Thermal Properties of Crystal Lattices

Peter Debye
(1884 – 1966)

The motion of a harmonic crystal can be described by a set of decoupled harmonic oscillators

$$H = \frac{1}{2} \sum_{\mathsf{k},s} |\mathsf{P}_s(\mathsf{k})|^2 + \omega_s^2(\mathsf{k}) \, |\mathsf{Q}_s(\mathsf{k})|^2$$

The occupancy of a given mode is

$$\langle n_s(\mathsf{k}) \rangle = \frac{1}{e^{\beta \omega_s(\mathsf{k})} - 1}$$

- Thermodynamic properties of the ionic lattice
- long-range order in the presence of lattice vibrations

$$
\begin{aligned}
\frac{d}{dt}\langle \mathsf{x}\cdot\mathsf{p}\rangle &= \frac{i}{\hbar}\langle [H,\mathsf{x}\cdot\mathsf{p}]\rangle = \frac{i}{\hbar}\langle H\mathsf{x}\cdot\mathsf{p} - \mathsf{x}\cdot\mathsf{p}H\rangle \\
&= \frac{iE}{\hbar}\langle \mathsf{x}\cdot\mathsf{p} - \mathsf{x}\cdot\mathsf{p}\rangle = 0
\end{aligned}
$$

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

$$
\begin{aligned}
0 &= \left\langle \left[\frac{p^2}{2m} + V(\mathsf{x}), \mathsf{x}\cdot\mathsf{p}\right]\right\rangle \\
&= \left\langle \left[\frac{p^2}{2m}, \mathsf{x}\cdot\mathsf{p}\right] + [V(\mathsf{x}), \mathsf{x}\cdot\mathsf{p}]\right\rangle \\
&= \left\langle \frac{1}{2m}\left[p^2, \mathsf{x}\right]\cdot\mathsf{p} + \mathsf{x}\cdot[V(\mathsf{x}), \mathsf{p}]\right\rangle
\end{aligned}
$$

Then as $[p^2,\boldsymbol{x}] = \boldsymbol{p}\,[p, \boldsymbol{x}] + [p, \boldsymbol{x}]\,\boldsymbol{p} = -2i\hbar\boldsymbol{p}$ and $\boldsymbol{p} = -i\hbar\nabla_x$,

$$
0 = \left\langle \frac{-i\hbar}{m}p^2 + i\hbar\mathsf{x}\cdot\nabla_x V(\mathsf{x})\right\rangle
$$

or, the Virial theorem:

$$2\langle T\rangle = \langle \mathsf{x}\cdot\nabla_x V(\mathsf{x})\rangle$$

Applied to the harmonic oscillator V = 1/2 $m\omega^2x^2$

$$\langle T\rangle = \langle V(\mathsf{x})\rangle = \frac{1}{2}\hbar\omega(n+\frac{1}{2})$$

Applying this to find the RMS excursion of a lattice site in an elemental lattice *r=1*

$$
\begin{aligned}
\langle s^2 \rangle &= \frac{1}{N} \sum_{n,i} \langle s_{n,i}^2 \rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathsf{q},s,\mathsf{k},r} Q_s(\mathsf{q}) \epsilon_i^s(\mathsf{q}) e^{i\mathsf{q}\cdot\mathsf{r}_n} Q_r(\mathsf{k}) \epsilon_i^r(\mathsf{k}) e^{i\mathsf{k}\cdot\mathsf{r}_n} \right\rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathsf{q},s,\mathsf{k},r} Q_s(\mathsf{q}) \epsilon_i^s(\mathsf{q}) e^{i\mathsf{q}\cdot\mathsf{r}_n} Q_r(-\mathsf{k}) \epsilon_i^r(-\mathsf{k}) e^{-i\mathsf{k}\cdot\mathsf{r}_n} \right\rangle \\
&= \frac{1}{N} \left\langle \sum_{n,i} \frac{1}{NM} \sum_{\mathsf{q},s,\mathsf{k},r} Q_s(\mathsf{q}) \epsilon_i^s(\mathsf{q}) e^{i\mathsf{q}\cdot\mathsf{r}_n} Q_r^*(\mathsf{k}) \epsilon_i^{*r}(\mathsf{k}) e^{-i\mathsf{k}\cdot\mathsf{r}_n} \right\rangle \\
&= \frac{1}{NM} \sum_{\mathsf{q},s} \left\langle |Q_s(\mathsf{q})|^2 \right\rangle \\
&= \frac{1}{NM} \sum_{\mathsf{q},s} \frac{2}{\omega_s^2(\mathsf{q})} \left\langle \frac{1}{2} \omega_s^2(\mathsf{q}) \, |Q_s(\mathsf{q})|^2 \right\rangle \\
&= \frac{1}{NM} \sum_{\mathsf{q},s} \frac{2}{\omega_s^2(\mathsf{q})} \frac{1}{2} \hbar \omega_s(\mathsf{q}) \left(n_s(\mathsf{q}) + \frac{1}{2} \right) \\
\langle s^2 \rangle &= \frac{1}{NM} \sum_{\mathsf{q},s} \frac{\hbar}{\omega_s(\mathsf{q})} \left(n_s(\mathsf{q}) + \frac{1}{2} \right)
\end{aligned}
$$

