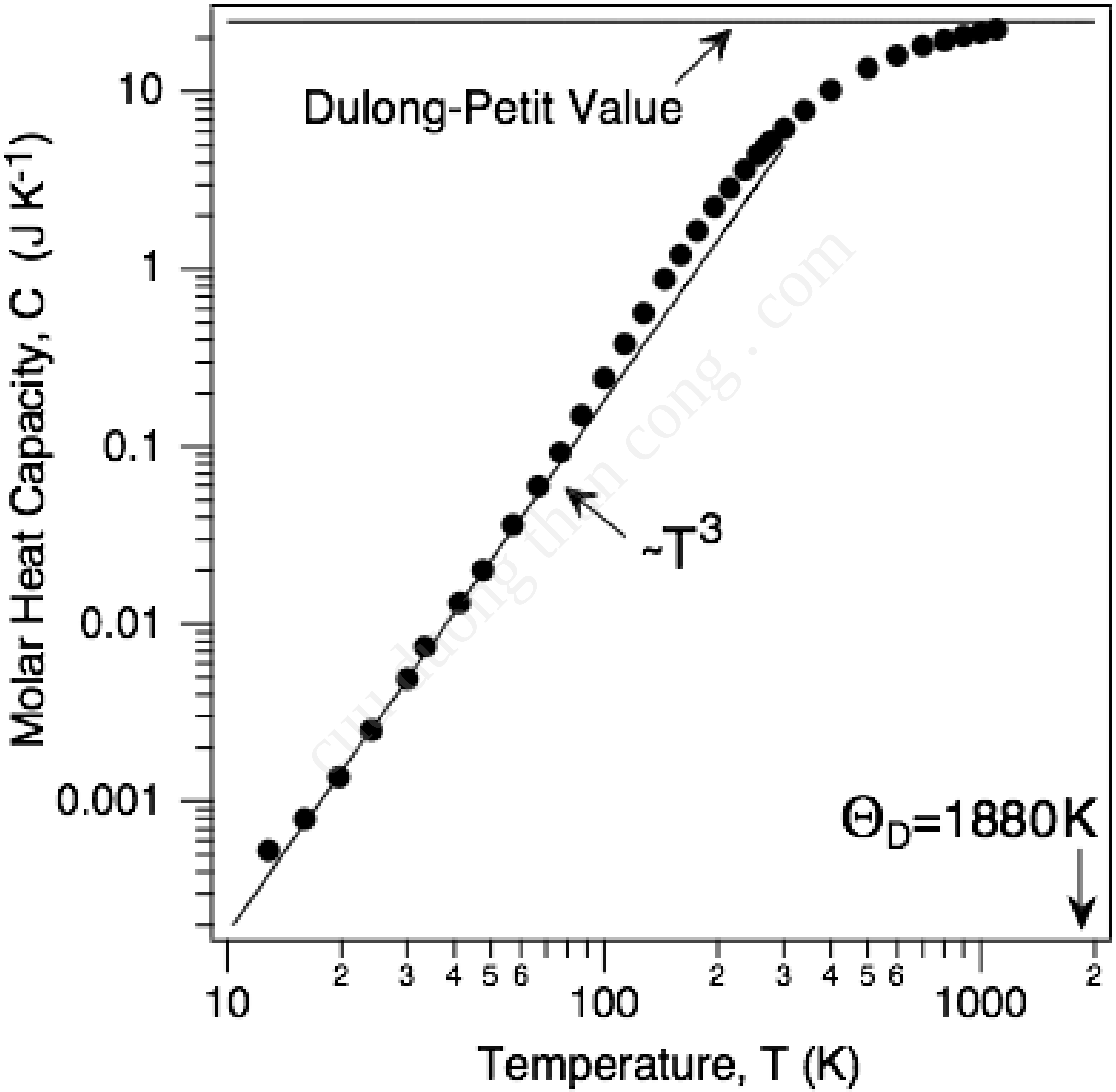
$$\int_0^{\infty}\frac{x^3}{e^x-1}dx = \frac{\pi^4}{15}$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

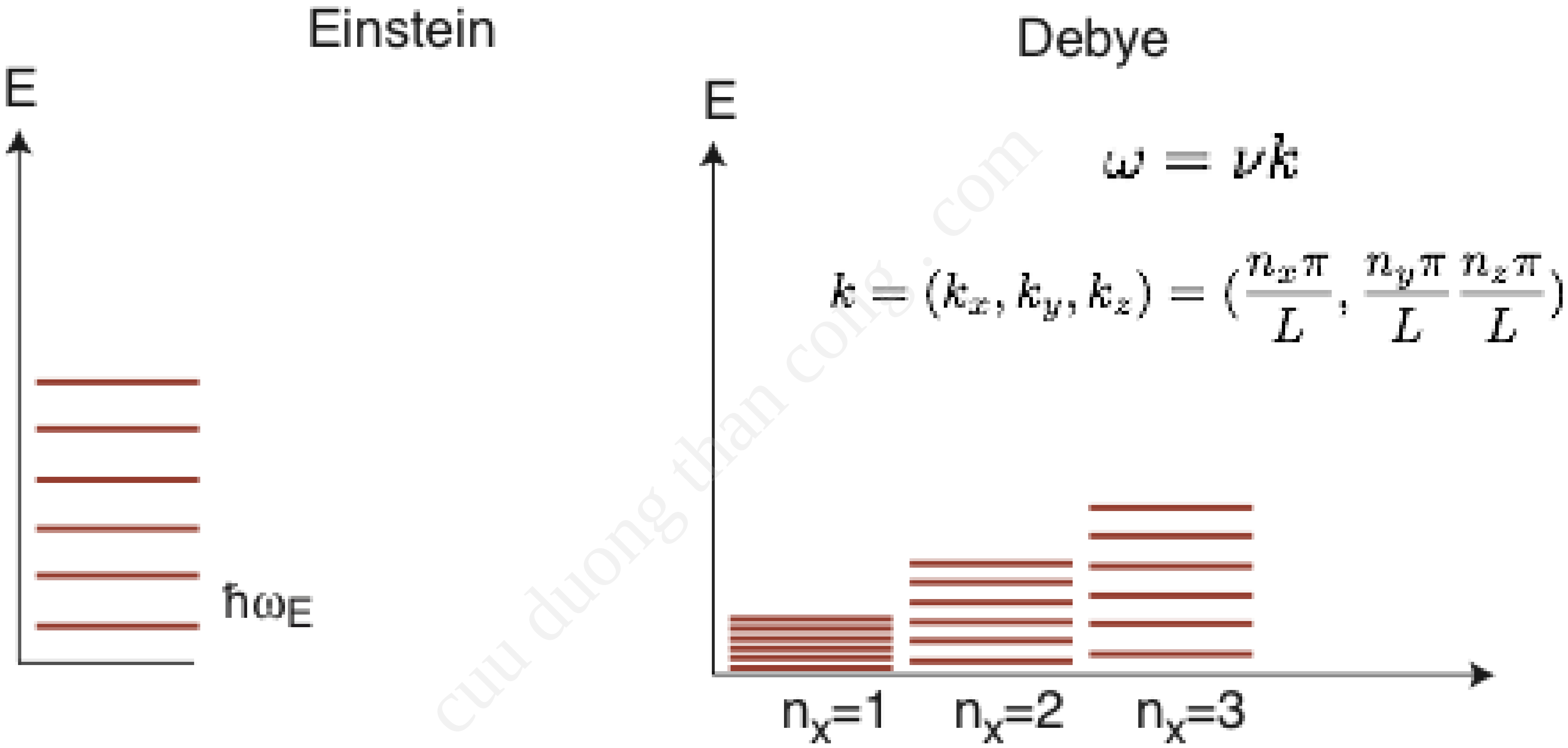
for one mole

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

Comparison Debye model - experiment



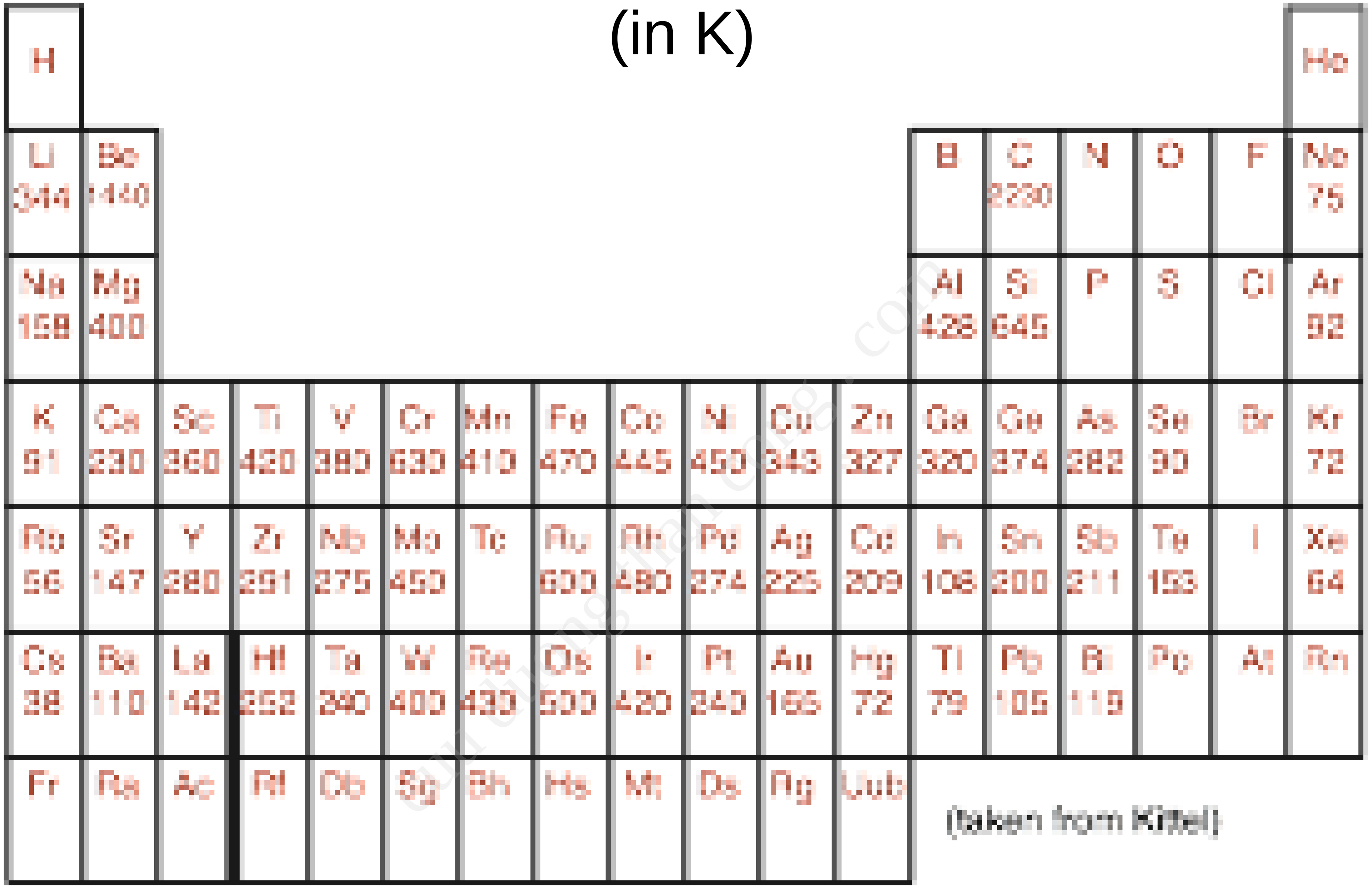
Why does the Debye model work better at low T than the Einstein model?



