

FYS3410 - Vår 2016 (Kondenserte fasers fysikk)

<http://www.uio.no/studier/emner/matnat/fys/FYS3410/v16/index.html>

**Pensum: Introduction to Solid State Physics
by Charles Kittel (Chapters 1-9 and 17, 18, 20)**

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2016 FYS3410 Lectures (based on C.Kittel's Introduction to SSP, Chapters 1-9, 17,18,20)

Module I – Periodic Structures and Defects (Chapters 1-3, 20)

M18/1: 9-12 am	Introduction. Crystal bonding. Periodicity and lattices, Brag diffraction and Laue condition, reciprocal space	3h
<i>W20/1 cancelled</i>		
M25/1: 9-12 am	Ewald construction, interpretation of a diffraction experiment , Brag planes, and Brillouin zones	3h
<i>W27/1 cancelled</i>		
M01/2: 10-12 am	Elastic strain and structural defects in crystals	2h
W03/2: 9-10 am	Atomic diffusion in solids	1h
M08/2: 10-12 am	Summary of Module I	2h

Module II – Phonons (Chapters 4 and 5)

W10/2: 9-10 am	Vibrations in monoatomic and diatomic chains of atoms	1h
M15/2: 10-12am	Periodic boundary conditions, phonons and density of states (DOS)	2h
W17/2: 9-10 am	Planck distribution	1h
M22/2 : 10-12am	Lattice heat capacity: Dulong-Petit, Einstein, and Debye models	2h
<i>W24/2 cancelled</i>		
M29/2: 9-12am	Comparison of different models for lattice heat capacity, thermal conductivity with phonons	3h
W02/3: 9-10 am	Thermal expansion	1h
M07/3: 10-12am	Summary of Module II.	2h

Module III – Electrons (Chapters 6, 7, 18 - pp.528-530, and Appendix D)

W09/3: 9-10 am	Free electron gas (FEG) versus free electron Fermi gas (FEFG)	1h
M14/3: 10-12am	DOS of FEFG in 3D. Effect of temperature – Fermi-Dirac distribution	2h
W16/3: 9-10 am	Heat capacity of FEFG in 3D	1h
W30/3: 9-10 am	DOS in 2D - quantum wells	1h
M04/4: 10-12am	DOS in 1D and 0D, i.e. quantum wires and quantum dots; transport properties of electrons	2h
W06/4: 9-10 am	Origin of the energy band gap	
M11/4: 10-12am	Nearly free electron model. Kronig-Penney model. Empty lattice approximation.	2h
W13/4: 9-10 am	Number of orbitals in a band	1h
M18/4: 10-12am	Summary of Module III.	2h

Module IV – Semiconductors and interfaces (Chapters 8, 9-pp 223-231, 17)

W20/4: 9-10 am	Metals versus semiconductors. Surfaces and interfaces.	1h
M25/4: 9-12 am	Effective mass method.	3h
W27/4: 9-10 am	Intrinsic carrier generation – electrons and holes.	1h
M02/5: 9-12 am	Localized levels for hydrogen-like impurities – donors and acceptors. Doping.	3h
W04/5: 9-10 am	Carrier statistics in semiconductors	1h
M09/5: 9-12 am	p-n junctions	3h
W11/5: 9-10 am	Optoelectronic semiconductor properties and devices	1h
M18/5: 9-12 am	Device demonstrations. Summary of Module IV	3h

Repetition

M23/5 9-12 am	The course in a nutshell	2h
<i>W25/5, M30/5 and W1/6 cancelled</i>		

Exam during week 22 (tentatively 30-31/5)

Lectures 7-8: Planck distribution; Lattice heat capacity: Dulong-Petit, Einstein and Debye models

- **Repetition of phonon DOS**
- **Classical theory for heat capacity of solids treating atoms as classical harmonic oscillators - Dulong-Petit model – success and problems**
- **Einstein model for heat capacity considering quantum properties of oscillators constituting a solid – success and problems**
- **Debye model**
- **Comparison of different models**

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Calculating phonon density of states – DOS – in 1-D

Since atoms s and $s+N$ have the same displacement, we can write:

$$u_s = u_{s+N} \longrightarrow ue^{i(ksa-\omega t)} = ue^{i(k(s+N)a-\omega t)} \longrightarrow 1 = e^{ikNa}$$

This sets a condition on allowed k values:

$$kNa = 2\pi n \rightarrow k = \frac{2\pi n}{Na} \quad n = 1, 2, 3, \dots$$

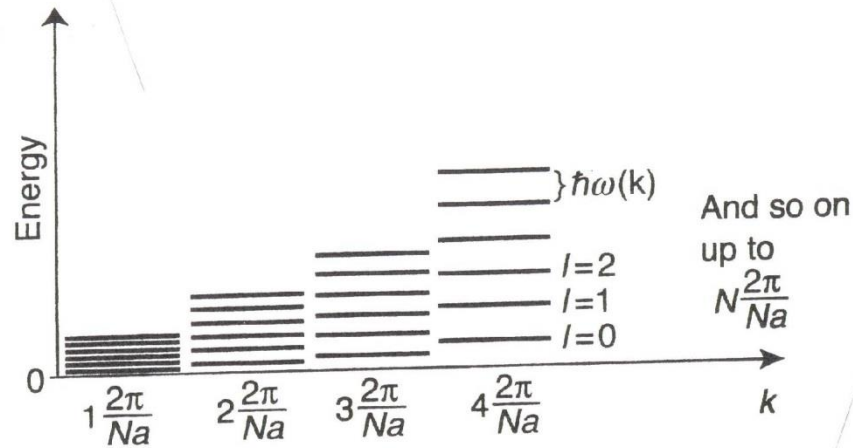
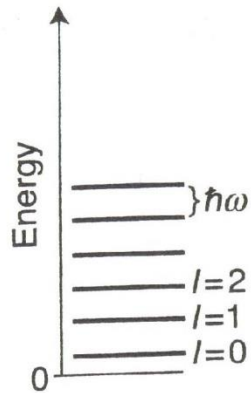
So the separation between allowed solutions (k values) is:

$$\Delta k = \frac{2\pi}{Na} \quad \Delta n = \frac{2\pi}{Na} \quad \text{independent of } k, \text{ so the density of modes in } k\text{-space is uniform}$$

Thus, in 1-D:

$$\frac{\text{\# of modes}}{\text{interval of } k\text{-space}} = \frac{1}{\Delta k} = \frac{Na}{2\pi} = \frac{L}{2\pi}$$

Energy level diagram for one harmonic oscillator



Energy level diagram for a chain of atoms with one atom per unit cell and a length of N unit cells

Lectures 7-8: Lattice heat capacity: Dulong-Petit, Einstein and Debye models

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Classical (Dulong-Petit) theory for heat capacity

For a solid composed of N such atomic oscillators: $\bar{E} = N\bar{E}_1 = 3Nk_B T$

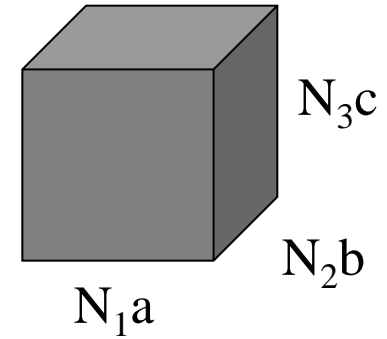
Giving a total energy per mole of sample: $\frac{\bar{E}}{n} = \frac{3Nk_B T}{n} = 3N_A k_B T = 3RT$

So the heat capacity at constant volume per mole is: $C_V = \frac{d}{dT} \left(\frac{\bar{E}}{n} \right)_V = 3R \approx 25 \frac{J}{mol K}$

This law of Dulong and Petit (1819) is approximately obeyed by most solids at high T (> 300 K).

Calculating phonon density of states – DOS – in 3-D

Now for a 3-D lattice we can apply periodic boundary conditions to a sample of $N_1 \times N_2 \times N_3$ atoms:



$$\frac{\# \text{ of modes}}{\text{volume of } k\text{-space}} = \frac{N_1a}{2\pi} \frac{N_2b}{2\pi} \frac{N_3c}{2\pi} = \frac{V}{8\pi^3} = N(k)$$

Now we know from before that we can write the differential # of modes as:

$$dN = N(\omega)d\omega = N(k)d^3\vec{k} = \frac{V}{8\pi^3} d^3\vec{k}$$

We carry out the integration in k -space by using a “volume” element made up of a constant ω surface with thickness dk :

$$d^3\vec{k} = (\text{surface area}) dk = \left[\int dS_\omega \right] dk$$

Calculating phonon density of states – DOS – in 3-D

Rewriting the differential number of modes in an interval:

$$dN = N(\omega)d\omega = \frac{V}{8\pi^3} \int dS_{\omega} dk$$

We get the result:

$$N(\omega) = \frac{V}{8\pi^3} \int dS_{\omega} \frac{dk}{d\omega} = \frac{V}{8\pi^3} \int dS_{\omega} \frac{1}{\frac{\partial \omega}{\partial k}}$$

A very similar result holds for $N(E)$ using constant energy surfaces for the density of electron states in a periodic lattice!

