F. **Density of states (DOS) for phonons**

— **Density of normal modes $D(\omega)$**

$$\boxed{\begin{array}{l} D(\omega)\,d\omega = \text{number of normal modes} \\ \quad \text{with angular frequency in the} \\ \quad \text{interval from } \omega \text{ to } \omega + d\omega \\ \quad (\text{include contributions from all branches}) \end{array}}$$

**Idea:** $\displaystyle \sum_{\vec{q}}^{3} \sum_{\vec{q}} (\cdots) \rightarrow \sum_{s}^{branch} \int \frac{V}{(2\pi)^3} d^3\vec{q}\,(\cdots) \rightarrow \int_0^\infty \underbrace{D(\omega)}_{\substack{\text{density of normal} \\ \text{modes}}} (\cdots)\,d\omega$

**Note:**
$\begin{cases} \text{For } \omega \text{ where there is no normal mode,} \\ \quad D(\omega) = 0 \end{cases}$

**Idea!**



$\omega(\vec{q}) \rightarrow \omega_{max}$

$D(\omega) \rightarrow D(\omega) = 0$ for $\omega > \omega_{max}$

# of allowed $\vec{q}$'s $= D(\omega)d\omega$

$\displaystyle \int_0^\infty D(\omega)\,d\omega = \begin{array}{c} \text{Total number} \\ \text{of normal modes} \end{array} = \underbrace{3}_{\substack{\text{number} \\ \text{of branches}}} \underbrace{p}_{\substack{p \text{ basis} \\ \text{atoms}}} \underbrace{N}_{\text{\# atoms}}$
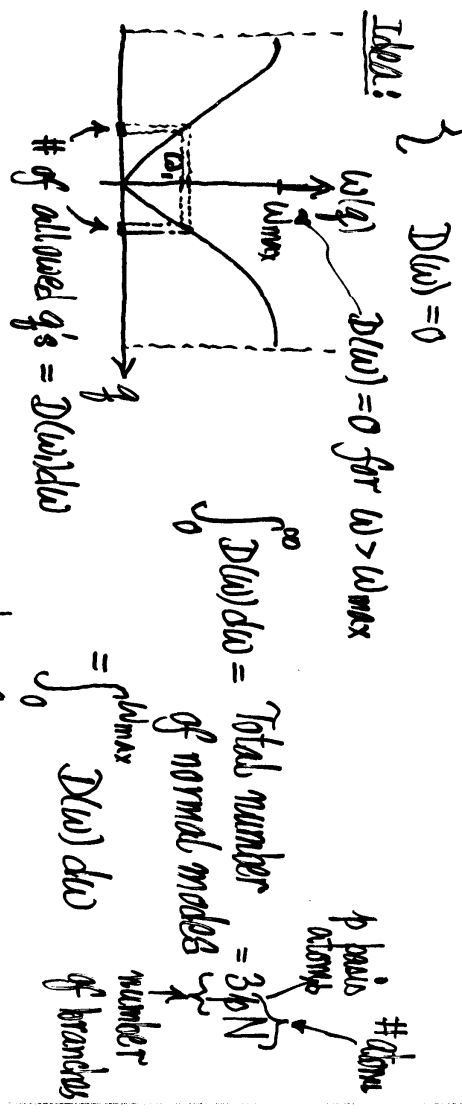
$\displaystyle = \int_0^{\omega_{max}} D(\omega)\,d\omega$

where for $\omega > \omega_{max}$,
there is no normal mode.

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$\boxed{\begin{array}{l} \text{If we consider only acoustic branches, there are} \\ 3N \text{ modes and } \displaystyle\int_0^{\omega_{max}} D_{acoustic}(\omega)\,d\omega = 3N. \quad \square \end{array}}$

In terms of $D(\omega)$,

$$\boxed{U = U_0 + \int_0^\infty \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\,D(\omega)\,d\omega} \quad \begin{array}{l}\text{due to}\\ \text{lattice}\\ \text{vibration}\end{array}$$

■ $T$-dependence in $\beta$

$$\therefore C_{vib} = k\int_0^\infty \left(\frac{\beta\hbar\omega}{e^{\beta\hbar\omega}-1}\right)^2 e^{\beta\hbar\omega}\,D(\omega)\,d\omega$$

Thus, a detailed calculation involves:
(i) find $\omega_s(\vec{q})$ ; (ii) find $D(\omega)$ ; (iii) calculate $C_{vib}$.