- The Debye model gives a better representation for the very low energy vibrations.
- At low temperatures, these vibrations matter most.

Debye temperatures of the elements

(in K)



H																	He
Li 344	Be 1440											B	C 2230	N	O	F	Ne 75
Na 158	Mg 400											Al 428	Si 645	P	S	Cl	Ar 92
K 91	Ca 230	Sc 360	Ti 420	V 380	Cr 630	Mn 410	Fe 470	Co 445	Ni 450	Cu 343	Zn 327	Ga 320	Ge 374	As 282	Se 90	Br	Kr 72
Rb 56	Sr 147	Y 280	Zr 291	Nb 275	Mo 450	Tc	Ru 600	Rh 480	Pd 274	Ag 225	Cd 209	In 108	Sn 200	Sb 211	Te 153	I	Xe 64
Cs 38	Ba 110	La 142	Hf 252	Ta 240	W 400	Re 430	Os 500	Ir 420	Pt 240	Au 165	Hg 72	Tl 79	Pb 105	Bi 119	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub						

(taken from Kittel)

$$\omega = \sqrt{\frac{\gamma}{M}},$$

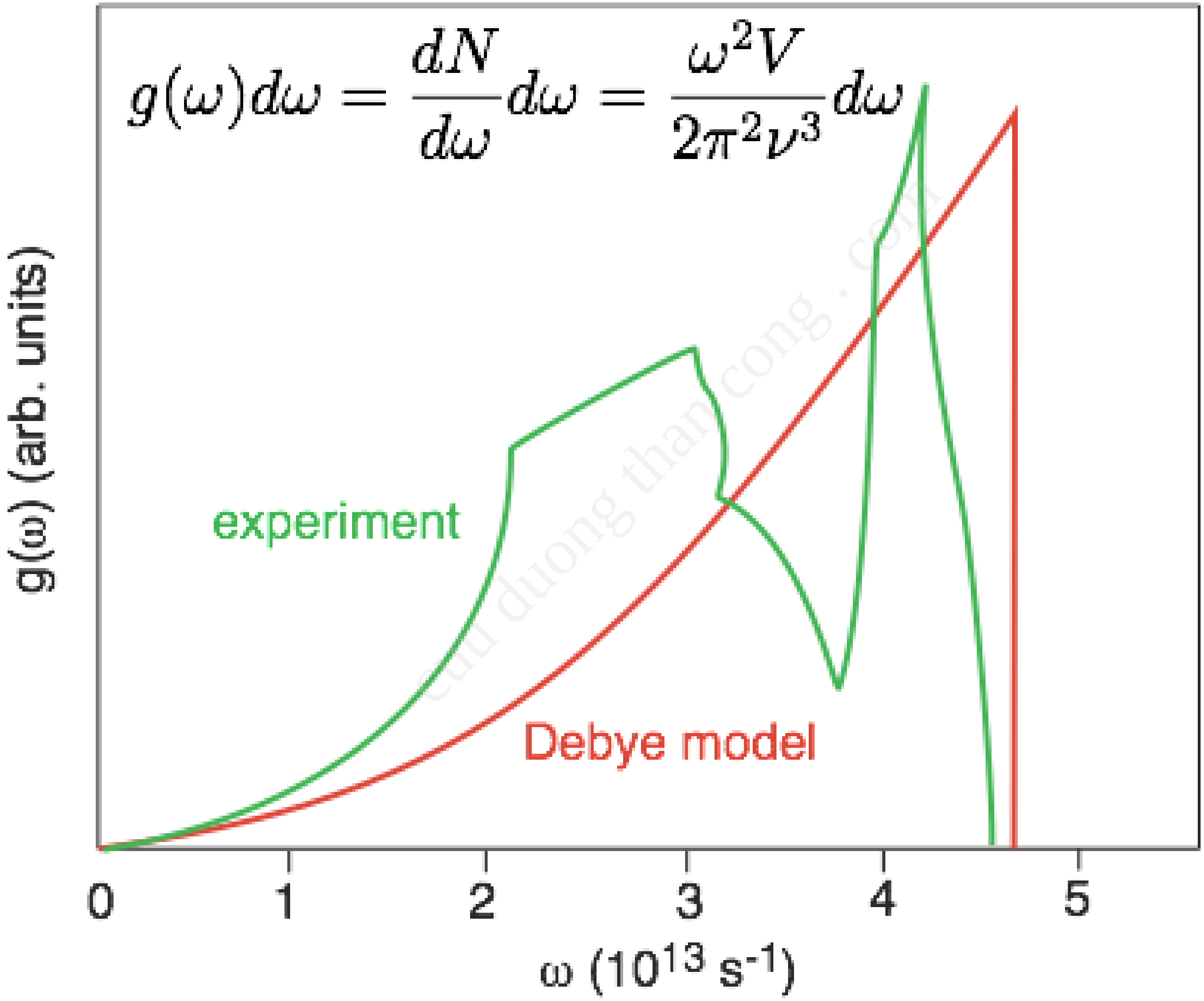
Comparison of the Dulong-Petit law to experiment

	77 K (JK^{-1})	273 K (JK^{-1})
classical value	24.9	24.9
copper	12.5	24.3
aluminium	9.1	23.8
gold	19.1	25.2
lead	23.6	26.7
iron	8.1	24.8
sodium	20.4	27.6
silicon	5.8	21.8

values of one mole of substance

- At high temperatures the Dulong-Petit law works quite well.
- At low temperatures, it does not. But we already know from basic principles that it wouldn’t.

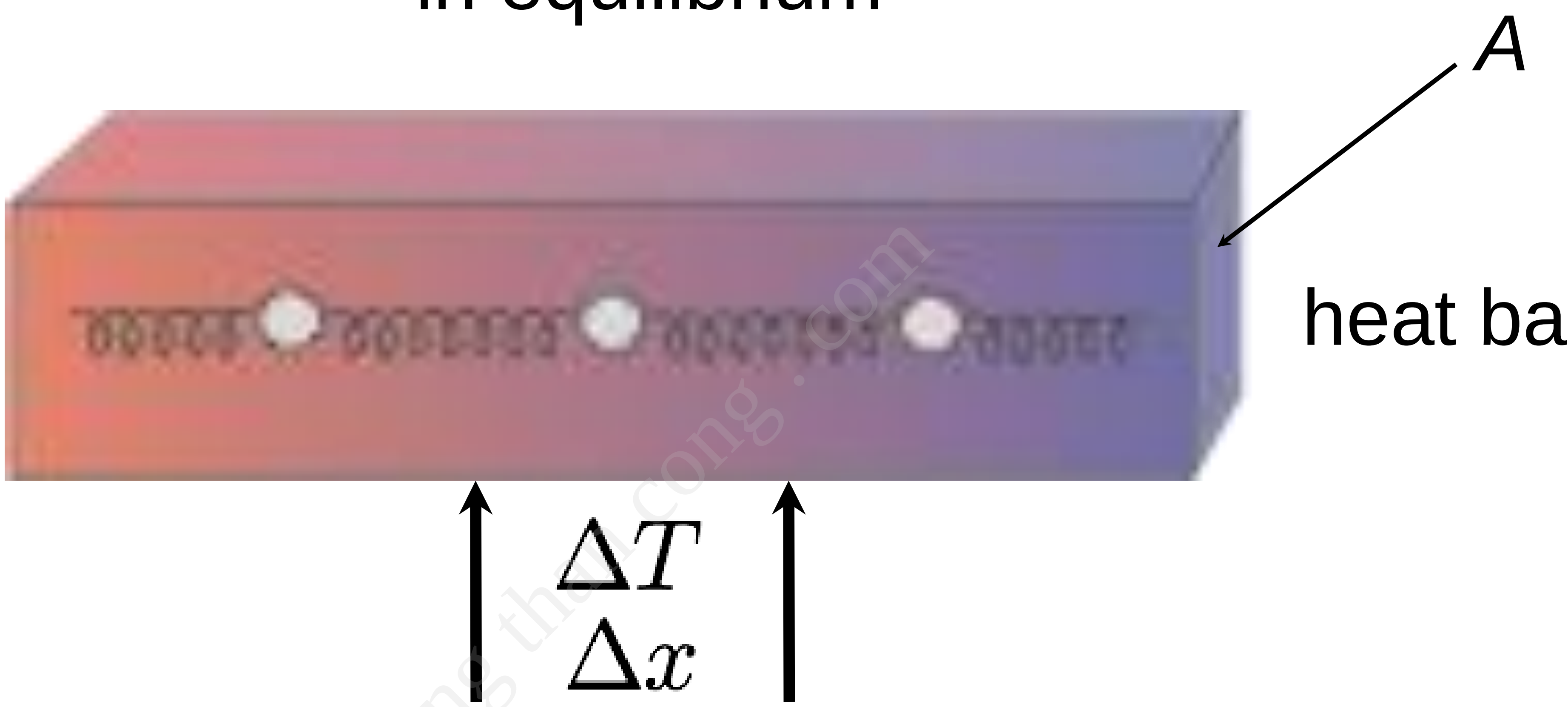
Limits of the Debye model



$$g(\omega)d\omega = \frac{dN}{d\omega}d\omega = \frac{\omega^2 V}{2\pi^2 \nu^3}d\omega$$