Temperature dependence of experimentally measured heat capacity

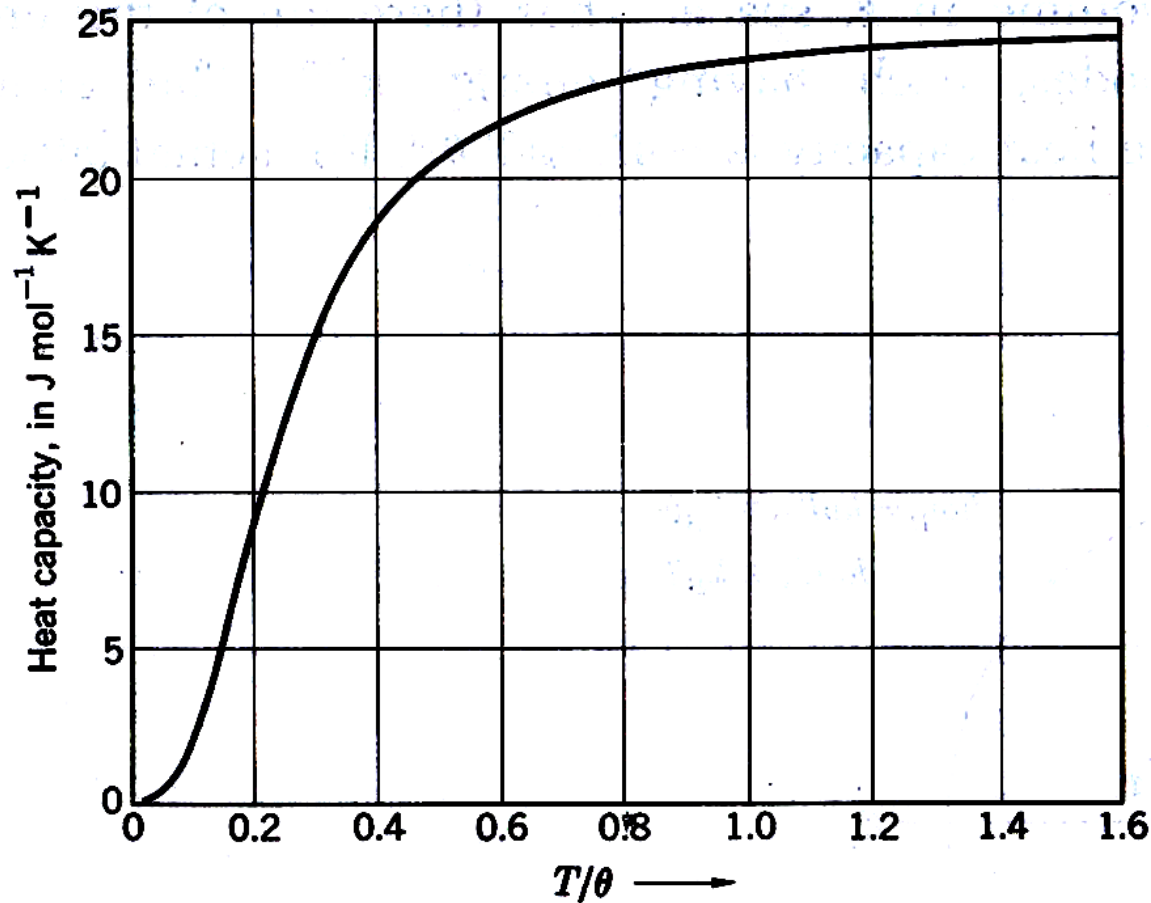


Figure 9a. Heat capacity C_V of a solid, according to the Debye approximation. The vertical scale is in $\text{J mol}^{-1} \text{K}^{-1}$. The horizontal scale is the temperature normalized to the Debye temperature θ . The region of the T^3 law is below 0.1θ . The asymptotic value at high values of T/θ is $24.943 \text{ J mol}^{-1} \text{ deg}^{-1}$.

Lectures 7-8: Lattice heat capacity: Dulong-Petit, Einstein and Debye models

- Repetition of phonon DOS
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- **Einstein model for heat capacity considering quantum properties of oscillators constituting a solid – success and problems**
- Debye model
- Comparison of different models

Einstein model for heat capacity accounting for quantum properties of oscillators constituting a solid

Planck (1900): vibrating oscillators (atoms) in a solid have quantized energies $E_n = n\hbar\omega$ $n = 0, 1, 2, \dots$

[later showed $E_n = (n + \frac{1}{2})\hbar\omega$ actually correct]

Einstein (1907): model a solid as a collection of $3N$ independent 1-D oscillators, all with constant ω , and use Planck's equation for energy levels

occupation of energy level n :
(probability of oscillator
being in level n)

$$f(E_n) = \frac{e^{-E_n/kT}}{\sum_{n=0}^{\infty} e^{-E_n/kT}} \quad \text{classical physics (Boltzmann factor)}$$

Average total
energy of solid:

$$E = U = 3N \sum_{n=0}^{\infty} f(E_n) E_n = 3N \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/kT}}{\sum_{n=0}^{\infty} e^{-E_n/kT}}$$

Boltzmann factor determines Planck distribution

$$e^{-E_i / kT}$$

Boltzmann factor is a weighting factor that determines the relative probability of a state i in a multi-state system in thermodynamic equilibrium at temperature T .

Where k_B is Boltzmann's constant and E_i is the energy of state i . The ratio of the probabilities of two states is given by the ratio of their Boltzmann factors.

Einstein model for heat capacity accounting for quantum properties of oscillators constituting a solid

Using Planck's equation:
$$U = 3N \frac{\sum_{n=0}^{\infty} n \hbar \omega e^{-n \hbar \omega / kT}}{\sum_{n=0}^{\infty} e^{-n \hbar \omega / kT}}$$
 Now let $x \equiv \frac{\hbar \omega}{kT}$

Which can be rewritten:
$$U = 3N \hbar \omega \frac{\sum_{n=0}^{\infty} n e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = 3N \hbar \omega \frac{-\frac{d}{dx} \sum_{n=0}^{\infty} e^{-nx}}{\sum_{n=0}^{\infty} e^{-nx}} = 3N \hbar \omega \frac{-\frac{d}{dx} \sum_{n=0}^{\infty} (e^{-x})^n}{\sum_{n=0}^{\infty} (e^{-x})^n}$$