However, the integral may be written as a function of $\omega_s(q)$ only

$$\langle s^2 \rangle = \frac{1}{NM} \sum_{\mathbf{q},s} \frac{\hbar}{\omega_s(\mathbf{q})} \left(\frac{1}{e^{\beta \omega_s(\mathbf{q})} - 1} + \frac{1}{2} \right)$$

It is convenient to introduce a density of phonon states

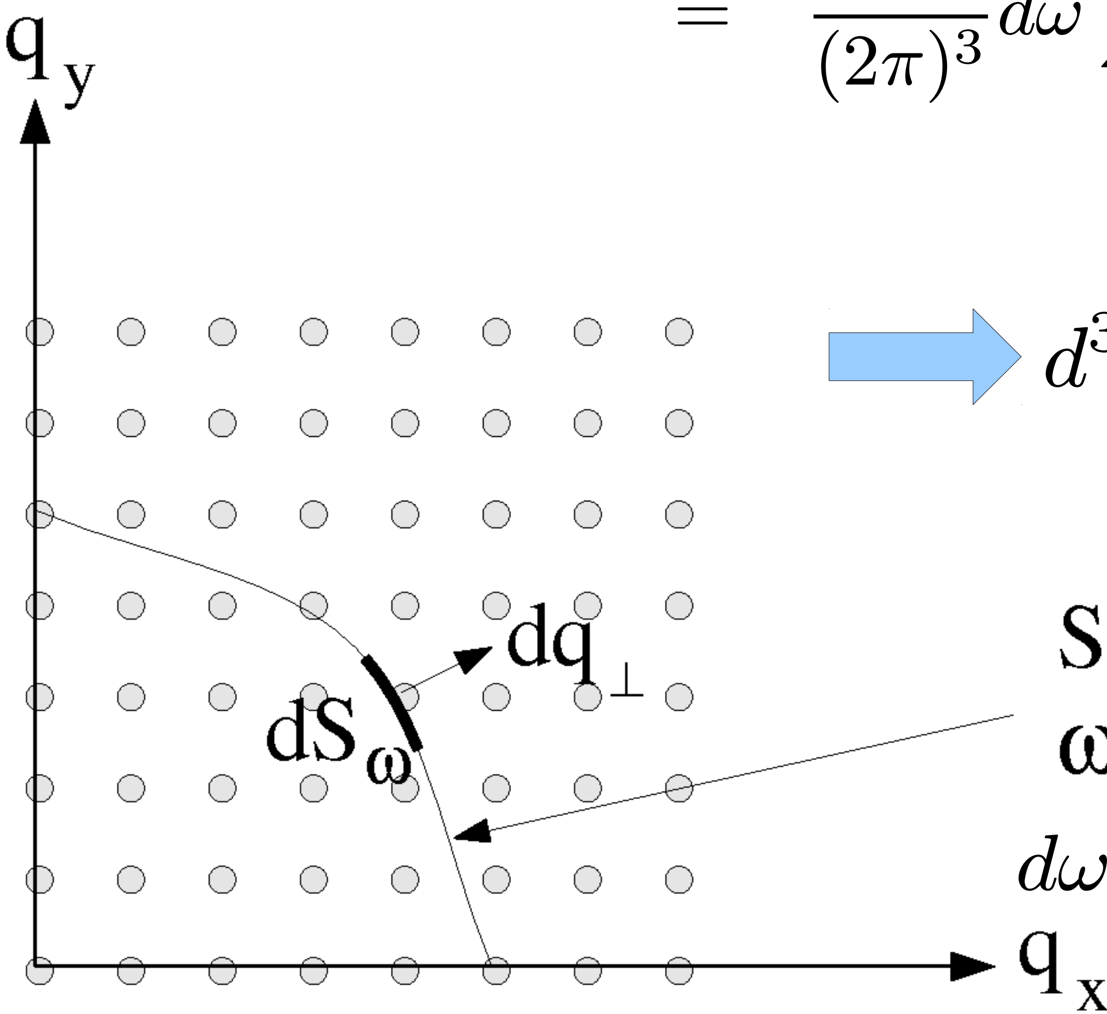
$$Z(\omega) = \frac{1}{N} \sum_{\mathbf{q},s} \delta\left(\omega - \omega_s(\mathbf{q})\right)$$

$$\Rightarrow \quad \langle s^2 \rangle = \frac{\hbar}{M} \int d\omega Z(\omega) \frac{1}{\omega} \left(n(\omega) + \frac{1}{2} \right)$$