**High temperature limit:** $\beta\hbar\omega \ll 1$ for all $\omega$ with $D(\omega) \neq 0$
i.e. $kT \gg \hbar\omega_{max}$ $\qquad$ each mode contributes $k$

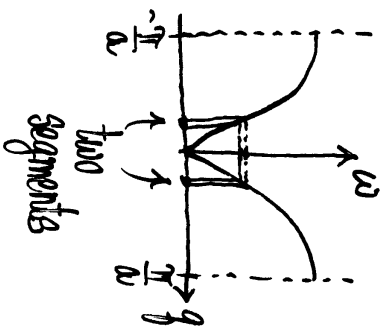then $\quad C_{vib} \approx k\int_0^\infty D(\omega)\,d\omega = k\int_0^{\omega_{max}} D(\omega)\,d\omega = k\cdot 3\underbrace{N^\circ}_{N^\circ = pN}$

$\therefore C_{vib} \sim 3N^\circ k$ $\qquad \begin{array}{l}\text{total number}\\ \text{of atoms}\end{array}$

this is called the **Dulong and Petit's law**
(equipartition theorem)

## E.g.: D(ω) for 1D monatomic chain (1 branch)

Recall: $\omega(q) = \sqrt{\dfrac{4K}{m}}\,\left|\sin\dfrac{qa}{2}\right|$   (thus $\omega_{max} = \sqrt{\dfrac{4K}{m}}$)

Recall: Each $q$ occupies $\left(\dfrac{2\pi}{L}\right)$ reciprocal space

$-\frac{\pi}{a}$ ← two segments → $\frac{\pi}{a}$  (ω vs q)

$$\therefore \sum_{q \text{ in } FBZ}(\cdots) \to \int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\left(\frac{L}{2\pi}\right) dq\,(\cdots)$$

$$\boxed{= \frac{L}{2\pi} = \text{DOS in } q\text{-space (1D)}}$$
  (a uniform DOS)
  = # allowed $q$-values per unit "length" of reciprocal space  (a constant)

If we restrict $q$ to __positive values__†, then

$$\int_{-\frac{\pi}{a}}^{\frac{\pi}{a}}\frac{L}{2\pi}(\cdots)\,dq = \int_{0}^{\frac{\pi}{a}}\frac{L}{\pi}(\cdots)\,dq = \int_{0}^{\omega_{max}}(\cdots)\,\underbrace{\frac{L}{\pi}\frac{1}{\left|\frac{d\omega}{dq}\right|}}_{\substack{\text{Here,} \\ \text{we} \\ \text{need} \\ D(\omega)}}\,d\omega$$

  from $dq$ to $d\omega$

For 1D chain,
$$D(\omega) = \frac{L}{\pi}\frac{1}{\left|\frac{d\omega}{dq}\right|} = \frac{2L}{\pi a}\frac{1}{\sqrt{\omega_{max}^{2}-\omega^{2}}}$$

$D(\omega)$ vs $\omega$,  Area $= N = \dfrac{L}{a}$,  $\omega_{max}$

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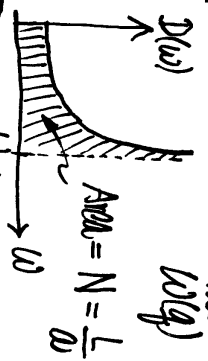
† This step is to prepare for treating 2D/3D cases. In 2D/3D, we use polar and spherical coordinates, and $q = |\vec{q}|$ is positive.