Now we can use the infinite sum: $\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$ for $|x| < 1$ To give: $\sum_{n=0}^{\infty} (e^{-x})^n = \frac{1}{1-e^{-x}} = \frac{e^x}{e^x - 1}$

So we obtain:
$$U = 3N \hbar \omega \frac{-\frac{d}{dx} \left(\frac{e^x}{e^x - 1} \right)}{\left(\frac{e^x}{e^x - 1} \right)} = \frac{3N \hbar \omega}{e^x - 1} = \frac{3N \hbar \omega}{e^{\hbar \omega / kT} - 1}$$

Einstein model for heat capacity accounting for quantum properties of oscillators constituting solids

Using our previous definition:

$$C_V = \frac{d}{dT} \left(\frac{U}{n} \right)_V = \frac{d}{dT} \left(\frac{3N_A \hbar \omega}{e^{\hbar \omega / kT} - 1} \right)$$

Differentiating:

$$C_V = \frac{-3N_A \hbar \omega \left[e^{\hbar \omega / kT} \left(\frac{-\hbar \omega}{kT^2} \right) \right]}{\left(e^{\hbar \omega / kT} - 1 \right)^2} = \frac{3R \left(\frac{\hbar \omega}{kT} \right)^2 e^{\hbar \omega / kT}}{\left(e^{\hbar \omega / kT} - 1 \right)^2}$$

Now it is traditional to define an “Einstein temperature”:

$$\theta_E \equiv \frac{\hbar \omega}{k}$$

So we obtain the prediction:

$$C_V(T) = \frac{3R \left(\frac{\theta_E}{T} \right)^2 e^{\theta_E / T}}{\left(e^{\theta_E / T} - 1 \right)^2}$$

Einstein model for heat capacity accounting for quantum properties of oscillators constituting solids

High T limit:

$$\frac{\theta_E}{T} \ll 1$$

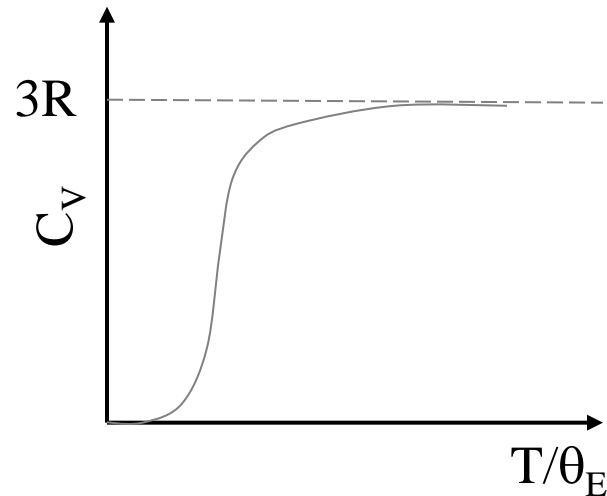
$$C_V(T) \approx \frac{3R \left(\frac{\theta_E}{T}\right)^2 \left(1 + \frac{\theta_E}{T}\right)}{\left(1 + \frac{\theta_E}{T} - 1\right)^2} \approx 3R$$

Low T limit:

$$\frac{\theta_E}{T} \gg 1$$

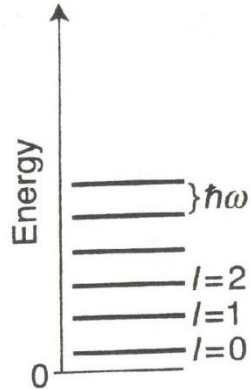
$$C_V(T) \approx \frac{3R \left(\frac{\theta_E}{T}\right)^2 e^{\theta_E/T}}{\left(e^{\theta_E/T}\right)^2} \approx 3R \left(\frac{\theta_E}{T}\right)^2 e^{-\theta_E/T}$$

These predictions are qualitatively correct: $C_V \rightarrow 3R$ for large T and $C_V \rightarrow 0$ as $T \rightarrow 0$:



Correlation with energy level diagram for a harmonic oscillator

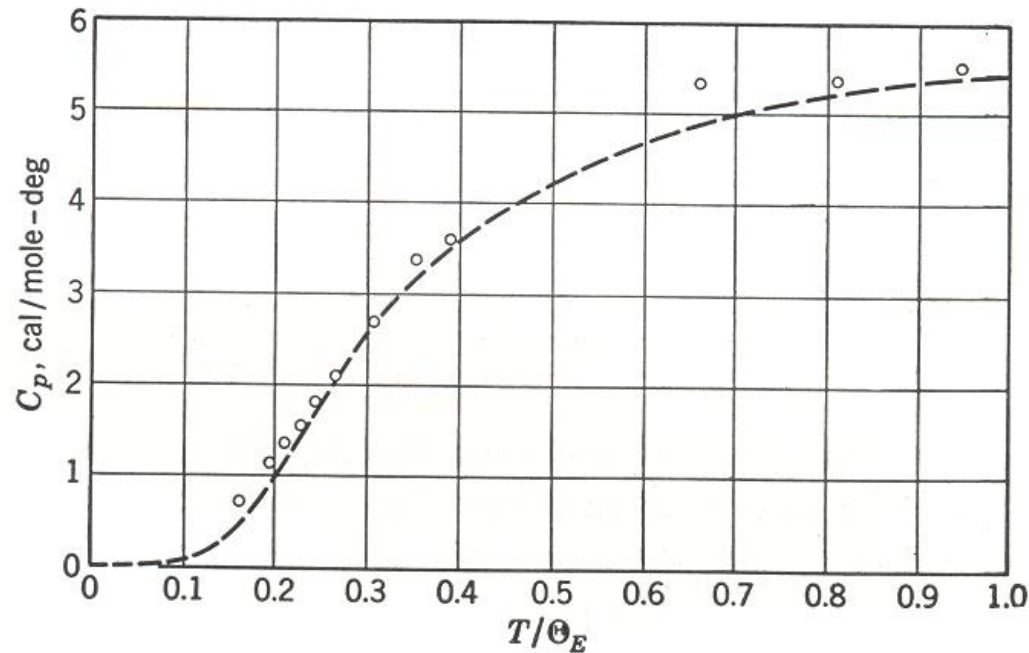
Energy level
diagram for one
harmonic oscillator