The Phonon Density of States

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3}\int_{\omega}^{\omega+d\omega} d^3q$$

$$= \frac{V}{(2\pi)^3}d\omega \sum_s \int d^3q\delta\left(\omega-\omega_s(\mathbf{q})\right)$$



$$\Rightarrow d^3q = dS_w dq_\perp = \frac{dS_\omega d\omega}{\nabla_q \omega_s(\mathbf{q})}$$

Surface

$\omega = \omega_S(q)$

$$d\omega = \nabla_q \omega_s(\mathbf{q}) dq_\perp$$

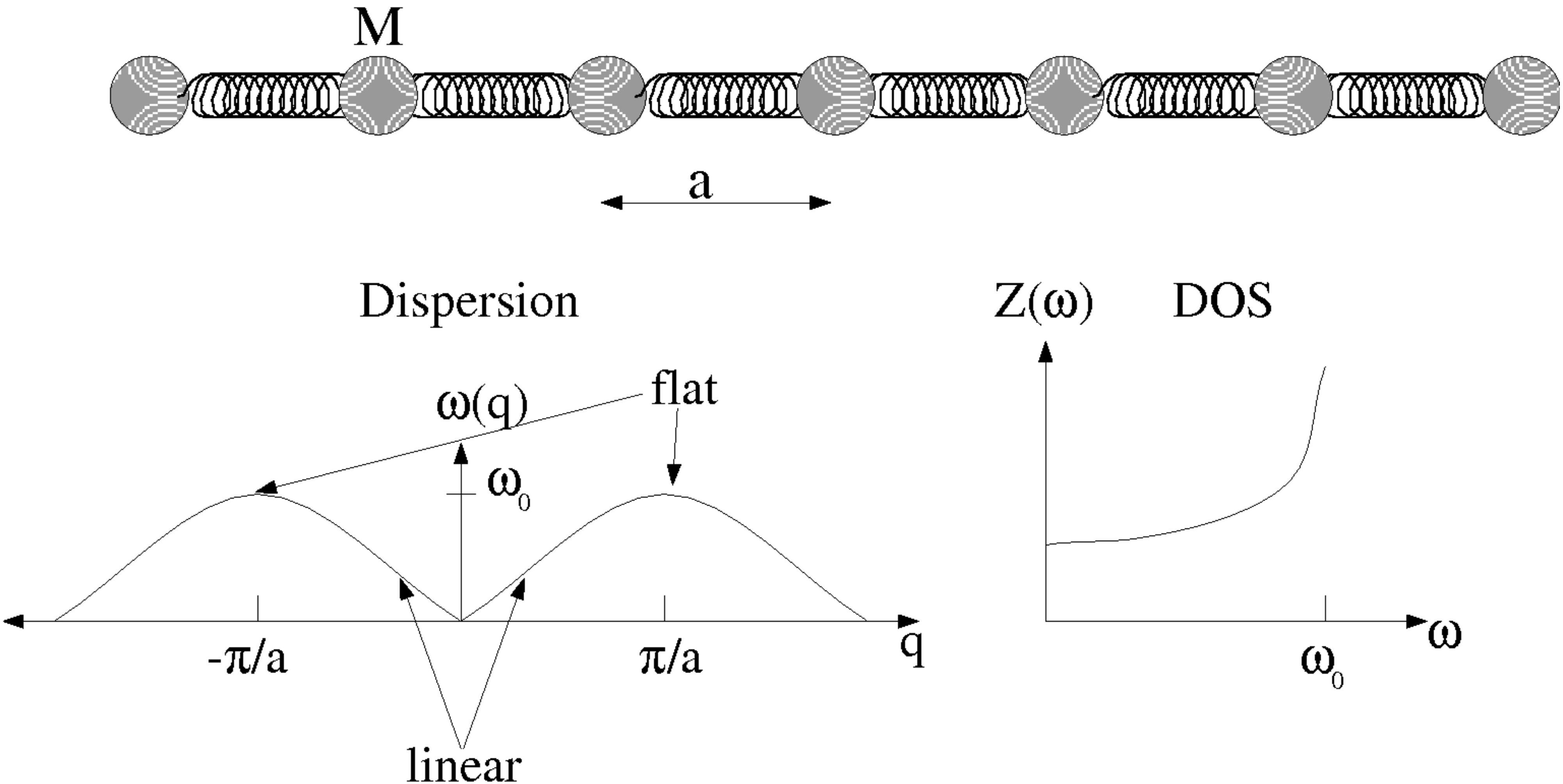
S_ω is the surface in q-space of constant $\omega = \omega_s(\mathbf{q})$, therefor

$$Z(\omega)d\omega = \frac{V}{(2\pi)^3} d\omega \sum_s \int_{\omega=\omega_s(\mathbf{q})} \frac{dS_\omega}{\nabla_q \omega_s(\mathbf{q})}$$

Thus the density of states is high in regions where the dispersion is flat so that $\nabla_q \omega_s(\mathbf{q})$ is small.