## Summarizing the steps in 1D:

$$D(\omega)\,d\omega = \frac{1}{2\pi}\,dq \cdot 2 \quad \leftarrow \text{two segments}$$
  ← need to know $\left(\dfrac{L}{2\pi}\right)$ as DOS in $q$-space (1D)

$$D(\omega) = \frac{L}{\pi}\frac{1}{\left|\frac{d\omega}{dq}\right|}$$
  ← transform RHS to involve $\omega$ instead of $q$
  ← need dispersion relation $\omega/q$
(by definition positive)

## Debye Approximation: Basic idea

- Low temperatures ⇒ important to _capture_ the small $q$ (small $\hbar\omega$) part of $\omega(q)$

$$\underbrace{\omega(q) \sim v \cdot q}_{\substack{kT \ll \hbar\omega_{optical}}} \quad \text{for small } q \text{ (acoustic branches)}$$

  (optical branches are un-important when $kT \ll \hbar\omega_{optical}$)
  $kT$ can't excite these optical modes

Actual   ≈   Debye Approximation

[graphs: $\omega$ vs $q$ from $-\frac{\pi}{a}$ to $\frac{\pi}{a}$, $\omega_{max}$, $\omega = vq$; Debye Approximation linear, $-q_D$ to $q_D$]

N $q$-values giving N modes per branch
$v = \sqrt{\dfrac{K}{m}}\,a$

← linear all the way
some $q_D$ to be determined
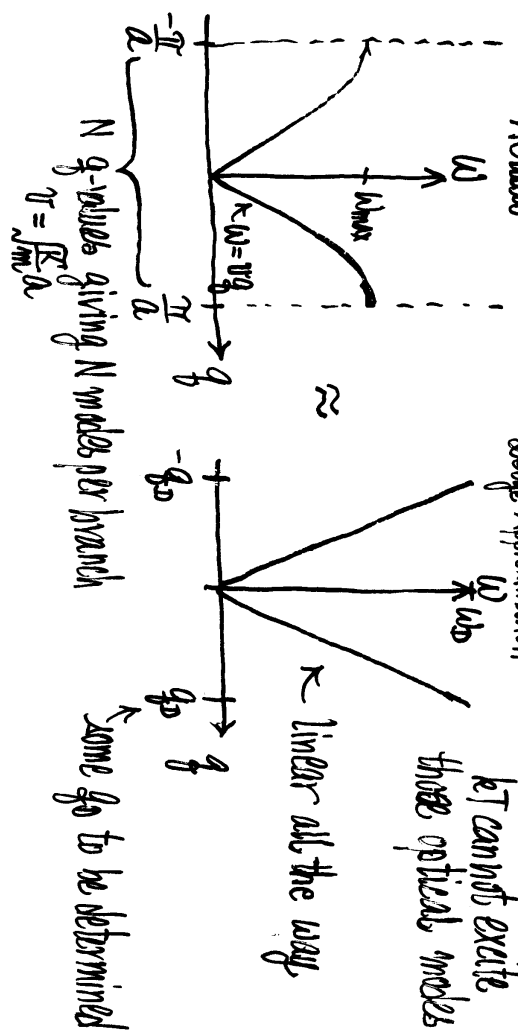
• Approximate $\omega(q)$ by

$$\omega(q) = v \cdot q \quad \text{all the way to some } q_D -$$

$\left.\begin{array}{c}\text{criteria}\\\text{to fix}\\ q_D\end{array}\right.$

so that exactly N modes are covered $\Big\{$ conserve the number of modes in a branch $\Big\}$

• In the 1D chain example,

$$q_0 = \frac{\pi}{a} \quad \text{as there are N modes for } \tfrac{-\pi}{a} q < \tfrac{\pi}{a}.$$

• $\omega_0 =$ Debye frequency
$\quad \equiv$ the highest frequency within the Debye approximation

In the 1D chain example,

$$\omega_D = v \cdot \frac{\pi}{a} = \sqrt{\frac{K}{m}}\, a \cdot \frac{\pi}{a} = \pi\sqrt{\frac{K}{m}} = \frac{\pi}{2}\sqrt{\frac{K}{m}} = \frac{\pi}{2}\omega_{max}$$

• Since $\omega = v \cdot q$, DOS within Debye approximation is:

$$D_{Debye}(\omega) = \frac{L}{\pi}\frac{1}{\left|\frac{d\omega}{dq}\right|} = \frac{1}{\pi}\frac{1}{v} \quad (\text{a constant})$$