Thermal conduction

in equilibrium



A

heating $\frac{\partial Q}{\partial t}$

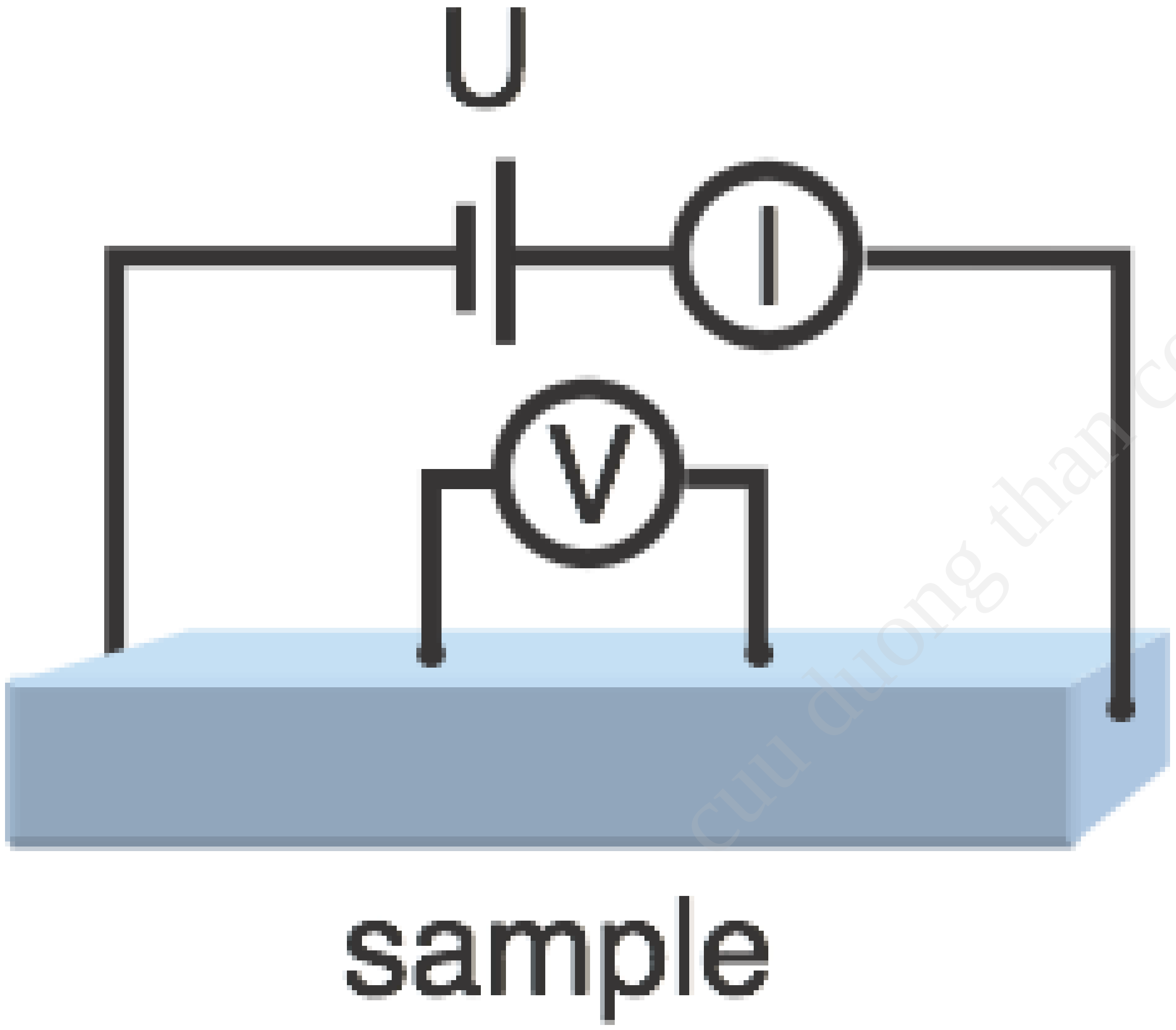
heat bath T

$\frac{\Delta T}{\Delta x}$

thermal conductivity $\kappa = \frac{1}{A}\frac{\partial Q}{\partial t}\frac{\Delta x}{\Delta T}$

$$\frac{1}{A}\frac{\partial Q}{\partial t} = \kappa\frac{\Delta T}{\Delta x}$$

How to measure the conductivity / resistivity



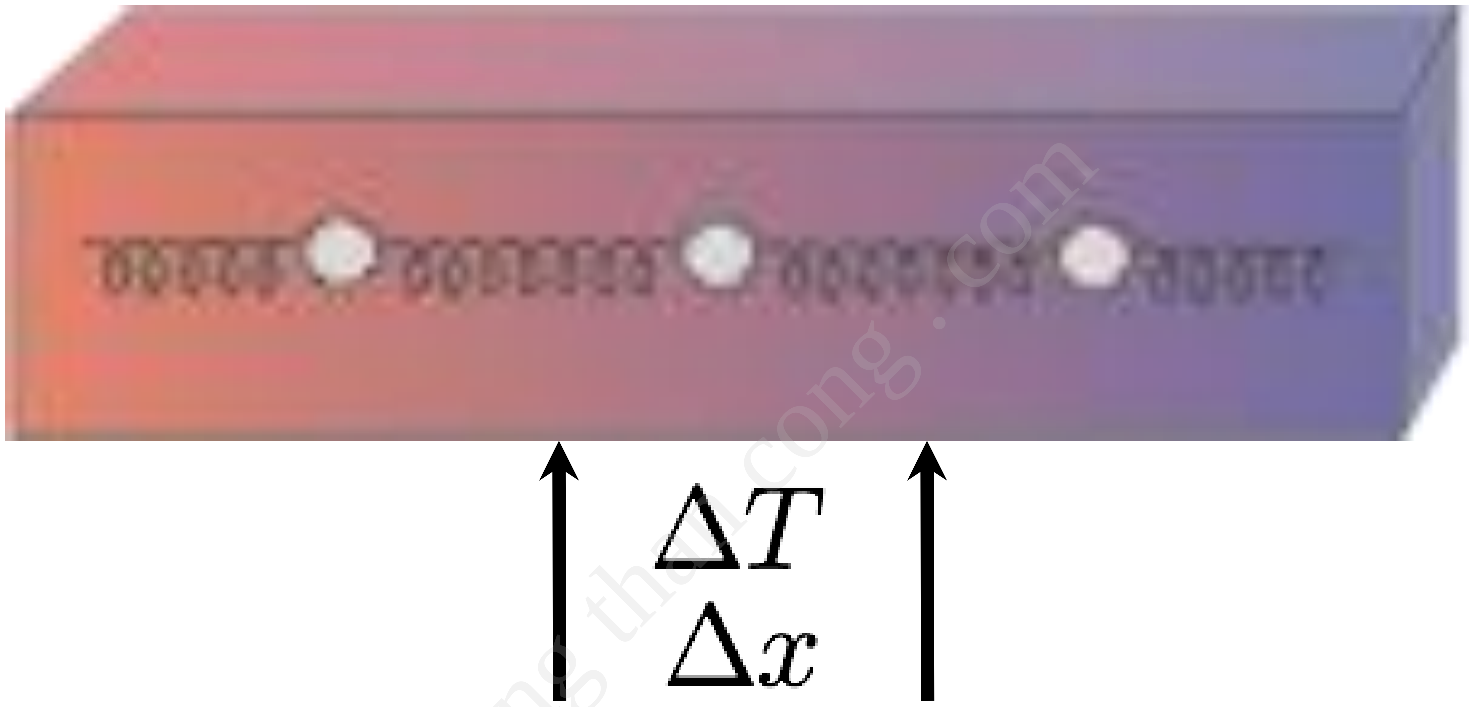
$$\sigma = \frac{j}{E} = \frac{I}{A}\frac{d}{U}$$

dimension $\frac{1}{\Omega m}$

Thermal conduction

in equilibrium

heating $\frac{\partial Q}{\partial t}$



heat bath T

$$\frac{\Delta T}{\Delta x}$$

current density

$$\kappa = \frac{1}{A}\frac{\partial Q}{\partial t}\frac{\Delta x}{\Delta T}$$

1/field

$$\kappa = \kappa_p + \kappa_e$$

electrical

$$\sigma = \frac{j}{E} = \frac{I}{A}\frac{d}{U}$$

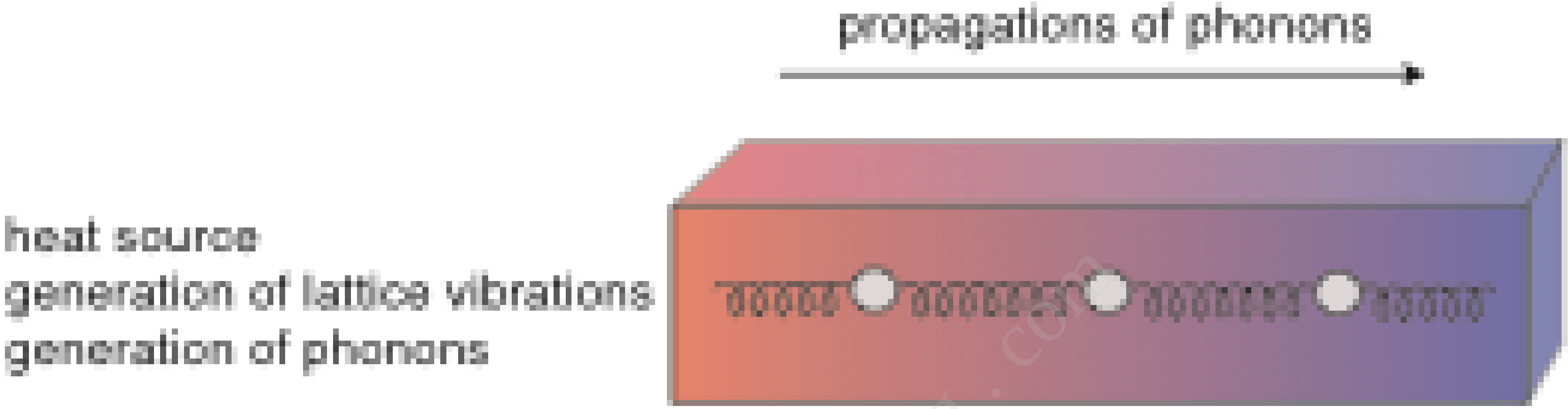
Thermal conduction (at room temperature)

$$\kappa = \kappa_p + \kappa_e$$

- Not only the electrons are important.
- A few insulators are also found to be good thermal conductors.
- The range of electrical conductivity of materials is much bigger than the range of thermal conductivity (24 vs 5 orders of magnitude)