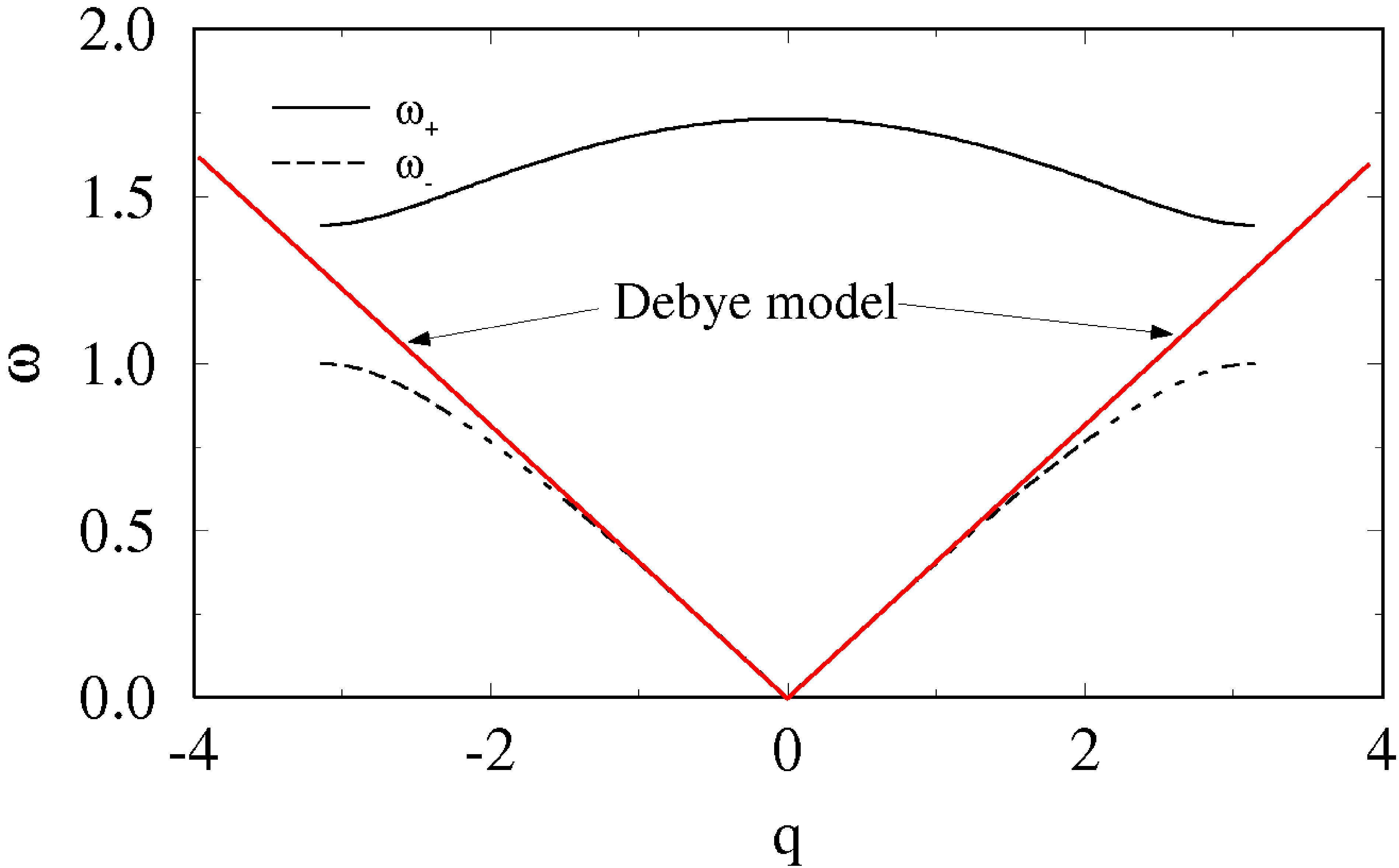
Example: 1-d Harmonic chain

1-d Harmonic chain



Models of Lattice Dispersion

The Debye Model



For small $\omega_s(\mathbf{q}) = c_s|\mathbf{q}|$ for all s and $\mathbf{q}$

$\rightarrow \nabla_q \omega_s(\mathbf{q}) = c_s$ for all s and $\mathbf{q}$

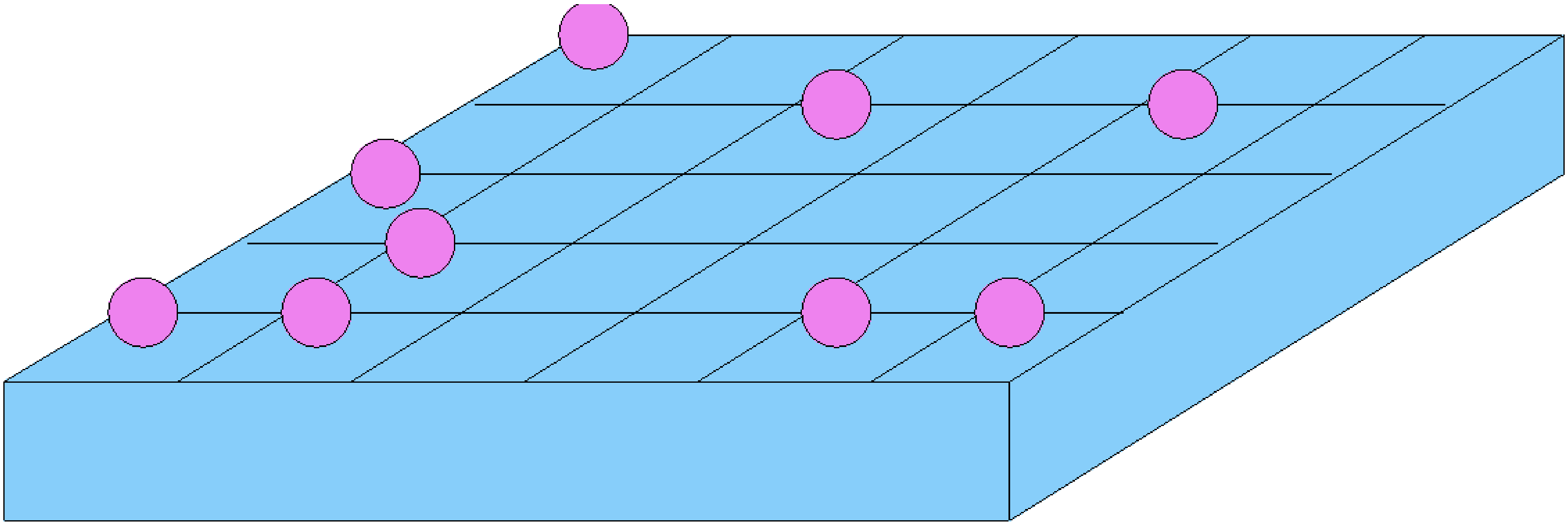
$$
\begin{aligned}
Z(\omega) &= \frac{V}{(2\pi)^3} \sum_s \int \frac{dS_\omega}{\nabla_q \omega_s(\mathsf{q})} \\
&= \frac{V}{(2\pi)^3} \sum_s \int \frac{dS_\omega}{c_s}
\end{aligned}
$$

$$
S_s(\omega = \omega(\mathsf{q})) = \begin{cases} 2 \text{ for } d = 1 \\ 2\pi q = 2\pi\omega/c \text{ for } d = 2 \\ 4\pi q^2 = 4\pi\omega^2/c^2 \text{ for } d = 3 \end{cases}
$$