• But $\omega_D$ cuts off Debye so that

$$\boxed{\int_0^{\omega_D} D_{Debye}(\omega)\, d\omega = N}$$

this also serves to define $\omega_D$

$D_{Debye}(\omega)$  1D chain
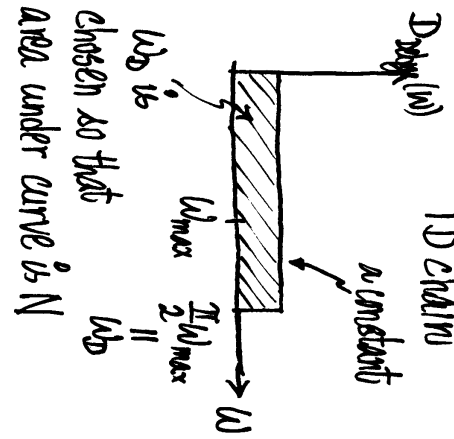


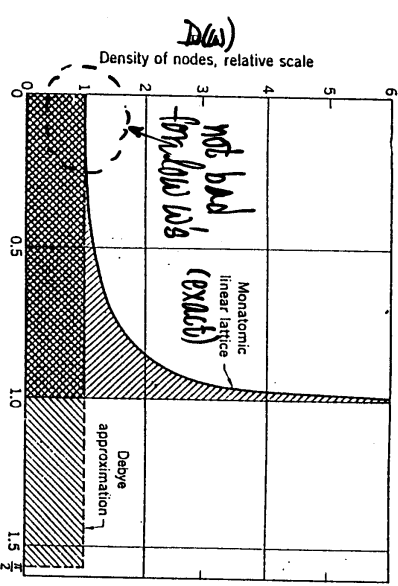$$D_{Debye}(\omega) = \begin{cases} \dfrac{1}{\pi}\dfrac{1}{v} & \omega < \omega_D \\[4pt] 0 & \omega > \omega_D \end{cases} \quad \text{with } \omega_D = \frac{\pi}{2}\omega_{max}$$

Note: Debye approximation in 1D $D(\omega)\sim\omega^0\sim$ constant

• 1D monatomic chain

$\omega_D$ is chosen so that area under curve is N

Same area under curve since the number of normal modes is fixed.



D(ω) — Density of nodes, relative scale

not bad for low ω's

Monatomic linear lattice (exact)

Debye approximation

$\frac{\omega}{\omega_{max}} \longrightarrow$

Density of phonon modes $\mathfrak{D}(\omega)$ for monatomic line of atoms with nearest-neighbor interactions, as compared with the density of modes in the Debye or continuum approximation calculated for the same velocity of sound in the limit of low frequencies. Note that the lattice model has a singularity which is absent in the Debye approximation. The Debye spectrum must be cut off at $\omega_D = \pi\omega_{max}/2$ if the total number of states is to be equal to the number of atoms.

• Note that the approximation is very good for small ω.

• One could carry out a Debye approximation for each acoustic branch.

• Same idea and procedure work for 2D, 3D cases.
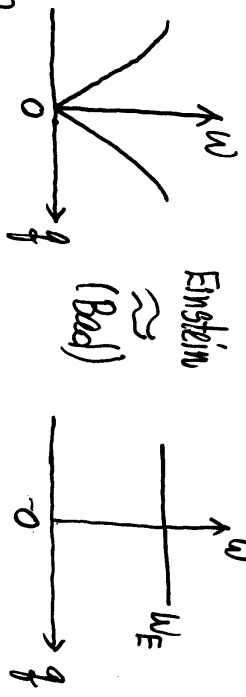
• Let's get some sense out of these!

<u>Einstein model</u>:    quantum nature of oscillators ✓

dispersion relation ✗

C drops to zero as T drops ✓

C drops too fast (bad) ✗

⇒ need to <u>consider dispersion relation</u>,

to do that, we need $D(\omega)$

<u>Physics</u>:



How bad?