High T limit: $\frac{\theta_E}{T} \ll 1$

Low T limit: $\frac{\theta_E}{T} \gg 1$

Problem of Einstein model to reproduce the rate of heat capacity decrease at low temperatures



High T behavior:
Reasonable
agreement with
experiment

Low T behavior:
 $C_V \rightarrow 0$ too quickly
as $T \rightarrow 0$!

Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320^\circ\text{K}$. [After A. Einstein, *Ann. Physik* **22**, 180 (1907).]

Lectures 7-8: Lattice heat capacity: Dulong-Petit, Einstein and Debye models

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More careful consideration of phonon occupancy modes as a way to improve the agreement with experiment

Debye's model of a solid:

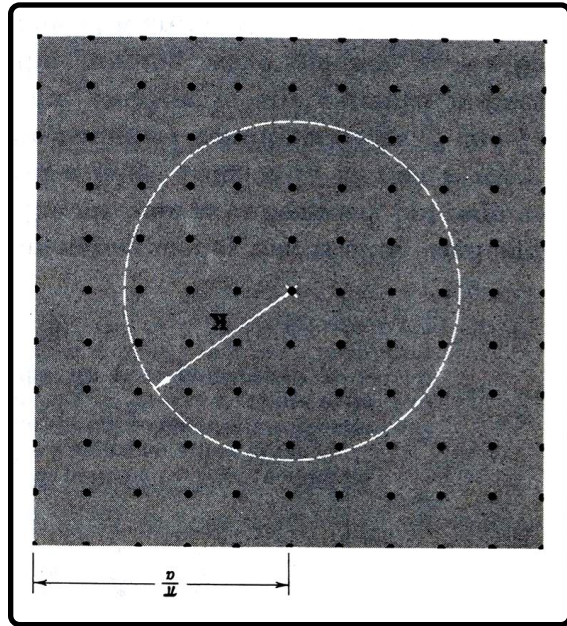
- $3N$ normal modes (patterns) of oscillations
- Spectrum of frequencies from $\omega = 0$ to ω_{\max}
- Treat solid as continuous elastic medium (ignore details of atomic structure)

This changes the expression for C_V because each mode of oscillation contributes a frequency-dependent heat capacity and we now have to integrate over all ω :

$$C_V(T) = \int_{\omega=0}^{\omega_{\max}} \underbrace{D(\omega)}_{\text{# of oscillators per unit } \omega, \text{ i.e. DOS}} \underbrace{C_E(\omega, T)}_{\text{Distribution function}} d\omega$$

of oscillators per unit ω , i.e. DOS Distribution function

Debye model



N_k : Allowed number of k points in a sphere with a radius k

$$k = v / \omega$$

$$N_k = \left(\frac{L}{2\pi} \right)^3 \frac{4\pi}{3} k^3 \quad \downarrow \quad N(\omega) = \left(\frac{L}{2\pi} \right)^3 \frac{4\pi\omega^3}{3v^3} = \frac{V\omega^3}{6\pi^2v^3}$$

Density of states of acoustic phonons for 1 polarization

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

Debye temperature θ

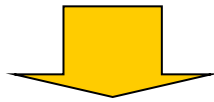
$$N = \frac{V\omega_D^3}{6\pi^2v^3} \quad \Rightarrow \quad \hbar\omega_D = k_B\theta$$

N : number of unit cell

$$\theta = \frac{\hbar v}{k_B} \left(\frac{6\pi^2 N}{V} \right)^{\frac{1}{3}}$$

Thermal energy U and lattice heat capacity C_V : Debye model

3 polarizations for acoustic modes



$$U = 3 \int d\omega D(\omega) n(\omega) \hbar \omega = 3 \int_0^{\omega_D} d\omega \frac{V \omega^2}{2\pi^2 v^3} \frac{\hbar \omega}{\exp(\hbar \omega / k_B T) - 1}$$

$$C_V = \left(\frac{\partial U}{\partial T} \right) \Big|_V = \frac{3V \hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 \exp(\hbar \omega / k_B T)}{[\exp(\hbar \omega / k_B T) - 1]^2}$$

$$C_V = 9Nk_B \left(\frac{T}{\theta} \right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2}$$

Debye model

Better agreement
than Einstein
model at low T

Universal behavior
for all solids!