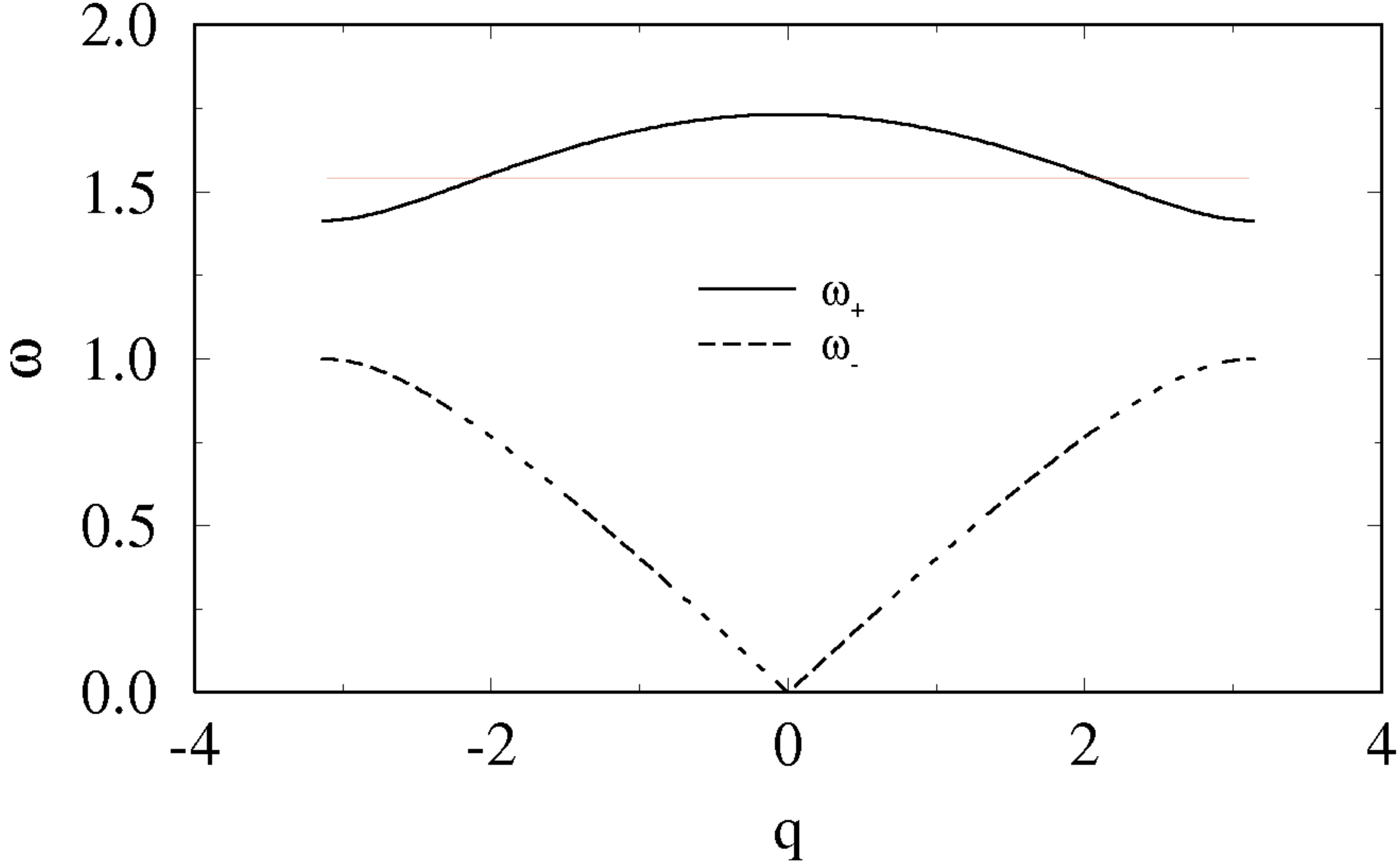
Number of modes = d:

$$
Z(\omega) = \frac{V}{(2\pi)^3} \left\{ \begin{array}{c} 2/c \text{ for } d = 1 \\ 2\pi q = 4\pi\omega/c^2 \text{ for } d = 2 \\ 4\pi q^2 = 12\pi\omega^2/c^3 \text{ for } d = 3 \end{array} \right\} \quad 0 < \omega < \omega_D
$$

The Einstein Model



The model is dispersionless $\omega(q) = \omega_0$, and the DOS for this system is a delta function $Z(\omega) = c\delta(\omega-\omega_0)$.



Thermodynamics of Crystal Lattices

Long-Range Order

$$\begin{aligned}\langle s^2 \rangle &= \frac{\hbar}{MN} \sum_{\mathbf{q},s} \frac{1}{\omega_s(\mathbf{q})} \left(\frac{1}{e^{\beta \omega_s(\mathbf{q})} - 1} + \frac{1}{2} \right) \\ &= \frac{\hbar}{2MN} \sum_{\mathbf{q},s} \frac{\sinh\left(\beta \omega_s(\mathbf{q})/2\right)}{\omega_s(\mathbf{q}) \cosh\left(\beta \omega_s(\mathbf{q})/2\right)}\end{aligned}$$

T → 0 limit:

$$\lim_{\beta \to \infty} \langle s^2 \rangle = \frac{\hbar}{2MN} \lim_{\beta \to \infty} \sum_{\mathbf{q},s} \frac{1}{\omega_s(\mathbf{q})} \left(\frac{1}{\beta \omega_s(\mathbf{q})} + \frac{1}{2} \right)$$