Normal mode analysis (invoke lattice vibrational waves)

⇒ a <u>continuous distribution</u> of $\omega(q)$ from

$$\omega = 0 \quad \text{to} \quad \omega = \omega_{max}$$

As T drops, only some oscillators cease to contribute ("frozen"), but those with small $\omega$ can still contribute

⇒ C drops less rapidly with T than in Einstein model.

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• To get some confidence in the approach, let's estimate $\omega_D$ for copper

$$\omega_D \sim v \cdot q \leftarrow \text{largest } q$$

$4759 \text{ ms}^{-1} = \text{sound speed for copper}$

$$\sim v \cdot \frac{\pi}{a} \leftarrow \text{nearest-neighbor spacing}$$

$(\sim 3\text{Å} \leftarrow \text{true for most materials})$

$$\sim 7.9 \times 10^{13} \text{ s}^{-1} \quad \text{(IR frequency)}$$

$$\frac{\hbar \omega_D}{k} = \theta_D = \text{Debye temperature}$$

$$\sim 600 \text{K}$$

so, for $T < \theta_D$, some oscillators cease to contribute to C

[see data in figure on p. VII-17]

⇒ estimate is within reasonable range of data.

G. A general way to get $D(\omega)$ in higher dimensions

Let's say, after some tedious calculations and/or measurements, we obtained the precise $\omega(\vec{q})$ (dispersion relation).

Q: Given $\omega(\vec{q})$, how to get $D(\omega)$?

Since the contributions to $D(\omega)$ can be considered branch by branch, we will consider how to get $D(\omega)$ for a single branch $\omega(\vec{q})$.
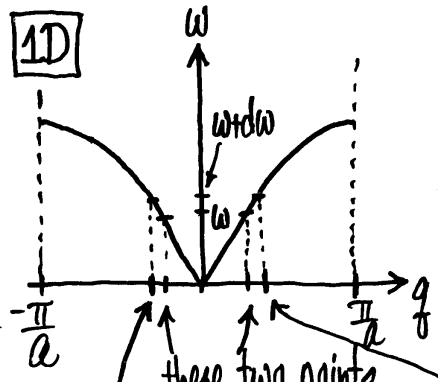
What we want to do is:

$$\sum_s \sum_{\vec{q}} (\cdots) \rightarrow \sum_s \int (\cdots) \frac{V}{(2\pi)^3} d^3q \qquad (3D)$$

and then turn $d^3q$ into an integral over $\omega$.

The idea is best shown by the following procedures+ in getting $D(\omega)$:

    (1) Cut at $\omega$

    (2) Cut at $\omega + d\omega$

    (3) Project on to $q$-space

    (4) Count "modes"

+ Important: When we treat electronic states, we get energy bands $E(\vec{k})$. The same procedure can be used to find $g(E)dE$, the electronic DOS.



1D
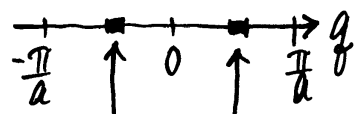
these two points form the constant $\omega$ "surface" for a cut at $\omega$

these two points form the constant $\omega$ "surface" for a cut at $(\omega + d\omega)$

look at $q$-space →



the two segments form the "volume" of $q$-space enclosed by the two constant-$\omega$-surfaces at $\omega$ and $\omega + d\omega$

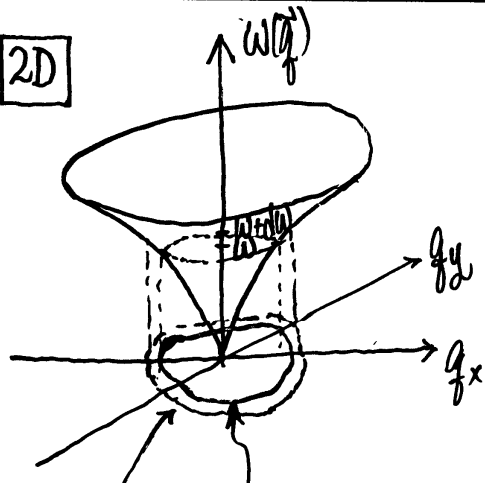Number of modes in the range $\omega$ to $\omega + d\omega = D(\omega)\,d\omega$

