Ch. 22: Classical Theory of Harmonic Crystal

Neglect of the thermal motion of ion cores in a lattice has led to failures to explain the following:

1. Equilibrium Properties
   - Specific Heat of Metals and Insulators
   - Equilibrium Density and Cohesive Energies
   - Thermal Expansion
   - Melting

2. Transport Properties
   - Temperature Dependence of Relaxation Time
   - Failure of Wiedemann-Franz Law
   - Superconductivity
   - Thermal Conductivity of Insulators
   - Transmission of Sound

3. Interaction With Radiation
   - Reflectivity of Ionic Crystals
   - Inelastic Scattering of Light
   - Scattering of X Rays
   - Scattering of Neutrons

The Harmonic Approximation

Assumptions:
1. Ions oscillate about lattice sites (= time averaged positions).
2. Amplitudes of ionic motion much smaller than interionic spacing.

For static lattice,
$$ U^{ex} = \frac{1}{2} \sum_{\bf{R}, \bf{R}'} \phi(\bf{R} - \bf{R}') = \frac{N}{2} \sum_{\bf{R}0} \phi(\bf{R}) $$

For dynamic lattice,
$$ \bar{U}(\bf{R}) = \bf{R} + \bar{u}(\bf{R}) $$
$$ U = \frac{1}{2} \sum_{\bf{R}, \bf{R}'} \phi(\bf{R} + \bar{u}(\bf{R}')) + \frac{1}{2} \sum_{\bf{R}, \bf{R}'} \phi(\bf{R} - \bf{R}') + \frac{1}{4} \sum_{\bf{R}, \bf{R}'} \phi(\bf{u}(\bf{R}) - \bf{u}(\bf{R}')) \cdot \nabla \phi(\bf{R} - \bf{R}') + O(u') $$

Taylor expansion,
$$ U = U^{ex} + \frac{1}{4} \sum_{\bf{R}, \bf{R}'} \left( [u_{\mu'}(\bf{R}) - u_{\mu'}(\bf{R}')] \phi_{\mu'}(\bf{R} - \bf{R}') \right) \cdot \left( [u_{\nu'}(\bf{R}) - u_{\nu'}(\bf{R}')] \phi_{\nu'}(\bf{R} - \bf{R}') \right) $$

Equivalently,
$$ U^{two} = \frac{1}{4} \sum_{\bf{R}, \bf{R}'} u_{\mu'}(\bf{R}) D_{\mu'}(\bf{R} - \bf{R}') u_{\nu'}(\bf{R}') $$

D for “dynamic”
$$ D_{\mu'}(\bf{R} - \bf{R}') = \delta_{\mu', \nu'} \sum_{\bf{R}} \phi_{\nu'}(\bf{R} - \bf{R}') - \phi_{\nu'}(\bf{R} - \bf{R}') $$
Lattice Specific Heat

\[ u = \frac{1}{V} \int dV e^{-\beta H} \]

\[ d\Gamma = \prod_{\mu} d\mu_i(\vec{R}) \prod_{\rho} dp_{\rho}(\vec{R}) \]

\[ u = \frac{1}{V} \frac{\partial}{\partial \beta} \ln \int dV e^{-\beta H} \]

change of variables

\[ \int dV e^{-\beta H} = e^{-\beta \mu \Gamma} \beta^{-3N} \exists \]

\[ u = u^{eq} + 3nk_B T \]

\[ c_v = \frac{\partial u}{\partial T} = 3nk_B \]

Dulong & Petit

Dulong and Petit law is exact. Follows from the quadratic dependence of elastic energy on coordinates. Should be reasonable in the classical limit, when energy distribution is continuous on the scale of kT.

Problems: (1) anharmonic oscillations (2) zero-point energy (3) discreteness of energy distribution at low T.