	κ ($Wm^{-1} K^{-1}$)
diamond	2000
copper	400
gold	310
aluminium	230
silicon	160
sodium	140
glass	1.0
polystyrene	0.02

Thermal conduction by phonons



heat capacity

mean free path of phonons

$$\kappa_p = \frac{1}{3} c_v \lambda_p v_p$$

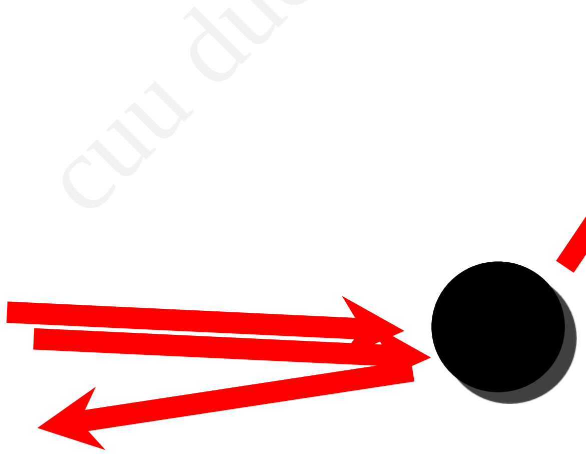
phonon (i.e. sound) speed

Thermal conduction by phonons

$$\kappa_p = \frac{1}{3} c_v \lambda_p v_p$$

at any temperature the mean free path is limited by

- scattering from defects or impurities
- scattering from the sample boundaries



Thermal conduction by phonons

$$\kappa_p = \frac{1}{3} c_v \lambda_p v_p$$

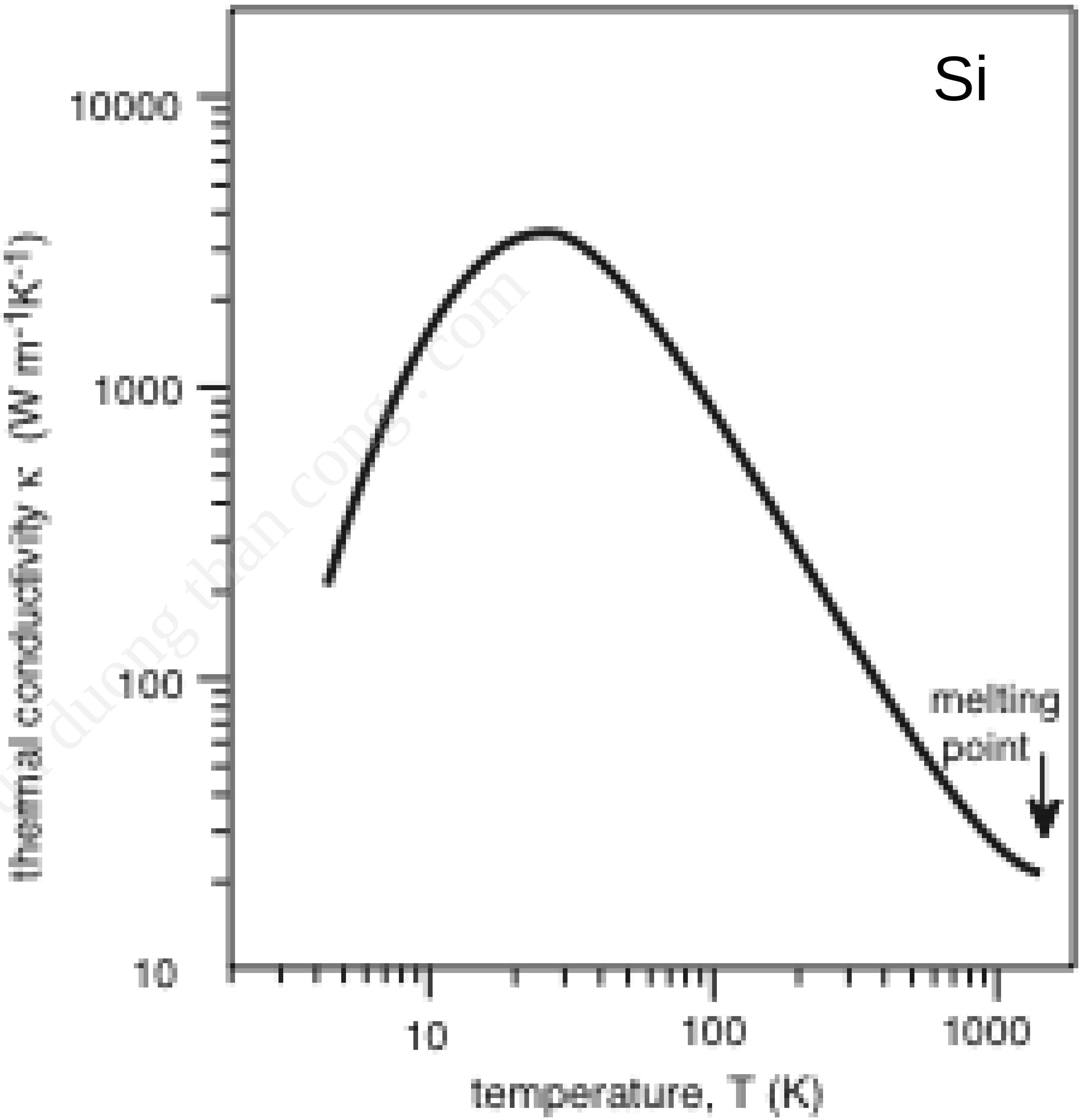
at high temperature the mean free path is limited by

- scattering from other phonons (but this is strictly spoken an anharmonic effect).

Thermal conduction by phonons

$$\kappa_p = \frac{1}{3} c_v \lambda_p v_p$$

- the mean free path decreases at high T
- the heat capacity decreases at low T
- there is a maximum in the conductivity at about 10% of θ_D



Thermal expansion

Thermal expansion

volume expansion

$$\alpha_V = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

linear expansion

$$\alpha = \frac{1}{L_0}\frac{\partial L}{\partial T}$$

$$L = L_0(1 + \alpha\Delta T)$$

$$\alpha = \frac{1}{3}\alpha_V$$

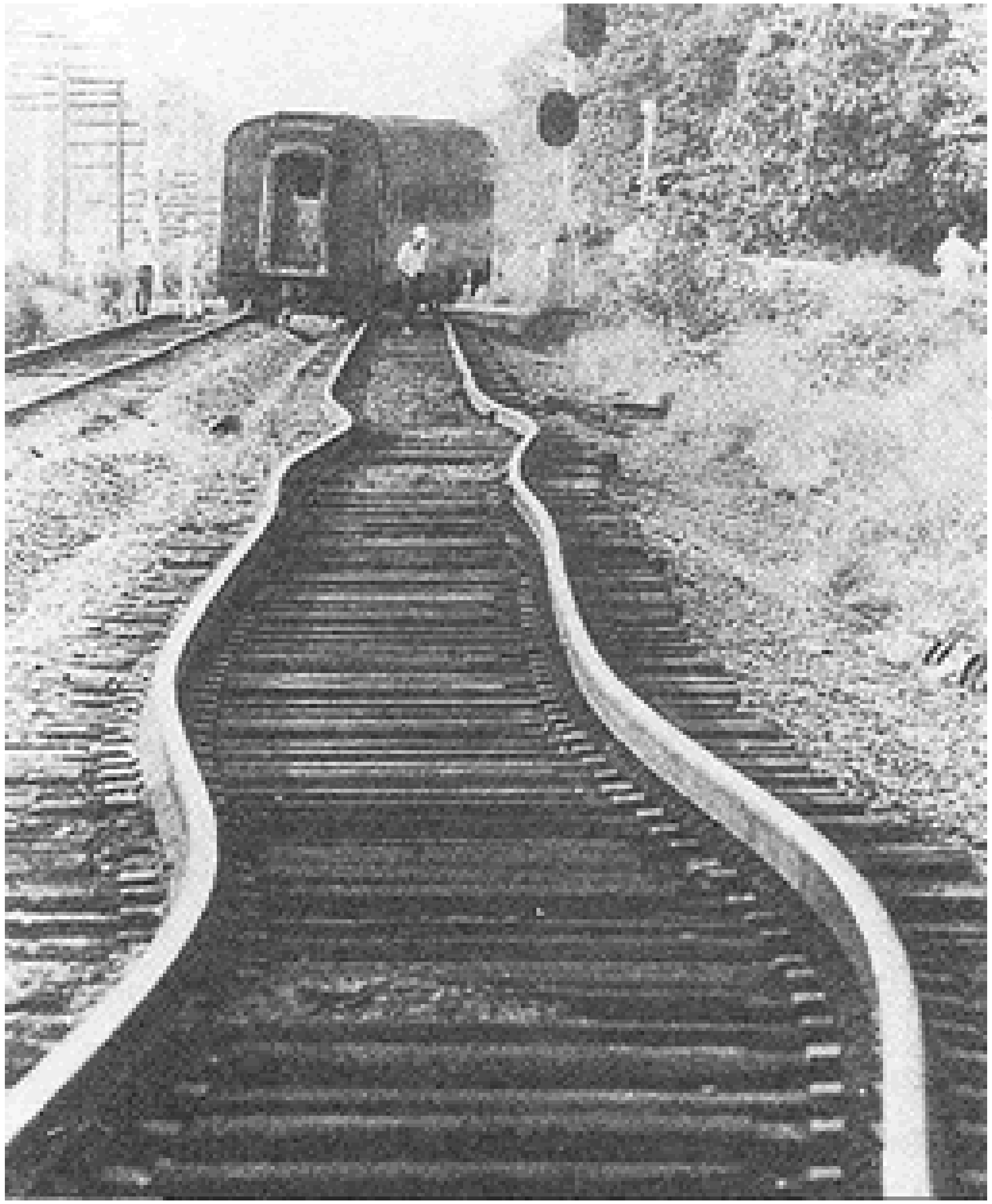
	α (10^{-5} K^{-1})
Lead	2.9
Aluminium	2.4
Brass	1.9
Copper	1.7
Steel	1.1
Glass	0.9
diamond	0.12
Invar	0.09

(at room temperature)

- α is temperature-dependent and vanishes at T=0.