$$= \left(\frac{L}{2\pi}\right) \cdot [\text{"volume" between two constant-}\omega\text{-surfaces}]$$

$$= \left(\frac{L}{2\pi}\right) \cdot [\text{"length" of two segments}]$$

• 1D

• $q$-values are uniformly distributed
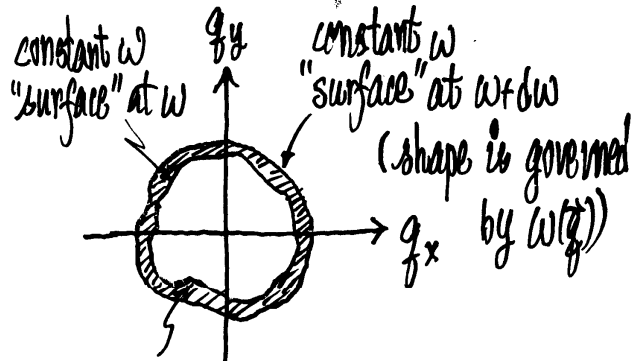
$\omega(\vec{q})$

$q_y$

$q_x$

$\omega + d\omega$

The line forms
the constant-$\omega$ "surface"
for a cut at $\omega$

The line forms the constant-$\omega$ "surface"
for a cut at $\omega + d\omega$

look at $q$-space →

constant $\omega$
"surface" at $\omega$

constant $\omega$
"surface" at $\omega + d\omega$
(shape is governed
by $\omega(\vec{q})$)

$q_y$

$q_x$

the shaded area forms the
"volume" of $q$-space enclosed
by two constant-$\omega$-surfaces
at $\omega$ and $\omega + d\omega$

Number of modes in the range $\omega$ to $\omega + d\omega$
$= D(\omega) d\omega$

$= \dfrac{A}{(2\pi)^2} \cdot$ ["volume" between two constant-$\omega$-surfaces]

$= \dfrac{A}{(2\pi)^2} \cdot$ ["area" of shaded region]

• 2D
• allowed $\vec{q}$s are
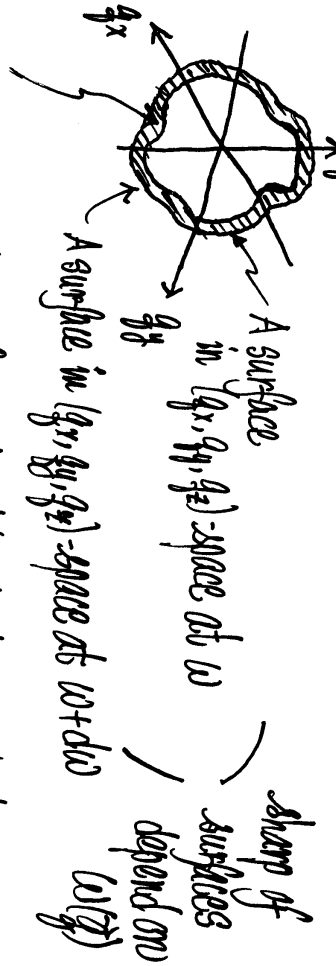uniformly distributed

<u>Constant frequency surface</u>

■ Given $\omega(\vec{q})$ for a branch, the <u>surface in the
reciprocal space</u> on which the $\vec{q}$s on the
surface all correspond to the same $\omega$ is a
<u>constant frequency surface</u>