Normal Modes of 1D Monatomic Bravais Lattice

\[ U^{bmn} = \sum_{k,\nu} ^{(n)} (\epsilon_{k,\nu}^{ \pm 1/2} +1/2)h\omega_{k,\nu} \]

\[ c_v = \frac{1}{V} \sum_{k,\nu} \frac{\partial}{\partial T} \frac{h\omega_{k,\nu}}{e^{h\omega_{k,\nu}/kT} - 1} \]

low T: acoustic phonons

\[ \sum_{\text{harm}} + \sum_{\text{non-harm}} \]

\[ \mu \omega_{k,\nu}, \omega_{k,\nu}^{2/1} \]

\[ k = \frac{2\pi j}{Na} \]

\[ \omega: \text{positive} \]

\[ k: -\pi/a \text{ to } \pi/a \]

N normal modes

small k

\[ c = \frac{\omega}{k} = \frac{1}{2} \sqrt{\frac{K}{M}} \frac{\partial \omega}{\partial k} = V \]

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1D Chain With Basis

Atoms M₁ and M₂ at na and (na+d),

\[ d = \frac{a}{2} \]

Spring constant K (intracell) and G (intercell). K ≥ G

\[
\begin{align*}
M_1 \ddot{u}_1(na) &= -K[u_1(na) - u_2(na)] - G[u_1(na) - u_2((n-1)a)] \\
M_2 \ddot{u}_2(na) &= -K[u_2(na) - u_1(na)] - G[u_2(na) - u_1((n+1)a)]
\end{align*}
\]

\[ u_1(na, t) = A_1 e^{i(kna - \omega t)} \quad u_2(na, t) = A_2 e^{i(kna - \omega t)} \]

\[
(M_1 \omega^2 - K - G)A_1 + (K + Ge^{-\omega t})A_2 = 0 \\
(K + Ge^{\omega t})A_1 + (M_2 \omega^2 - K - G)A_2 = 0
\]

determinant = 0

\[
\omega^2 = \frac{K + G}{2M'} \left[ 1 \pm \sqrt{1 - \frac{4M'}{M_1 + M_2} \frac{4K'}{K + G} \sin^2(ka/2)} \right]
\]

M' = \frac{M_1M_2}{M_1 + M_2}
K' = \frac{KG}{K + G}

Two branches:

\[
\begin{align*}
A_2 &= \frac{K + G}{K + Ge^{-\omega t}} \left( \frac{M_2 - M_1}{2M_2} \right) + \frac{M_1 + M_2}{2M_2} \sqrt{1 - \frac{4M'}{M_1 + M_2} \frac{4K'}{K + G} \sin^2(ka/2)} \\
A_1 &= \frac{K + G}{K + Ge^{\omega t}} \left( \frac{M_2 - M_1}{2M_2} \right) - \frac{M_1 + M_2}{2M_2} \sqrt{1 - \frac{4M'}{M_1 + M_2} \frac{4K'}{K + G} \sin^2(ka/2)}
\end{align*}
\]

1D Behavior

\[
\omega^2 = \frac{K + G}{2M'} \left[ 1 \pm \sqrt{1 - \frac{4M'}{M_1 + M_2} \frac{4K'}{K + G} \sin^2(ka/2)} \right]
\]

when M₁ → M₁, M₁' → M₂ when M₁ >> M₂ when M₂ ↓ M₁
K' → K/2 when K → G
K' → K when K ↓ G

\[
\omega_{acoustics} = \frac{K'}{\sqrt{M_1 + M_2}} \quad A_1 = A_2
\]
\[
\omega_{optics} = \frac{K + G}{\sqrt{M'}} \quad A_2 = -A_1
\]

1D Behavior:

\[
\omega = \frac{K + G}{2M'} \sqrt{K' \left( \frac{K'}{M_1 + M_2} \right)}
\]

when K → ∞, K' → ∞
K' → K when K ↓ G
K' → K/2 when K → G
K' → K when K ↓ G

\[
\omega_{acoustics} = \frac{4G}{\sqrt{M_1 + M_2}} | \sin(ka/2) | \quad A_1 ≈ A_2
\]
\[
\omega_{optics} = \frac{K}{M'} \quad A_2 = -A_1
\]
1D Behavior ($M_1 = M_2$)

$$\omega^2 = \frac{K + G}{M_1} \pm \frac{1}{M_1} \sqrt{\left(\frac{K + G}{M_1}\right)^2 + 2KG \cos ka}$$