Debye temperature
is related to
“stiffness” of solid,
as expected

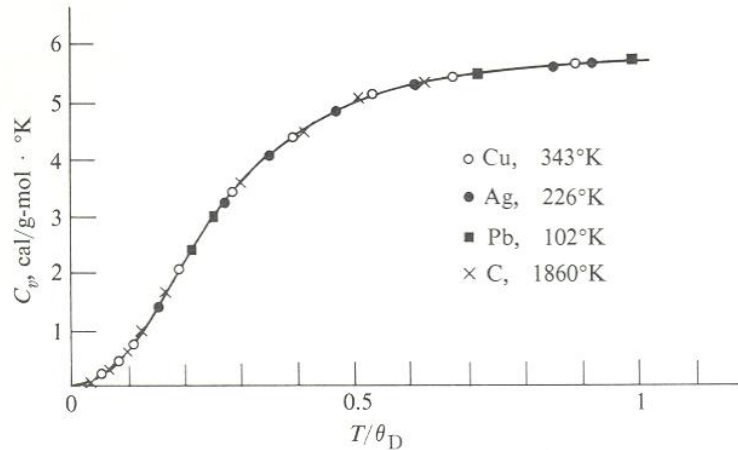


Fig. 3.13 Specific heats versus reduced temperature for four substances. Numbers refer to Debye temperatures. Note the high Debye temperature for diamond.

Table 3.1
Debye Temperatures

Element	$\theta_D, ^\circ\text{K}$	Compound	$\theta_D, ^\circ\text{K}$
Li	335	NaCl	280
Na	156	KCl	230
K	91.1	CaF ₂	470
Cu	343	LiF	680
Ag	226	SiO ₂ (quartz)	255
Au	162		
Al	428		
Ga	325		
Pb	102		
Ge	378		
Si	647		
C	1860		

Debye model

Quite impressive agreement with predicted $C_V \propto T^3$ dependence for Ar! (noble gas solid)

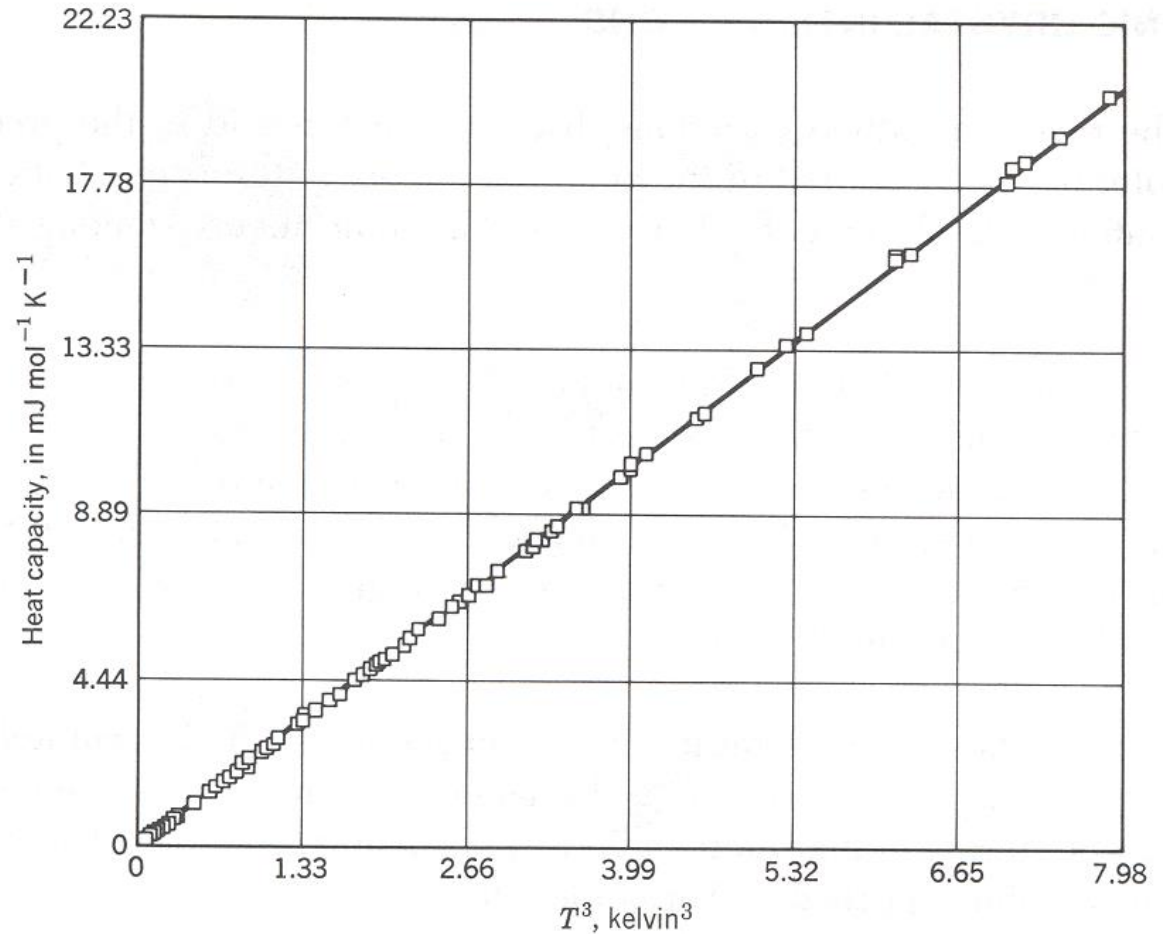
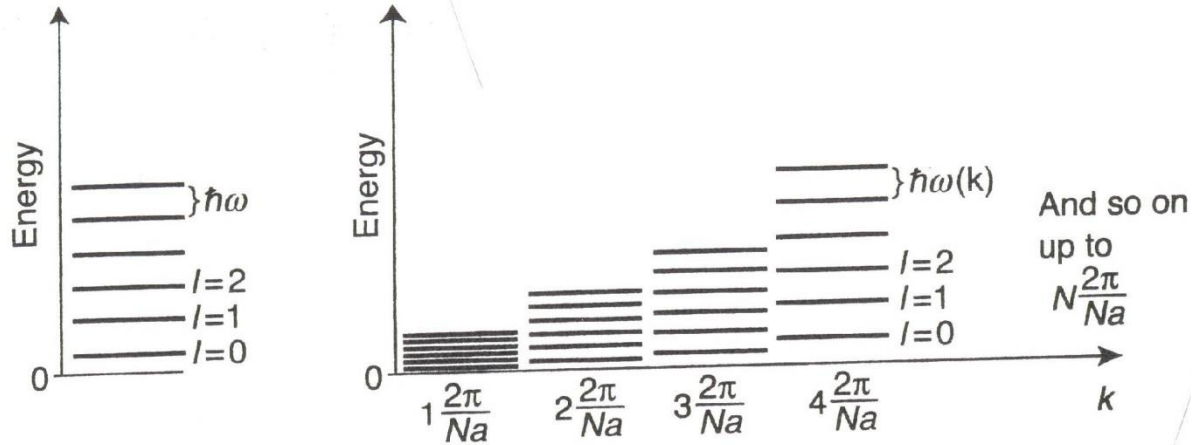