Thermal expansion: examples

not so smart design

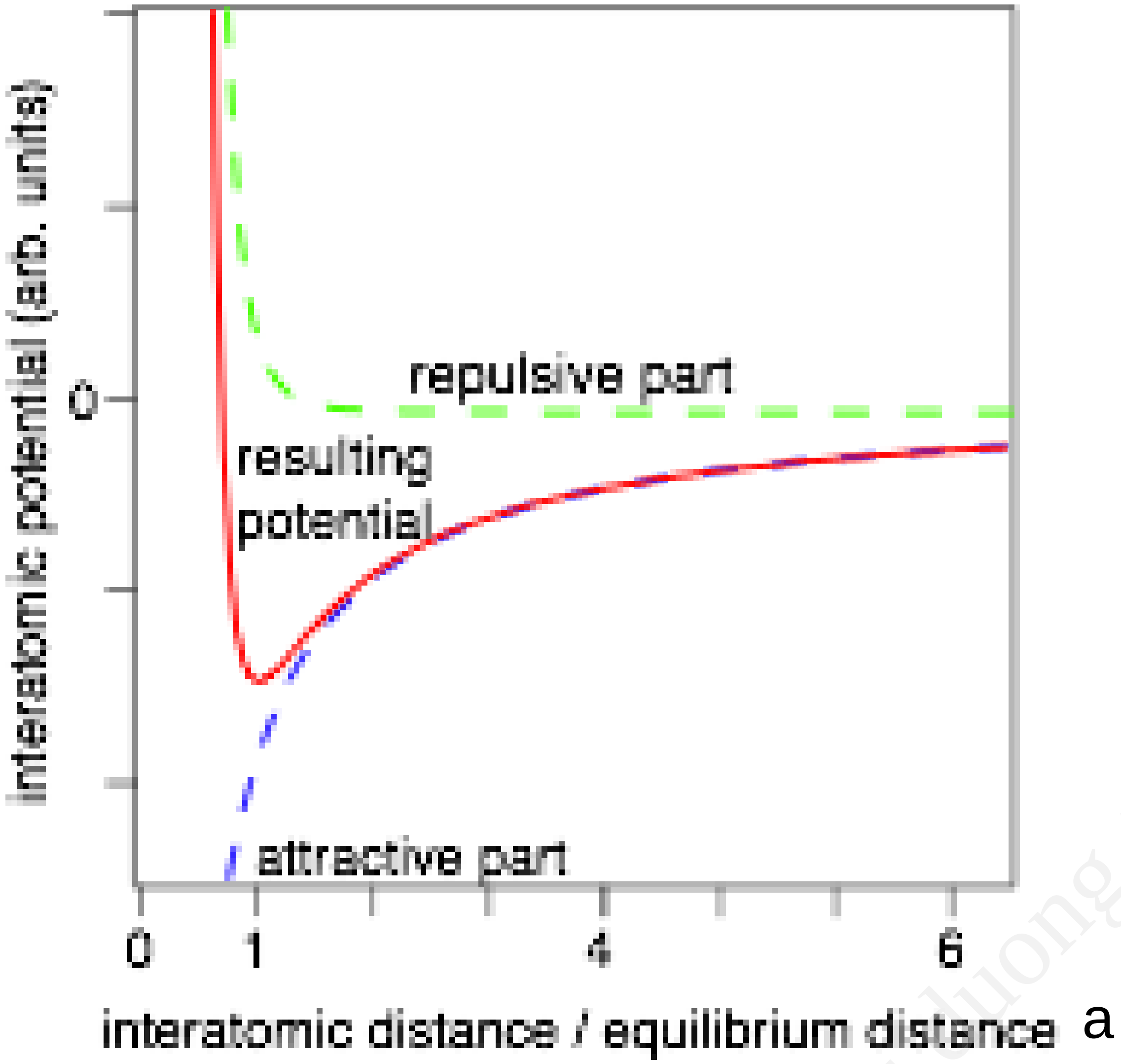


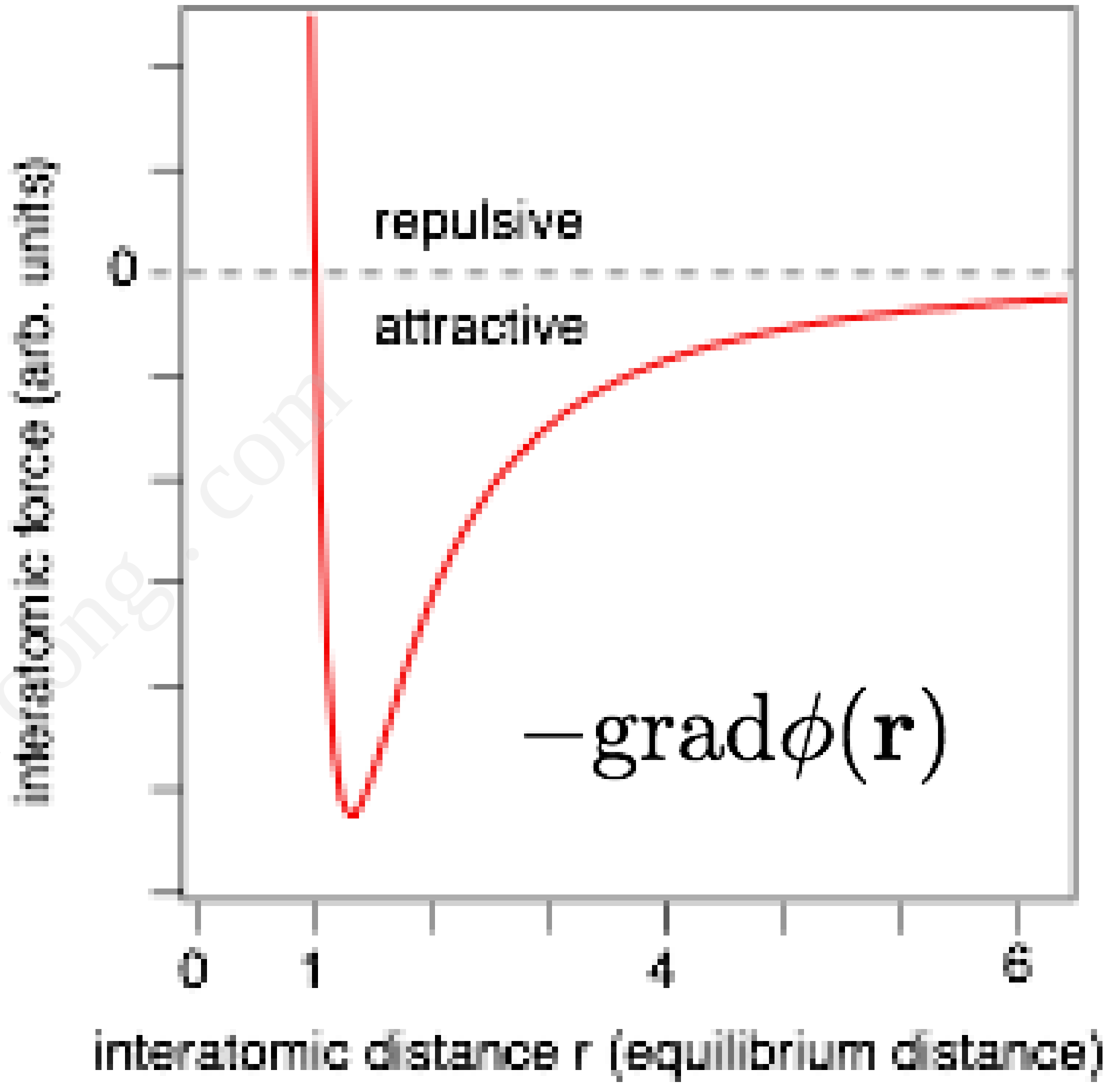
better design

Invar

- Invar is a 63% NiFe alloy with the lowest coefficient of thermal expansion of all metallic compounds.
- Commonly used in thermostats, thermal switches, precision instruments...
- Nobel prize to Charles-Edouard Guillaume, 1920.