small $k$

$$\omega_{\text{small}} = \frac{ka}{2M_1}$$
$$A_1 = A_2$$

$$\omega_{\text{vp}} = \frac{\sqrt{2(K + G)}}{M_1}$$
$$A_1 = -A_2$$

$k \approx \frac{\pi}{a}$

$$\omega_{\text{small}} = \frac{\sqrt{2G}}{M_1}$$
$$A_1 = A_2$$

$$\omega_{\text{vp}} = \frac{\sqrt{2K}}{M_1}$$
$$A_1 = -A_2$$

$K \gg G$

$$\omega_{\text{small}} = \frac{2G}{M_1} \sin(ka/2) \Rightarrow A_1 \approx A_2$$

$$\omega_{\text{vp}} = \frac{\sqrt{2K}}{M_1} \Rightarrow A_1 = -A_2$$

Monatomic 3D Bravais Lattice

$$U^\text{bare} = \frac{1}{2} \sum_{\vec{k}} \bar{u}(\vec{R}) \bar{D}(\vec{R} - \vec{R}') \bar{u}(\vec{R}')$$

$$D_{\nu\nu}(\vec{R} - \vec{R}') = D_{\nu\nu}(\vec{R}' - \vec{R})$$

$$D_{\nu\rho}(\vec{R}) = D_{\rho\nu}(\vec{R}) = 0$$

$$M_{\mu\nu}(\vec{R}) = -\frac{\partial U^\text{bare}}{\partial u_\mu(\vec{R})} = -\sum_\rho D_{\nu\rho}(\vec{R} - \vec{R}') u_\rho(\vec{R}')$$

$$\bar{u}(\vec{R},t) = \bar{A}(\vec{R},t) e^{i\vec{k} \cdot \vec{R} - \omega t}$$

$$\bar{M}\omega^2 \bar{A} = \bar{D}(\vec{k}) \bar{A}$$

$$\bar{D}(\vec{k}) = \sum_{\vec{R}} \bar{D}(\vec{R}) e^{-i\vec{k} \cdot \vec{R}}$$

$$\bar{D}(\vec{k}) = \frac{1}{2} \sum_{\vec{R}} \bar{D}(\vec{R}) [e^{i\vec{k} \cdot \vec{R}} + e^{-i\vec{k} \cdot \vec{R}}] = -2\sum_{\vec{R}} \bar{D}(\vec{R}) \sin^2(\vec{k} \cdot \vec{R}/2)$$

$$\bar{D}(\vec{k})\text{ matrix is real and even.}$$

3 eigen vectors for any allowed $k$.

$$\bar{D}(\vec{k}) \bar{A}_i(\vec{k}) = \lambda_i \bar{A}_i(\vec{k})$$

$$\bar{A}_i(\vec{k}) \cdot \bar{A}_j(\vec{k}) = \delta_{ij}$$

$$\omega_i(\vec{k}) = \frac{\lambda_i(\vec{k})}{M}$$

long wavelength limit

$$\bar{D}(\vec{k}) = -\frac{k^2}{2} \sum_{\vec{R}} \bar{D}(\vec{R}) (\vec{k} \cdot \vec{R})^2$$

$$\omega_i(\vec{k}) = kc_i(\vec{k})$$
Monatomic lattices have three acoustic branches. Cells with basis have, in addition to the three acoustic branches, $3n-3$ optical branches. One can think of the acoustic branches as motions of center of mass of the basis and the optical branches as relative motions amongst atoms in the same basis.

Theory of Elasticity (Lattice ↔ Continuum)

- **monatomic 3D lattice**
  
  \[
  U_{\text{form}} = \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \left( \hat{u}(\mathbf{R}) \hat{D}(\mathbf{R} - \mathbf{R}') \hat{u}(\mathbf{R}') \right)
  \]
  
  \[
  U_{\text{form}} = -\frac{1}{4} \sum_{\mathbf{R}} \left( \hat{u}(\mathbf{R}) - \hat{u}(\mathbf{R}) \hat{D}(\mathbf{R}^- \mathbf{R}') \hat{u}(\mathbf{R}') - \hat{u}(\mathbf{R}) \hat{D}(\mathbf{R}^- \mathbf{R}') \hat{u}(\mathbf{R}') \right)
  \]
  
  \[
  \hat{u}(\mathbf{R}'') = \hat{u}(\mathbf{R}) + (\mathbf{R}' - \mathbf{R}) \nabla \hat{u}(\mathbf{R}) |_{\mathbf{R} = \mathbf{R}'}
  \]
  