Figure 11 Low temperature heat capacity of solid argon, plotted against T^3 . In this temperature region the experimental results are in excellent agreement with the Debye T^3 law with $\theta_0 = 92.0$ K. (Courtesy of L. Finegold and N. E. Phillips.)

More careful consideration of phonon occupancy modes as a way to improve the agreement with experiment

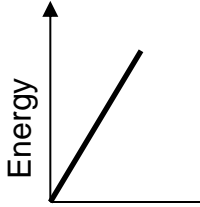


Energy level diagram for a chain of atoms with one atom per unit cell and a length of N unit cells

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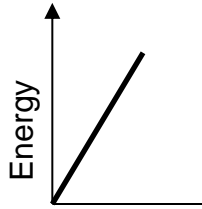
Ensemble of $3N$ independent harmonic oscillators modeling vibrations in a solid



**Classical
oscillators**

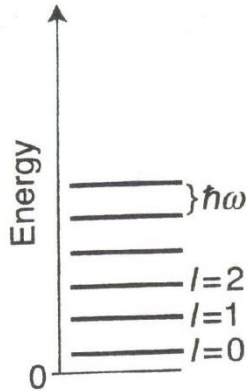
Any energy state is accessible for any oscillator in form of $k_B T$, i.e. no distribution function is applied and the total energy is $\bar{E} = N\bar{E}_1 = 3Nk_B T$

Ensemble of 3N independent harmonic oscillators modeling vibrations in a solid



**Classical
oscillators**

Any energy state is accessible for any oscillator in form of $k_B T$, i.e. no distribution function is applied and the total energy is $\bar{E} = N\bar{E}_1 = 3Nk_B T$



**Quantum
oscillators**

Not all energies are accessible, but only those in quanta of $\hbar\omega n$, and Planck distribution is employed to calculate the occupancy at temperature T, so that $E = 3N \cdot \langle n \rangle \cdot \hbar\omega$

$$E = 3N \sum_{n=0}^{\infty} f(E_n) E_n = 3N \frac{\sum_{n=0}^{\infty} E_n e^{-E_n/k_B T}}{\sum_{n=0}^{\infty} e^{-E_n/k_B T}} = 3N \frac{1}{e^{\hbar\omega/k_B T} - 1} \cdot \hbar\omega$$