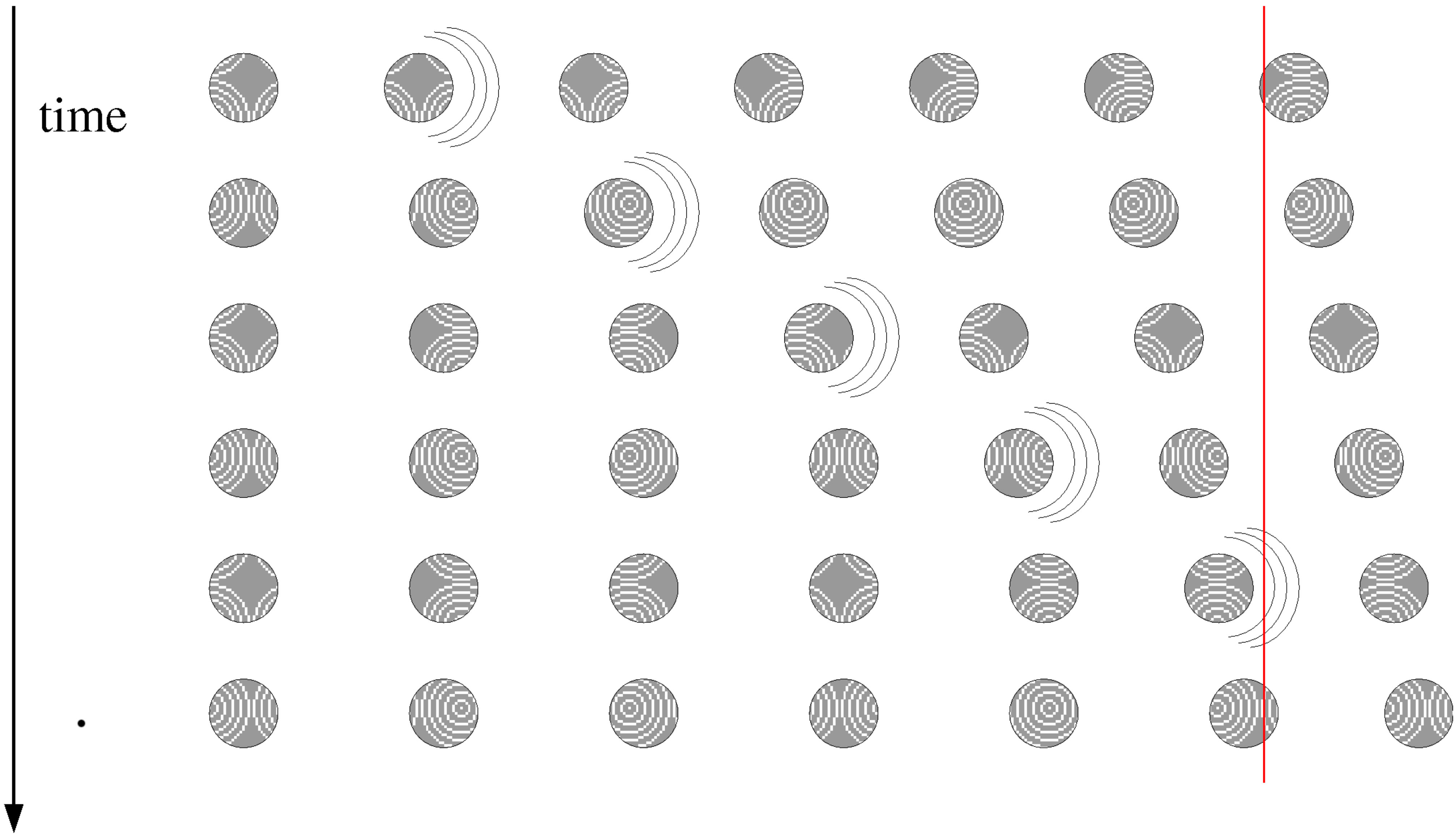
Low frequency modes are most important → Debye model

$$\lim_{\beta\to\infty}\langle s^2\rangle \approx \frac{\hbar}{2MN}\int_0^{\omega_D} d\omega Z(\omega)\frac{1}{\omega}\left(\frac{1}{\beta\omega}+\frac{1}{2}\right)$$

$$Z(\omega) = \frac{V}{(2\pi)^3}\left\{\begin{array}{c} 2/c \ \text{ for } d=1 \\ 2\pi q = 4\pi\omega/c^2 \ \text{ for } d=2 \\ 4\pi q^2 = 12\pi\omega^2/c^3 \ \text{ for } d=3 \end{array}\right\} \quad 0<\omega<\omega_D$$

<*s*^2> for lattices of different dimension

$\langle s^2\rangle$	$d=1$	$d=2$	$d=3$
$T=0$	∞	finite	finite
$T\neq 0$	∞	∞	finite


time

Thermodynamics

The probability that any state in the subsystem is occupied

$$P\left(\{n_s(\mathsf{k})\}\right) \propto e^{-\beta E(\{n_s(\mathsf{k})\})}$$

$$\begin{aligned}
\mathcal{Z} &= \sum_{\{n_s(\mathsf{k})\}} e^{-\beta E(\{n_s(\mathsf{k})\})} \\
&= \sum_{\{n_s(\mathsf{k})\}} e^{-\beta \sum_{\mathsf{k},s} \hbar\omega_s(\mathsf{k})\left(n_s(\mathsf{k})+\frac{1}{2}\right)} \\
&= \prod_{s,\mathsf{k}} \mathcal{Z}_s(\mathsf{k})
\end{aligned}$$