  \[
  U_{\text{form}} = \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \left( \frac{\partial \hat{u}(\mathbf{R})}{\partial x_x} \frac{\partial \hat{u}(\mathbf{R})}{\partial x_x} \right) E_{\text{stress}}
  \]
  
  \[
  E_{\text{stress}} = -\frac{1}{2} \sum_{\mathbf{R}} \hat{R}_x D_{\mu \nu}(\mathbf{R}) \hat{R}_x
  \]
  
  \[
  U_{\text{form}} = \frac{1}{2V_{\text{cell}}} \sum_{x \mu \nu \tau} \left( \frac{\partial \hat{u}(\mathbf{F})}{\partial x_x} \frac{\partial \hat{u}(\mathbf{F})}{\partial x_x} \right) E_{\text{stress}}
  \]

- E unchanged $\mu \leftrightarrow \nu$ or $\sigma \leftrightarrow \tau$
- E specified for 6 values of $\mu \nu$:
  
  \[
  xx, yy, zz, yz, zx, xy
  \]
- U unchanged upon rotation as a whole, can depend only on symmetric strain $X$

  \[
  X_{\mu \nu} = \frac{1}{2} \left( \frac{\partial u_\mu}{\partial x_\nu} + \frac{\partial u_\nu}{\partial x_\mu} \right)
  \]
  
  \[
  U_{\text{form}} = \frac{1}{2} \int \! d^3 \mathbf{r} \sum_{\mu \nu} X_{\mu \nu} c_{\mu \nu} X_{\tau \tau}
  \]
  
  \[
  c_{\mu \nu} = -\frac{1}{2V_{\text{cell}}} \sum_{\mathbf{R}} \left[ \hat{x}_\mu D_{\mu \nu}(\mathbf{R}) \hat{x}_\tau + \hat{x}_\nu D_{\mu \nu}(\mathbf{R}) \hat{x}_\tau + \hat{x}_\tau D_{\mu \nu}(\mathbf{R}) \hat{x}_\mu + \hat{x}_\tau D_{\mu \nu}(\mathbf{R}) \hat{x}_\nu \right]
  \]
  
  UNCH. $\sigma \mu \leftrightarrow \tau \nu$, $\sigma \leftrightarrow \mu$, OR $\tau \leftrightarrow \nu$

- $c$ matrix is symmetric, only 21 independent parameters.
Continuum Linear Elastic Theory

Stress has the units of pressure (force per area). $\sigma_{ij}$ is the force per area exerted on the $i$-th surface with the force in the $j$-th direction ($x$, $y$, $z$).

$$\sigma_{ij} = \lim_{\Delta x \to 0} \frac{\Delta F_{ij}}{\Delta A_{ij}}$$

For an object to remain stationary, the shear components $\sigma_{ij} = \sigma_{ji}$.

Strain, a number, is the (small) fractional change of the dimension of a crystal from equilibrium.

$$\varepsilon_{xx} = \frac{\partial u_x}{\partial x} \quad \varepsilon_{yy} = \frac{1}{2} \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right)$$

In a 1D wire, linear stress $\sigma = (L' - L)/L$ is proportional to the linear stress (tension per cross section) by Hooke’s law. The Young’s modulus, $E$, is a measure of the stiffness, or strength, of the material.

$$\varepsilon_{xx} = E \sigma_{xx}$$

In general, the stress and the strain are related through the stiffness tensor (modulus) $C'$, or, equivalently, through the compliance tensor $S'$.

$$\sigma_{ij} = \sum_{k,l} C'_{ijkl} \varepsilon_{kl} \quad \varepsilon_{ij} = \sum_{k,l} S'_{ijkl} \sigma_{kl} \quad (9x9 matrices)$$

Elastic energy (work stored):

$$U_{elas} = \frac{1}{2} \sum_{i,j} \varepsilon_{ij} \sigma_{ij} = \frac{1}{2} \sum_{i,j} \varepsilon_{ij} C'_{ijkl} \varepsilon_{kl} = \frac{1}{2} \sum_{i,j} \varepsilon_{ij} S'_{ijkl} \sigma_{kl}$$