Ensemble of $3N$ independent harmonic oscillators modeling vibrations in a solid

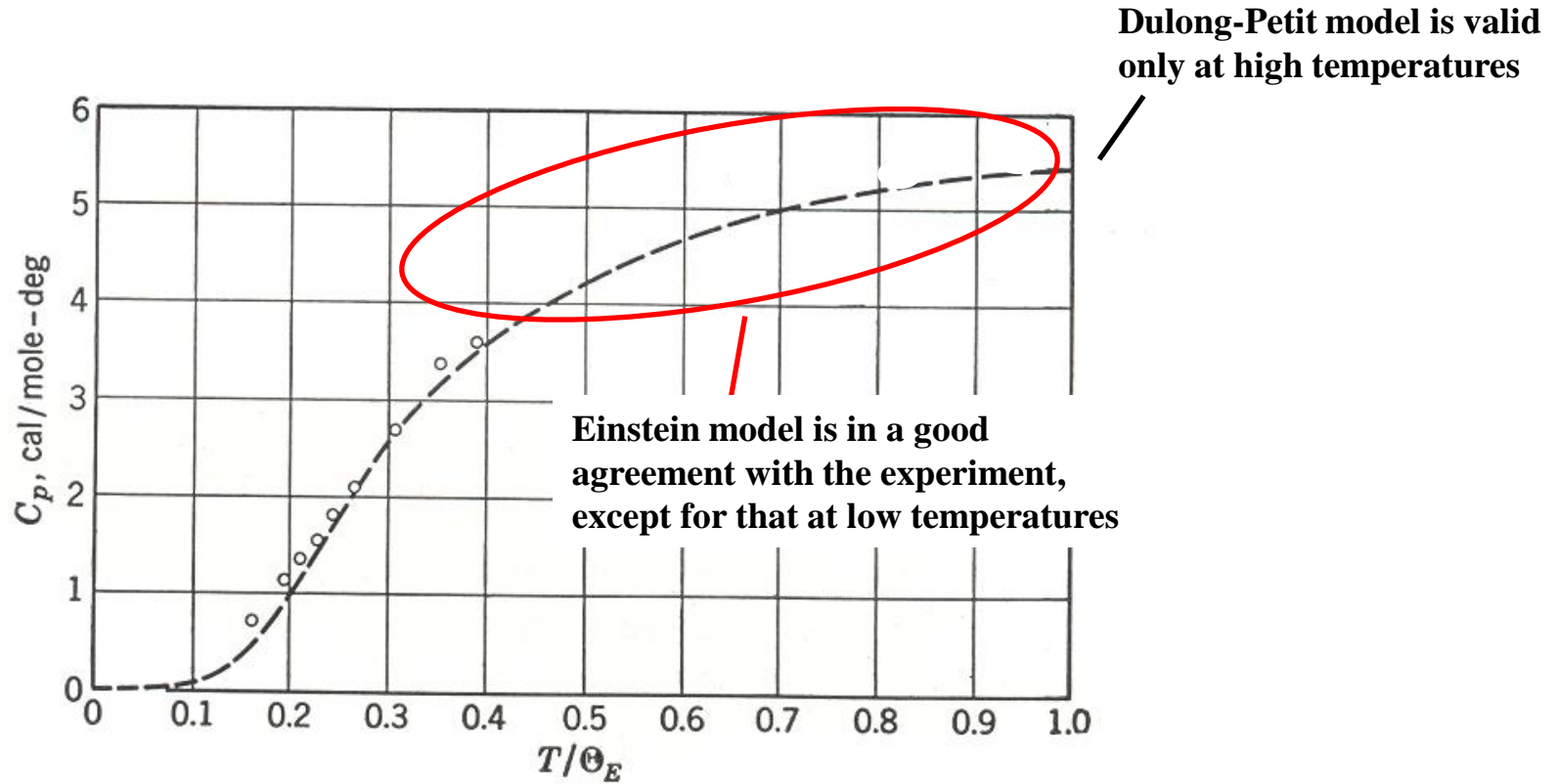
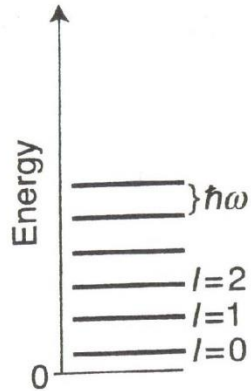
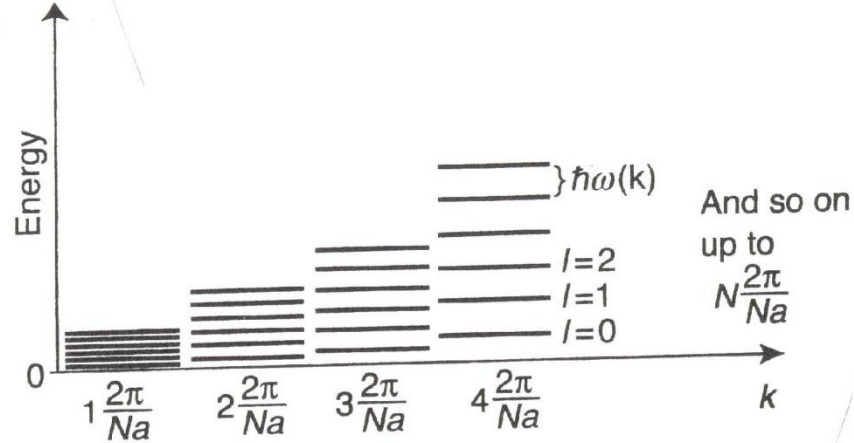


Fig. 6.2. Comparison of experimental values of the heat capacity of diamond and values calculated on the Einstein model, using $\Theta_E = 1320^\circ\text{K}$. [After A. Einstein, *Ann. Physik* **22**, 180 (1907).]

Energy level diagram for one harmonic oscillator



Energy level diagram for a chain of atoms with one atom per unit cell and a length of N unit cells



$$E = 3N \cdot \langle n \rangle \cdot \hbar\omega$$

$$E = 3 \int_{\omega_{\min}}^{\omega_{\max}} d\omega D(\omega) \langle n \rangle \hbar\omega$$