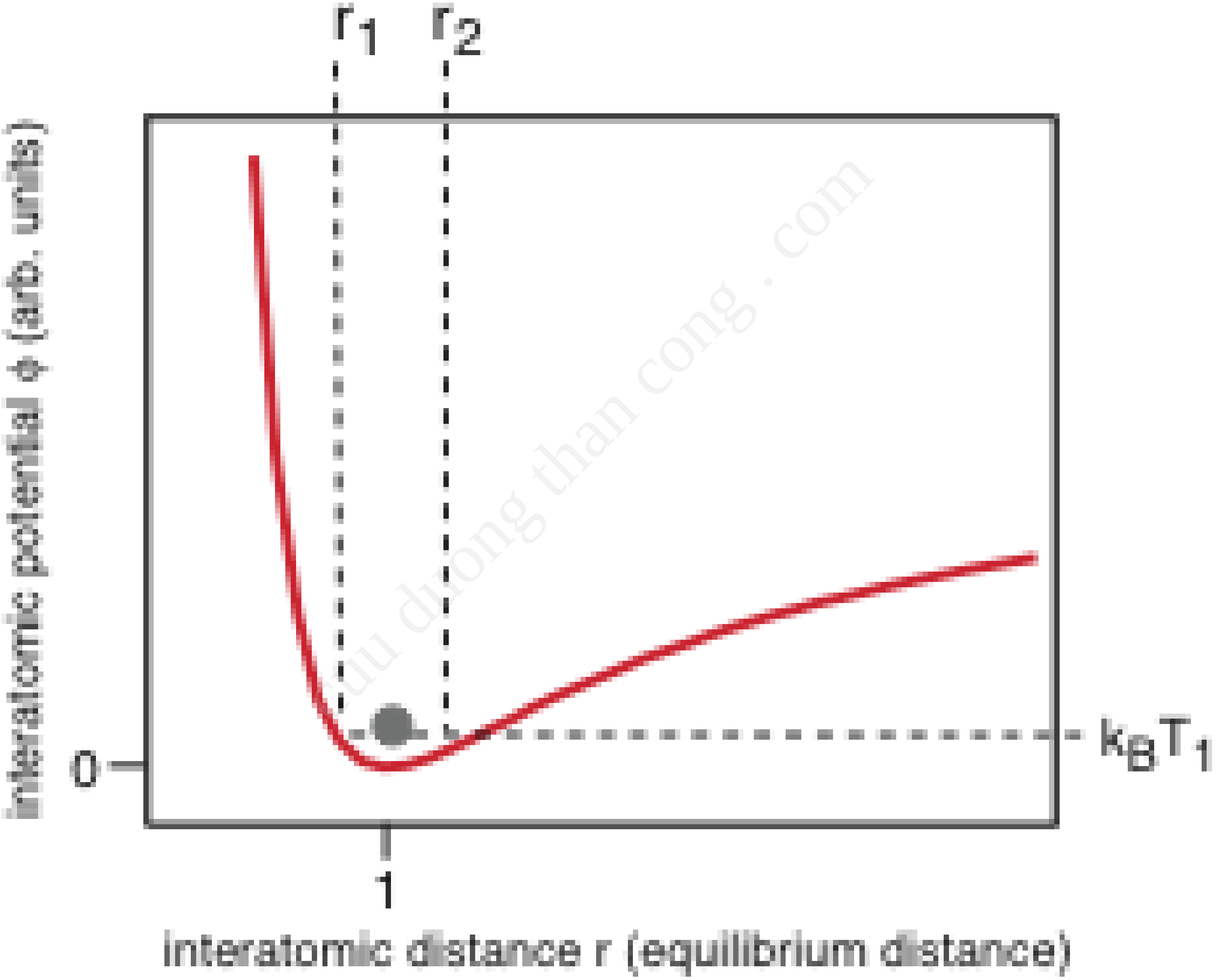
Lattice vibratons



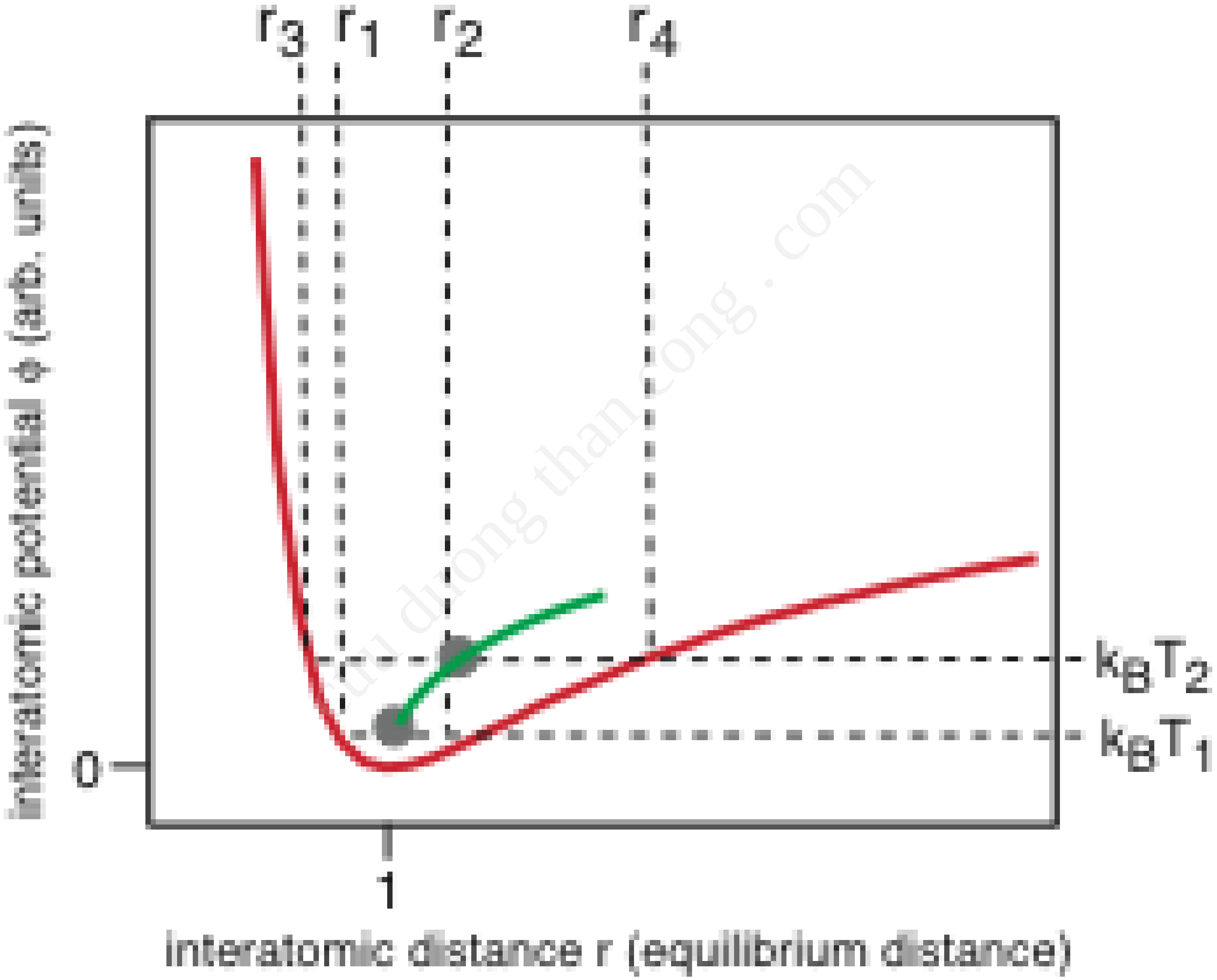


$$\phi(x) = \underbrace{\phi(a)}_{\text{energy offset}} + \underbrace{\frac{d\phi(a)}{dx}}_{=0}(x-a) + \underbrace{\frac{1}{2}\frac{d^2\phi(a)}{dx^2}}_{\text{harmonic potential linear force.}}(x-a)^2 + \underbrace{\frac{1}{6}\frac{d^3\phi(a)}{dx^3}(x-a)^3}_{\text{first anharmonic term}} + \ldots$$

Thermal expansion on the atomic scale (classical)



Thermal expansion on the atomic scale (classical)



Thermal expansion on an atomic scale

- The bottom line: for the harmonic solid, there is no thermal expansion. Thermal expansion is caused by anharmonicity.
- For a quantum treatment, we get the same qualitative result.
- The shallower the interatomic potential, the more anharmonic effects are expected.

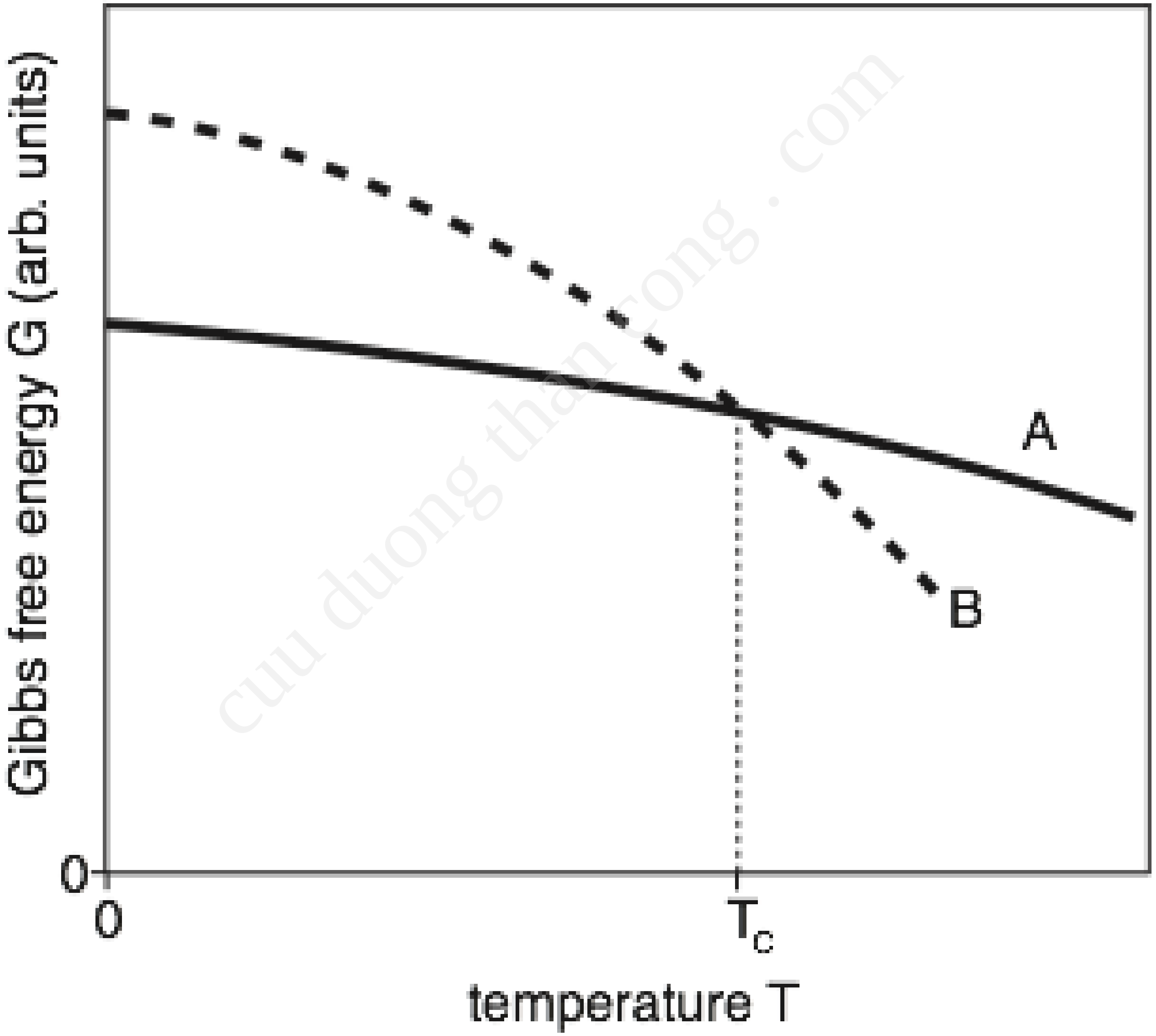
Allotropic phase transitions

- phase transition from one solid phase to another solid phase.
- transitions involving latent heat (first order phase transitions) with a singularity in the heat capacity.
- ultimate reason: minimum in the free energy (for constant T,V,N) and more practically the Gibbs free energy (for constant T,P,N).