Continuum Elastic Theory

Only 6 elements of the 3x3 $\sigma$ and $\varepsilon$ matrices are independent

$xx \to 1, \quad yy \to 2, \quad zz \to 3, \quad yz \to 4, \quad zx \to 5, \quad xy \to 6$

$\sigma = C' \varepsilon$ and $\varepsilon = S' \sigma$ still hold if $C'$ and $S'$ were simply truncated to $6x6$. However, elastic energy would be wrong. Solution: double the shear strain!
Continuum Elasticity

\[
\begin{bmatrix}
\sigma_{xx} \\
\sigma_{yy} \\
\sigma_{zz} \\
\sigma_{xy} \\
\sigma_{yz} \\
\sigma_{zx}
\end{bmatrix} =
\begin{bmatrix}
c_{11} & c_{12} & c_{13} & c_{14} & c_{15} & c_{16} \\
c_{21} & c_{22} & c_{23} & c_{24} & c_{25} & c_{26} \\
c_{31} & c_{32} & c_{33} & c_{34} & c_{35} & c_{36} \\
c_{41} & c_{42} & c_{43} & c_{44} & c_{45} & c_{46} \\
c_{51} & c_{52} & c_{53} & c_{54} & c_{55} & c_{56} \\
c_{61} & c_{62} & c_{63} & c_{64} & c_{65} & c_{66}
\end{bmatrix}
\begin{bmatrix}
\varepsilon_{xx} \\
\varepsilon_{yy} \\
\varepsilon_{zz} \\
\varepsilon_{xy} \\
\varepsilon_{yz} \\
\varepsilon_{zx}
\end{bmatrix}
\]

Continuum Theory of Wave Propagation

Write Lagrangian for the elastic medium

\[ T = \rho \int d\mathbf{r} \frac{\dot{u}(\mathbf{r}, t)^2}{2} \quad \rho = MN / V \]

\[ T - U = \frac{1}{2} \int d\mathbf{r} \left[ \rho \ddot{u}(\mathbf{r})^2 - \frac{1}{4} \sum_{\mu \nu \tau \omega} \left( \frac{\partial u_\mu(\mathbf{r})}{\partial x_\sigma} + \frac{\partial u_\mu(\mathbf{r})}{\partial x_\mu} \right) \left( \frac{\partial u_\nu(\mathbf{r})}{\partial x_\tau} + \frac{\partial u_\nu(\mathbf{r})}{\partial x_\tau} \right) c_{\mu \nu \tau \omega} \right] \]

\[ \delta \int dt L = 0 \quad \Rightarrow \quad \rho \dddot{u}_\mu = \sum_{\sigma \tau \nu} c_{\mu \sigma \tau \nu} \frac{\partial^2 u_\sigma}{\partial x_\sigma \partial x_\nu} \]

Seek solutions

\[ \ddot{u}(\mathbf{r}, t) = A e^{(k \cdot \mathbf{r} - \omega t)} \quad \rho \omega^2 A_\mu = \sum_c A_c \sum_{\sigma \nu} c_{\mu \sigma \tau \nu} k_\sigma k_\nu \]

At long wavelength, same as discrete lattice.
Historic context: $T^3$ dependence of specific heat at low temperature inconsistent with electronic heat capacity.

Classically, 

$$ u = \frac{1}{V} \int dV e^{-\beta H} \quad \quad \quad d\Gamma = \prod_{\mu} d\mu_{\mu}(\vec{R}) d\vec{p}_{\mu}(\vec{R}) $$

Quantum mechanically, 

$$ u = \frac{1}{V} \sum_{i} E_i e^{-\beta E_i} \quad \quad \quad i = \text{stationary states}, \quad \text{given by Hamiltonian} $$

For monatomic lattice, 

$$ H_{\text{ho}} = \frac{1}{2} \sum_{s} \left( \frac{\vec{p}(\vec{R})^2}{2M} + \frac{1}{2} \sum_{s,s'} \vec{u}(\vec{R}) \cdot \vec{D}(\vec{R} - \vec{R}') \cdot \vec{u}(\vec{R}') \right) $$

Look for solution ($s$: band index) 

$$ \vec{u}(\vec{R}, t) = \vec{A}_s(\vec{k}) e^{i \vec{k} \cdot \vec{r} - \omega_s t} $$

Find $\omega_s$ as function of $\vec{k}$.