3D: Need a 4D plot to show $\omega(\vec{q}) = \omega(q_x, q_y, q_z)$
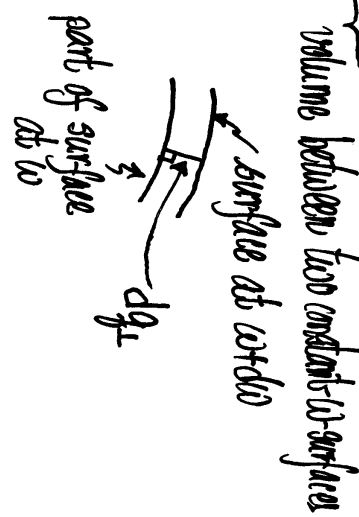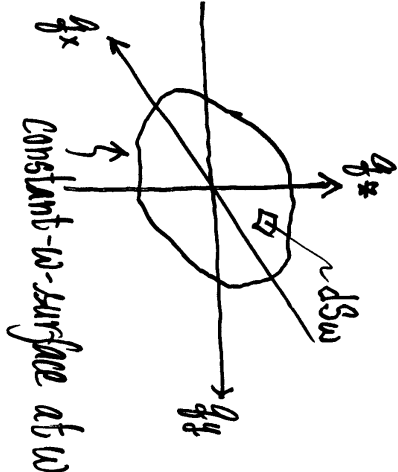
A cut at $\omega$ gives a surface in $q$-space

shape of
surfaces
depend on
$\omega(\vec{q})$

A surface in $(q_x, q_y, q_z)$-space at $\omega$

A surface in $(q_x, q_y, q_z)$-space at $\omega + d\omega$

$q_x$

$q_z$

$q_y$

The shaded <u>volume</u> is enclosed by the two constant-$\omega$-surfaces
at $\omega$ and $\omega + d\omega$ (the volume of the shell between two surfaces)

$D(\omega) d\omega = $ number of modes in the range $\omega$ to $\omega + d\omega$

$= \dfrac{V}{(2\pi)^3} \cdot$ [volume between two constant-$\omega$-surfaces]

$$\therefore\ D(\omega)d\omega = \frac{Y}{(2\pi)^3}\int_{shell} d^3q$$

volume between two constant-ω-surfaces



$q_x$, $q_y$, $q_z$, $dS_\omega$

constant-ω-surface at $\omega$

$dS_\omega$ = an area element on surface

For the volume of the shell, a volume element is of the form



$dS_\omega$ — $dq_\perp$

part of surface at $\omega$

part of surface at $\omega + d\omega$

the volume of the volume element = $dS_\omega\, dq_\perp$

$$\therefore\ \int_{shell} d^3q = \text{Add up volume elements}$$
$$= \oint dS_\omega\, dq_\perp$$

over the surface area of the constant-ω-surface at $\omega$

$$\underbrace{\vec{\nabla}_{\vec{q}}\, \omega(\vec{q})}_{\text{scalar}} = \text{gradient of } \omega \text{ with respect to } \vec{q}$$

a vector

$$\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})$$

$$\therefore\ |\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})| \perp \text{constant-}\omega\text{-surface}$$

$$\therefore\ |\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})|\, dq_\perp = d\omega$$

$$\text{or}\quad dq_\perp = \frac{d\omega}{|\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})|}$$

$$dS_\omega\, dq_\perp = \frac{dS_\omega}{|\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})|}\, d\omega$$

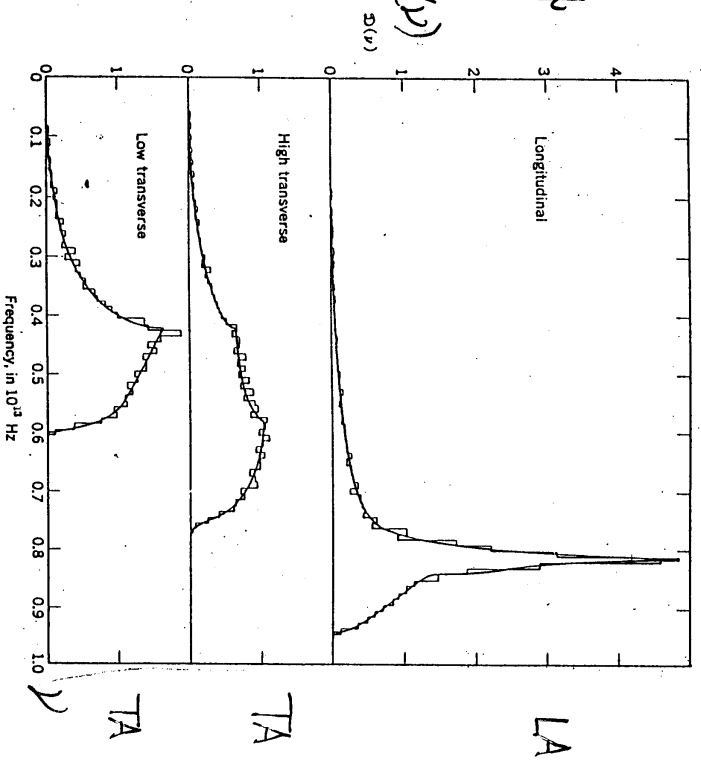$$\therefore\ D(\omega)d\omega = \frac{Y}{(2\pi)^3}\oint \frac{dS_\omega}{|\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})|}\, d\omega \quad \text{for each branch}$$