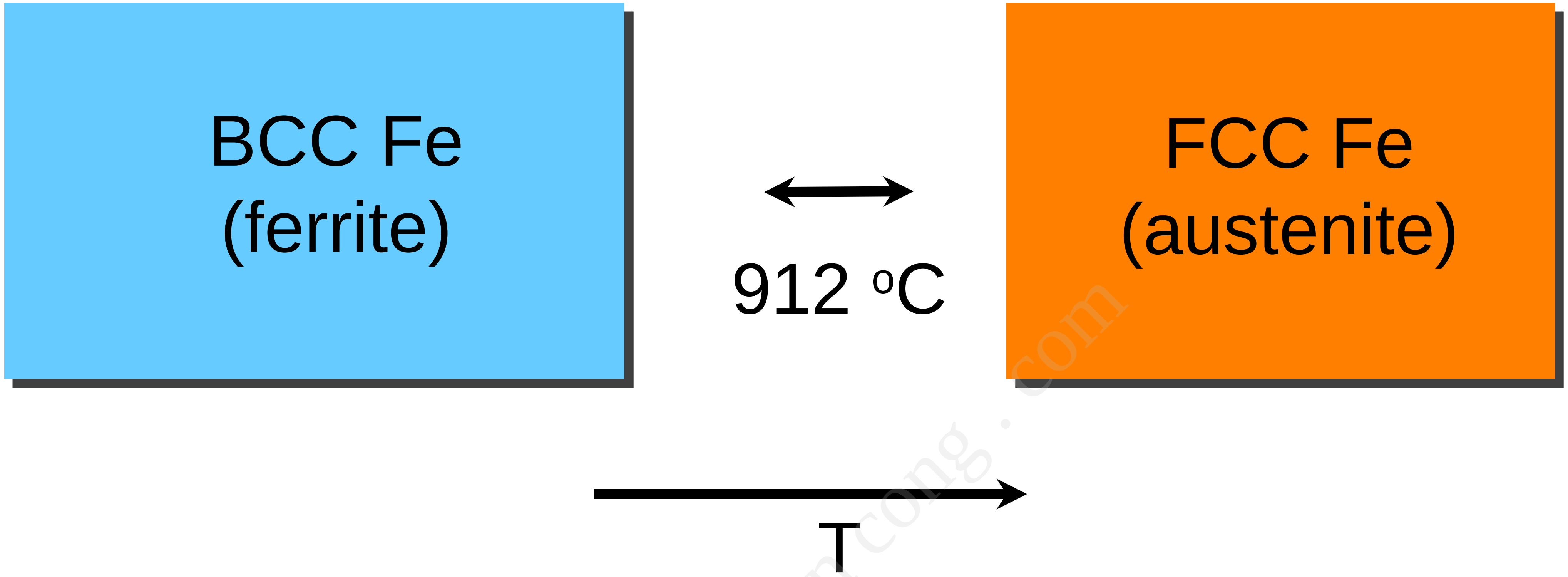
$$F = U - TS \qquad dF = -SdT - PdV + \mu dN$$

$$G = U + PV - TS \qquad dG = -SdT + VdP + \mu dN$$

Allotropic phase transitions



Allotropic phase transitions: example I



BCC Fe
(ferrite)

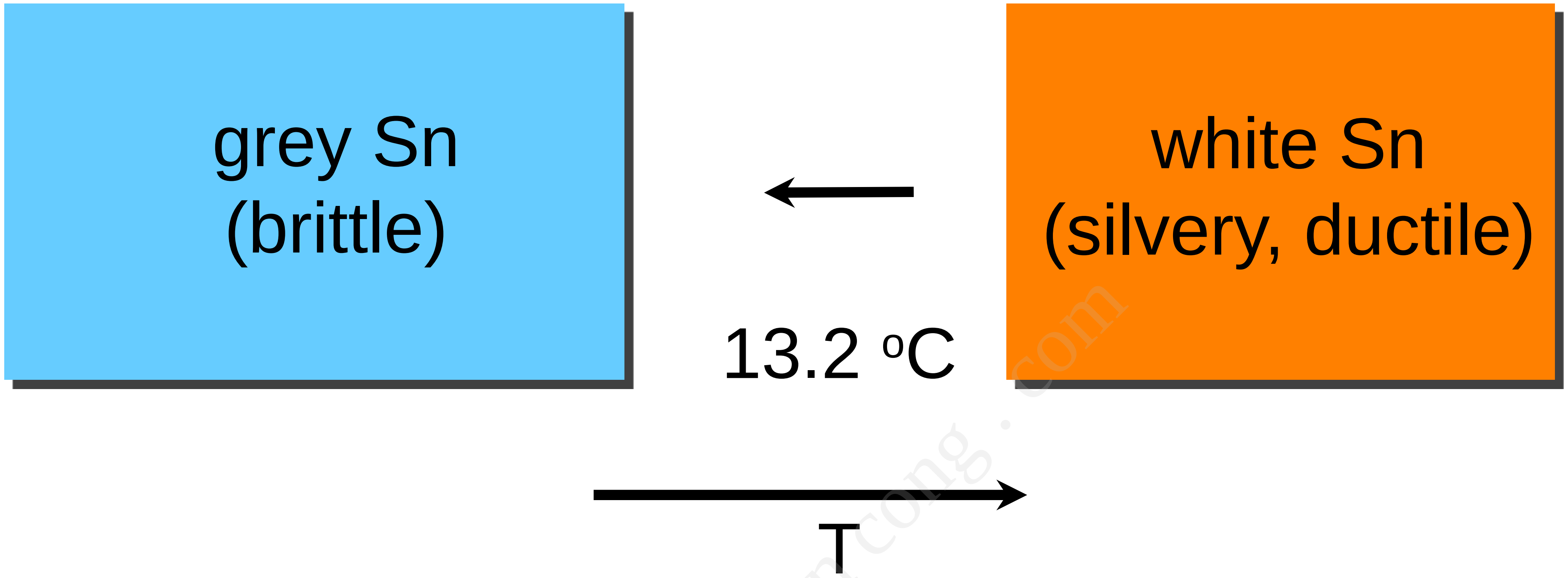
912 ^{o}C

FCC Fe
(austenite)

T

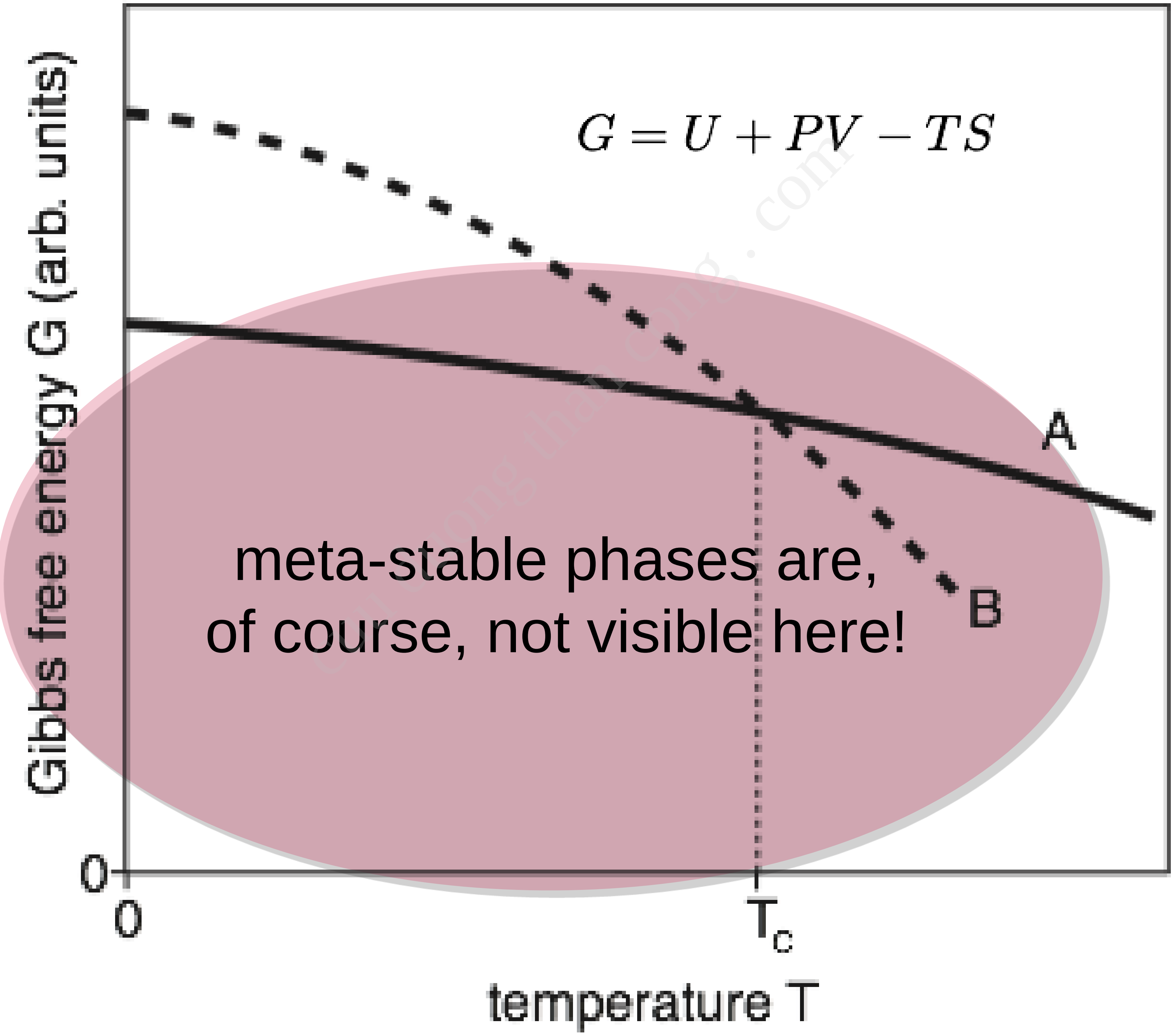
- In the fcc phase, a small amount of carbon atoms can be put into the interstitial positions (C radius is 61% of Fe radius)
- in the bcc phase this is not possible. The re-distribution of C while cooling affects the strength of the steel (influenced by cooling rate)