**Second Quantization**

Semiclassical treatment: particles quantized, field classical

Full quantum treatment: field quantized

Define annihilation and creation operators

$$ a_{\vec{k}s} = \frac{1}{\sqrt{N}} \sum_{s'} e^{-i s' \vec{k} \cdot \vec{r}} \tilde{A}_{s'}(\vec{k}) \quad \quad \quad a_{\vec{k}s}^* = \frac{1}{\sqrt{N}} \sum_{s'} e^{i s' \vec{k} \cdot \vec{r}} \tilde{A}_{s'}(\vec{k}) $$

Commutation relations

$$ [a_{\vec{k}s}, a_{\vec{k}'s'}^*] = \delta_{\vec{k},\vec{k}'} \delta_{s,s'} \quad \quad [a_{\vec{k}s}, a_{\vec{k}'s'}] = 0 $$

$$ \tilde{u}(\vec{R}) = \frac{1}{\sqrt{N}} \sum_{s} e^{i s \vec{k} \cdot \vec{r}} \tilde{A}_s(\vec{k}) \quad \quad \quad \frac{\hbar}{2M\omega_s(\vec{k})} (a_{\vec{k}s} + a_{\vec{k}s}^*) $$

$$ \tilde{p}(\vec{R}) = -i \frac{1}{\sqrt{N}} \sum_{s} \epsilon^{\vec{k} \cdot \vec{r}} \tilde{A}_s(\vec{k}) \sqrt{\frac{\hbar M\omega_s(\vec{k})}{2}} (a_{\vec{k}s} - a_{\vec{k}s}^*) $$
Statistical Mechanics Of Quantum Oscillators

\[ H^{\text{harm.}} = \sum_{k, S} \hbar \omega_k (\bar{k}) (a_{kS}^+ a_{kS} + \frac{1}{2}) \]

eigenstates of \( H \) are characterized by
\( 3N \) population numbers of the
independent oscillators (=\# phonons)

\[ E(n_{kS}, n_{kS}, \ldots) = \sum_{k, S} \hbar \omega_k (\bar{k}) (n_{kS} + \frac{1}{2}) \]

define
\[ f = \frac{1}{V} \ln \left( \sum_i e^{-\beta E_i} \right) \]
\[ u = -\frac{\partial f}{\partial \beta} \]

for oscillators
\[ f = \frac{1}{V} \ln \prod_{k, S} \frac{e^{-\beta \hbar \omega_k (\bar{k}) / 2}}{1 - e^{-\beta \hbar \omega_k (\bar{k})}} \]
\[ u = n^* + \frac{1}{V} \sum_{k, S} \hbar \omega_k (\bar{k}) + \frac{1}{V} \sum_{k, S} \frac{\hbar \omega_k (\bar{k})}{e^{\beta \hbar \omega_k (\bar{k})} - 1} \]
\[ n_{kS}(\bar{k}) = \frac{1}{e^{\beta \hbar \omega_k (\bar{k})} - 1} \]

High Temperature Specific Heat

\[ c_v = \frac{1}{V} \sum_{k, S} \frac{\hbar \omega_k (\bar{k})}{e^{\beta \hbar \omega_k (\bar{k})} - 1} \]
cancels zero point energy

High Temp
\[ x = \beta \hbar \omega \ll 1 \]
\[ \frac{1}{e^x - 1} = \frac{1}{x} \left( 1 + \frac{x}{2} + \frac{x^2}{12} + \ldots \right) \]

leading term
Dulong-Petit
\[ c_v^0 = \frac{1}{V} \sum_{k, S} k_S T = \frac{3N k_B T}{V} \]

\[ c_v = c_v^0 \left( 1 - \frac{\hbar^2}{12(k_S T)^2} \frac{1}{3N} \sum_{k, S} \omega_k (\bar{k})^2 + \ldots \right) \]
competing with
anharmonic contrib.
Low Temperature Specific Heat

Modes with $\hbar \omega \gg kT$ will contribute negligibly to specific heat. However, portions of the three acoustic branches will always contribute significantly, even at low $T$, because $\omega \to 0$ as $k \to 0$.