$$\boxed{D(\omega) = \frac{Y}{(2\pi)^3}\oint \frac{dS_\omega}{|\vec{\nabla}_{\vec{q}}\,\omega(\vec{q})|}}$$

over the surface area (in $\vec{q}$-space) of the constant frequency surface at $\omega$

- Good for a branch
- Total $D(\omega)$ is obtained by summing up all branches
- Realistic/Complicated $\omega(\vec{q})$, $D(\omega)$ can be computed numerically
- Debye approximation, easy to evaluate $D(\omega)$

Numerically obtained
D(ν)

D(ν)



Phonon density o' modes $D(\nu)$ for the three branches of aluminum; here $\nu = \omega/2\pi$. The histograms are obtained from computed frequencies for 2791 wavevectors.
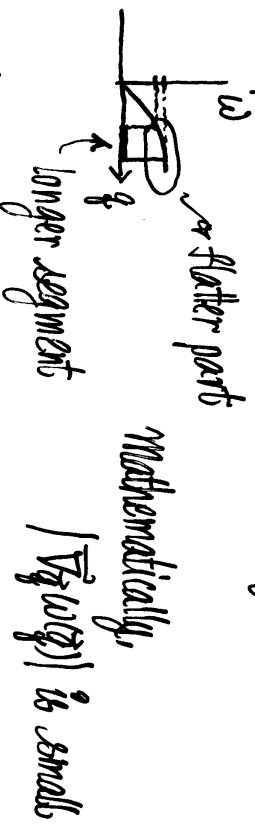
Typical total DOS

Density of modes



Angular frequency ($10^{13}$ rad/s)
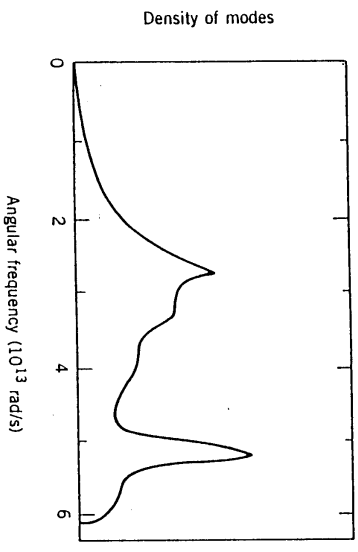
A typical density of modes function. For low frequencies the function is well represented by the Debye approximation, but high-frequency portions show complicated structure.

## Remarks:

• Flat dispersion relation $\Rightarrow D(\omega)$ is large

Mathematically,



flatter part

longer segment

$|\vec{\nabla}_{\vec{q}} \omega(\vec{q})|$ is small

• Note that $\vec{\nabla}_{\vec{q}} \omega(\vec{q}) =$ group velocity $= v_{group}$

in general, not a constant

$\therefore D(\omega) = \dfrac{V}{(2\pi)^3} \oint \dfrac{dS_\omega}{v_g}$

• Concept of $D(\omega)$ is valid even for non-periodic (random) system

e.g. ⌒○⌒○⌒○⌒○⌒○⌒○⌒○⌒

masses are randomly picked from a distribution

• Not periodic $\Rightarrow$ cannot talk about $\omega/q$

• But still can solve $N \times N$ eigenvalue problem $\Rightarrow N \;\omega$'s

∴ Can still find $D(\omega) d\omega = \#$ modes in the interval $\omega$ to $\omega + d\omega$