Allotropic phase transitions: example II



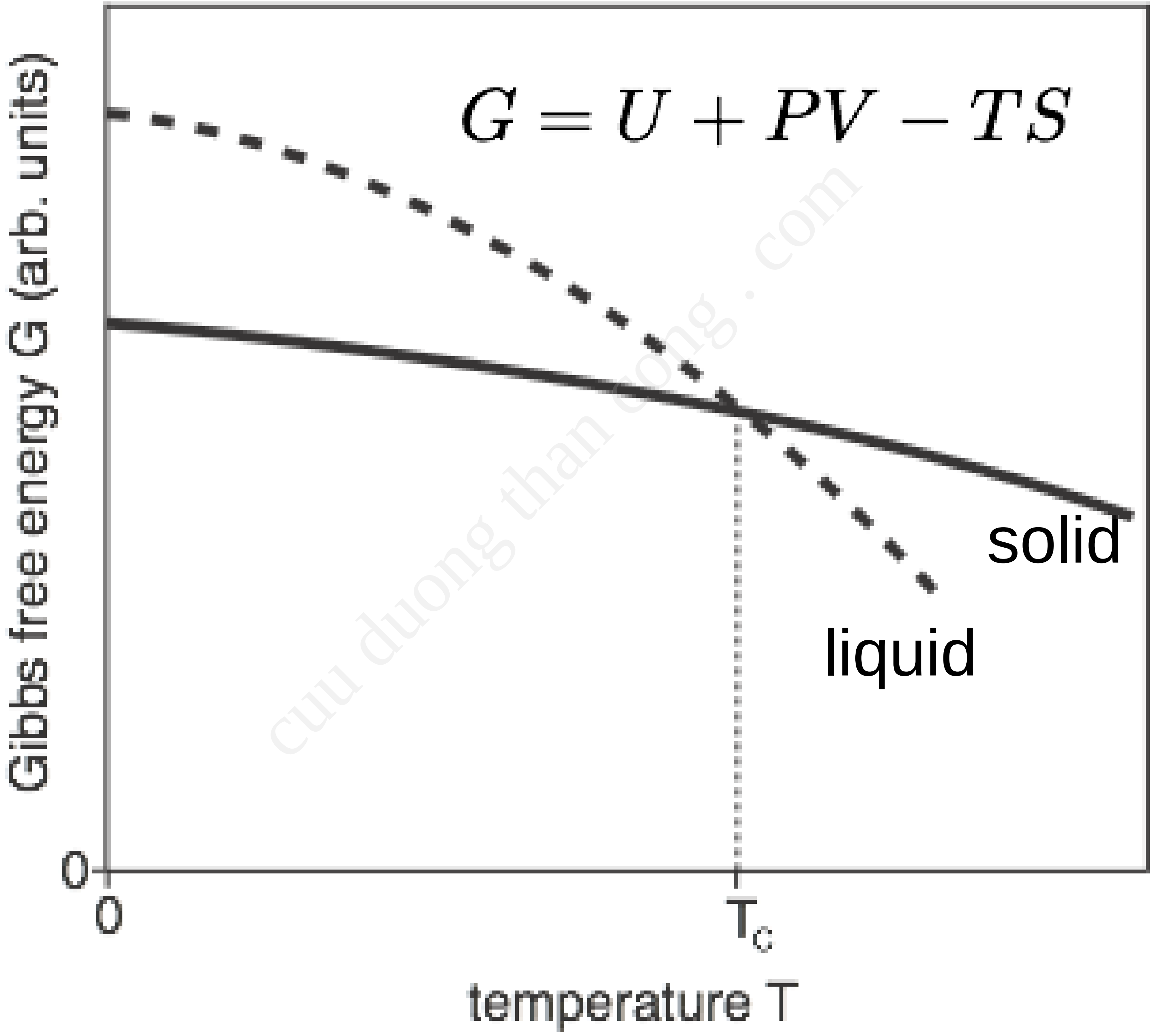
- The transition temperature can be lower for none-pure samples.
- The transition is auto-catalytic.
- Problems for organ pipes in nordic countries (tin pest).
- ...and polar expeditions.
- The problem can be avoided by alloying Sb, Bi or Pb into Sn.

Allotropic phase transitions



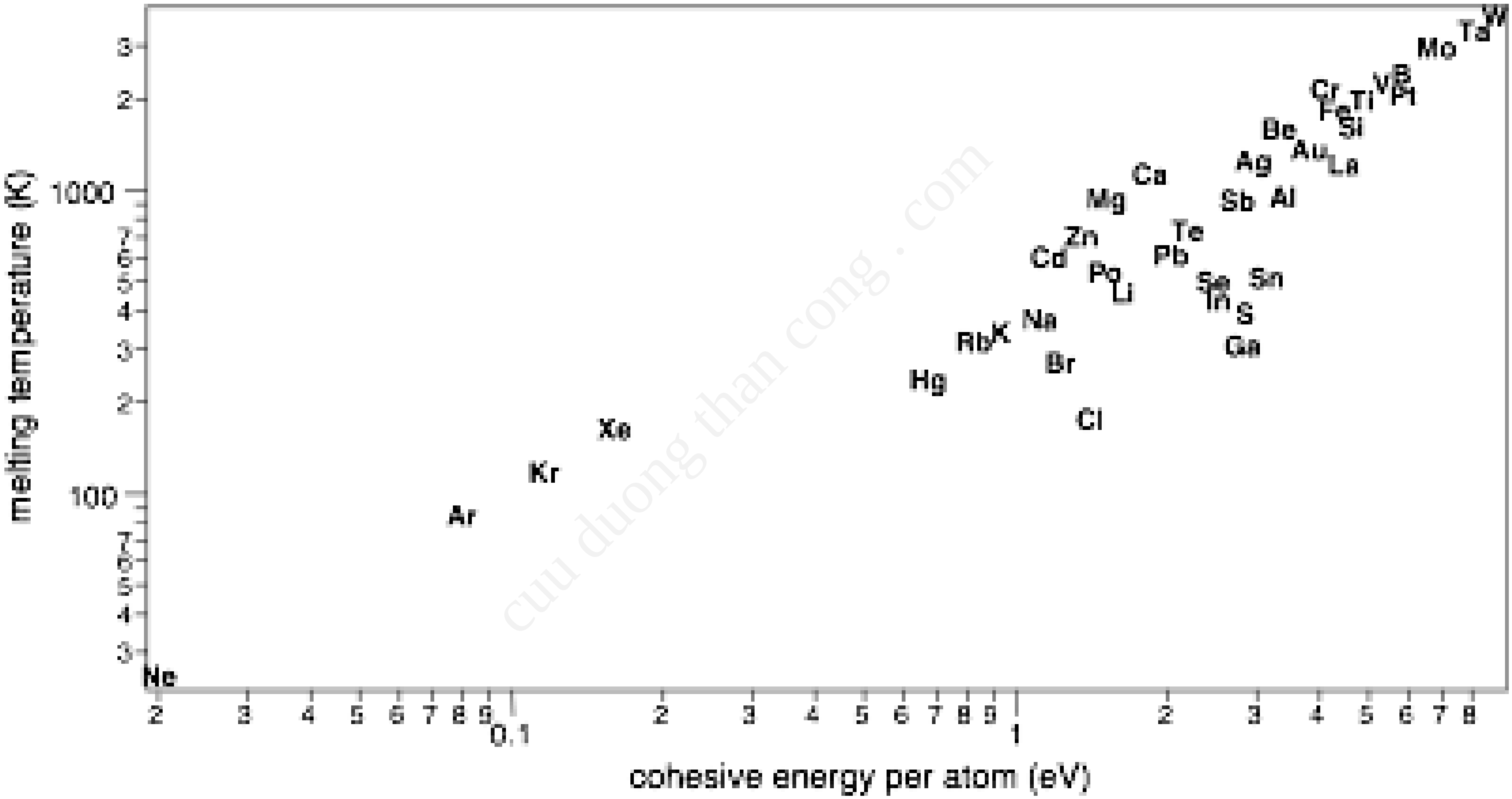
meta-stable phases are,
of course, not visible here!

Melting



$G = U + PV - TS$
solid
liquid
Gibbs free energy G (arb. units)
0
0
T_C
temperature T

Melting temperature and cohesive energy



Lindemann criterion (F. Lindemann, 1911)

The crystal melts when the vibrational amplitude reaches some fraction of the interatomic spacing (e.g. 5% or so).

$$x_{\max} = \left(\frac{2k_BT}{\gamma}\right)^{1/2}$$

$$T_m = \frac{x_{\max}^2\gamma}{2k_B}$$

$$T_m = \frac{(0.05a)^2\gamma}{2k_B} = \frac{(0.05a)^2\omega^2 M}{2k_B}$$

with $\omega = \sqrt{\frac{\gamma}{M}}$.

$$T_m = \frac{(0.05a)^2\Theta_D^2 k_B M}{2\hbar^2}$$

with $\hbar\omega = k_B\Theta_D$

Lindemann criterion (F. Lindemann, 1911)

$$T_m = \frac{(0.05a)^2 \Theta_D^2 k_B M}{2\hbar^2}$$