1. Consider only contributions from acoustic branches, even if crystal has a basis.

2. Approximate the dispersion relation by long-wavelength linear form $\omega = c k$.

3. Replace summation with integral over all $k$-space. Little contribution outside of first BZ anyways.

$$c_v = \frac{\partial}{\partial T} \sum \int \frac{dk}{8\pi^2} \left( \frac{\hbar c \nu k}{e^{\hbar c \nu k/T} - 1} \right)$$

$$c_v = \frac{\partial}{\partial T} \left( \frac{k_B T}{\hbar c \nu \rho} \right)^3 \frac{\pi^2}{10}$$

Why is this not $4\pi^2$?

$$\int_0^\infty \frac{x^4}{e^x - 1} \frac{\pi^4}{15}$$ average phonon phase velocity $T^3$ dependence

Intermediate Temperature $C_V$

DEBYE INTERPOLATION SCHEME

1. Replaces all branches with three acoustic branches with same linear dispersion relation, $\omega = ck$.

2. Each branch is integrated to a sphere of radius $k_D$, such that the total number of modes equals the total number of ions (all ions), $n$, i.e.

$$n = \frac{k_D^3}{6\pi^2}$$

$$c_v = \frac{\partial}{\partial T} \left( \frac{3\hbar c k_D}{2\pi^2} \int_0^{k_D} k^3 dk \right)$$

$$\omega_D = k_D c \quad k_B \Theta_D = \hbar \omega_D = \hbar k_D c$$

define

$$c_v = \left( \frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D/T} x^4 e^x dx \left( \frac{T}{\Theta_D} \right)^3$$

Could compare this with experiment to get Debye temperature.

$$c_v \approx \frac{12\pi^4}{5} nk_B \left( \frac{T}{\Theta_D} \right)^3 = 234 nk_B \left( \frac{T}{\Theta_D} \right)^3$$

However, often assume the low $T$ equation and assume Debye temperature to vary with temperature.
Einstein Model

1. Only acoustic modes are treated with Debye approximation.
2. Assume constant frequency $\omega_e$ for any optical branches present.

\[
c_i^{\text{E}} = c_i^{\text{ac}} + c_i^{\text{opt}}
\]

\[
c_i^{\text{opt}} = p n k_B \frac{(\hbar \omega_e / k_B T)^2 e^{\hbar \omega_e / k_B T}}{(e^{\hbar \omega_e / k_B T} - 1)^2}
\]

Density of Normal Modes

\[
g(\omega) = \sum S \int \frac{d\boldsymbol{k}}{8\pi^3} \delta\left(\omega - \omega_S(\boldsymbol{k})\right)
\]

Debye model

\[
g(\omega) = \begin{cases} 
3\omega^2 \pi^{-2} c^{-3} / 2, & \omega < \omega_D \\
0, & \omega > \omega_D
\end{cases}
\]

aluminum
Blackbody Radiation

- Experimental data for distribution of energy in blackbody radiation: As the temperature increases, the total amount of energy increases.
- As the temperature increases, the peak of the distribution shifts to shorter wavelengths, following Wien’s Law $\lambda_{\text{max}} T = 0.2898 \times 10^{-2} \text{ m} \cdot \text{K}$
- At short wavelengths, classical theory predicted infinite energy, experiment showed no energy. This contradiction is called the ultraviolet catastrophe.

\[
\frac{8\pi f^2}{c^3} - \frac{hf}{e^{\frac{hf}{k_B T}} - 1}^{-1}
\]

Blackbody Radiation

The number of standing waves that can be maintained inside a cavity is identical to the number of oscillators in a crystal, except for a factor of 2/3.
The energy of a mode is quantized $E = n \hbar \omega$
There is no upper limit to the wave vector, photon’s case is identical to acoustic phonon’s modes at low temperature.

\[
u_{cavity} = \int_0^\infty \frac{dk}{4\pi^3} \frac{hck}{e^{\frac{hck}{\beta \hbar c}} - 1} = \frac{\pi^2}{15} (k_B T)^4
\]

Stefan-Boltzmann $T^4$ law

spectral energy density $\frac{\hbar \omega^3}{\pi^2 c^3} e^{\beta \hbar \omega} - 1$
Planck radiation law