$$
\begin{aligned}
\mathcal{Z}_s(\mathsf{k}) &= \sum_n e^{-\beta\hbar\omega_s(\mathsf{k})\left(n_s(\mathsf{k})+\frac{1}{2}\right)} \\
&= e^{-\beta\hbar\omega_s(\mathsf{k})/2} \sum_n e^{-\beta\hbar\omega_s(\mathsf{k})(n_s(\mathsf{k}))} \\
&= \frac{e^{-\beta\hbar\omega_s(\mathsf{k})/2}}{1-e^{-\beta\hbar\omega_s(\mathsf{k})}} \\
&= \frac{1}{2\sinh\left(\beta\omega_s(\mathsf{k})/2\right)}
\end{aligned}
$$

$$
\mathcal{F} = -k_B T \ln\left(\mathcal{Z}\right) = k_B T \sum_{\mathsf{k},s} \ln\left(2\sinh\left(\beta\hbar\omega_s(\mathsf{k})/2\right)\right)
$$

Since $dE=TdS-PdV$ and $dF=TdS-PdV-TdS-SdT$, the entropy is

$$\mathcal{S} = -\left(\frac{\partial \mathcal{F}}{\partial T}\right)_V$$

and system energy is then given by

$$\mathcal{E} = \mathcal{F} + T\mathcal{S} = \mathcal{F} - T\left(\frac{\partial \mathcal{F}}{\partial T}\right)_V$$

where constant volume V is guaranteed by the harmonic approximation (since $\langle s \rangle = 0$)

$$\mathcal{E} = \sum_{\mathsf{k},s} \frac{1}{2}\hbar\omega_s(\mathsf{k})\coth\left(\beta\omega_s(\mathsf{k})/2\right)$$

The specific heat is then given by

$$C = \left(\frac{d\mathcal{E}}{dT}\right)_V = k_B \sum_{\mathsf{k},s} \left(\beta\hbar\omega_s(\mathsf{k})\right)^2 \operatorname{csch}^2\left(\beta\omega_s(\mathsf{k})/2\right)$$

where *csch (x) = 1/sinh (x)*

Consider the specific heat of our 3-dimensional Debye model.

$$\begin{aligned} C &= k_B \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) \left(\beta\omega/2\right)^2 \operatorname{csch}^2\left(\beta\omega/2\right) \\ &= k_B \int_0^{\omega_D} d\omega \left(\frac{12V\pi\omega^2}{(2\pi c)^3}\right) \left(\beta\omega/2\right)^2 \operatorname{csch}^2\left(\beta\omega/2\right) \end{aligned}$$

Debye frequency ω_D is determined by the requirement that

$$3rN = \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) = \int_0^{\omega_D} d\omega \left(\frac{12V\pi\omega^2}{(2\pi c)^3} \right)$$

or $V/(2\pi c)^3 = 3rN/(4\omega_D^3)$.

At high temperatures
$\beta\hbar\omega_D/2 \ll 1$

$$C \approx k_B \int_0^{\omega_D} d\omega \mathcal{Z}(\omega) = 3Nrk_B$$

At low temperatures

$\beta\hbar\omega_D/2 \gg 1$

$$\mathrm{csch}^2\left(\beta\omega/2\right) \approx 2e^{-\beta\omega/2}$$

$$C \approx 12\pi k_B \frac{3rN}{4\omega_D^2}\int_0^\infty d\omega\omega^2\left(\frac{\beta\hbar\omega}{2}\right)^2 2e^{-\beta\omega_s(\mathsf{k})/2}$$

$$C \approx \frac{9k_B rN\pi}{2}\left(\frac{1}{\omega_D\beta\hbar}\right)^3\int_0^\infty dx x^4 e^{-x}$$

$$\approx \frac{9k_B rN\pi}{2}\left(\frac{1}{\omega_D\beta\hbar}\right)^3 24$$

Then, if we identify the Debye temperature $\theta_D=\hbar\omega_D/k_B$, we get

$$C \approx 96\pi rNk_B\left(\frac{T}{\theta_D}\right)^3$$

Einstein Model:

$$C = pnk_B \frac{(\hbar\omega_E/k_BT)^2 \, e^{\hbar\omega_E/k_BT}}{\left(e^{\hbar\omega_E/k_BT} - 1\right)^2}$$

At low temperatures
$T \ll \Theta_E$

Constant

At high temperatures
$T \gg \Theta_E$

Exponential

Were we have used the Debye temperature

$$\Theta_E = \hbar\omega_e/k_B$$

Specific Heat