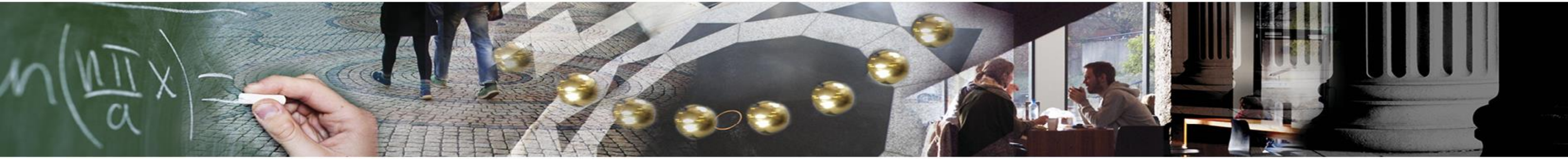
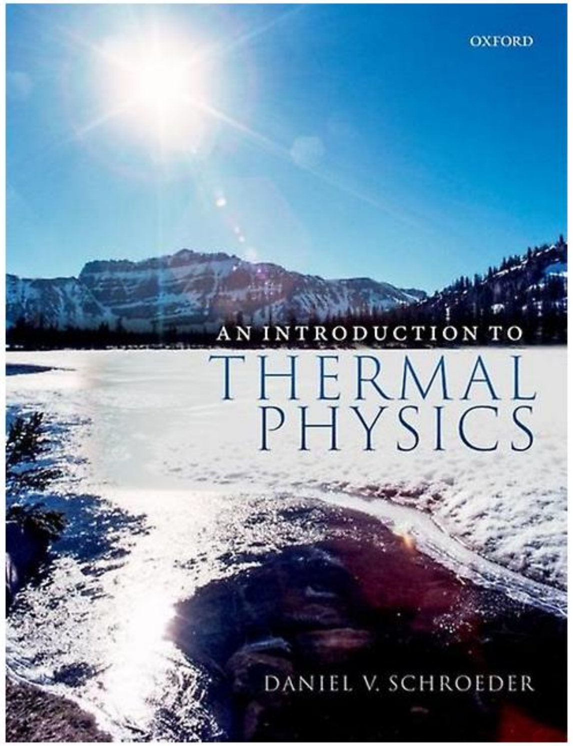


UiO : University of Oslo

Heat capacity



7.5 Debye Theory of Solids

[Misconceptions About Temperature - YouTube]

Heat capacity

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} \qquad \left(\frac{\partial S}{\partial U}\right)_{N,V} \equiv \frac{1}{T} \qquad \frac{\partial S}{\partial U \partial T} \equiv \frac{1}{T \partial T} \qquad T\frac{\partial S}{\partial T} \equiv \frac{\partial U}{\partial T} \equiv C_V$$

$$dU = TdS - PdV \qquad C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P.$$

Equipartition theorem: $U = Nf\frac{1}{2}kT$ $\qquad k = 1.381\ 10^{-23}\ J/K$

Ideal gas: $PV = NkT$

Single-atom ideal gas

$$C_V = \frac{3}{2}Nk = \frac{3}{2}nR$$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{NfkT}{2}\right) = \frac{Nfk}{2}$$

$$C_P = C_V + Nk = C_V + nR$$

$$c_V = f\frac{R}{2}, \quad c_p = (f+2)\frac{R}{2}$$

$$c_p - c_V = R = 8.314\,4598(48)\ \mathrm{J/(K \cdot mol)}.$$

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Adiabatic compression

$$dU = \cancel{TdS} - PdV$$

Equipartition theorem: $U = Nf\frac{1}{2}kT$

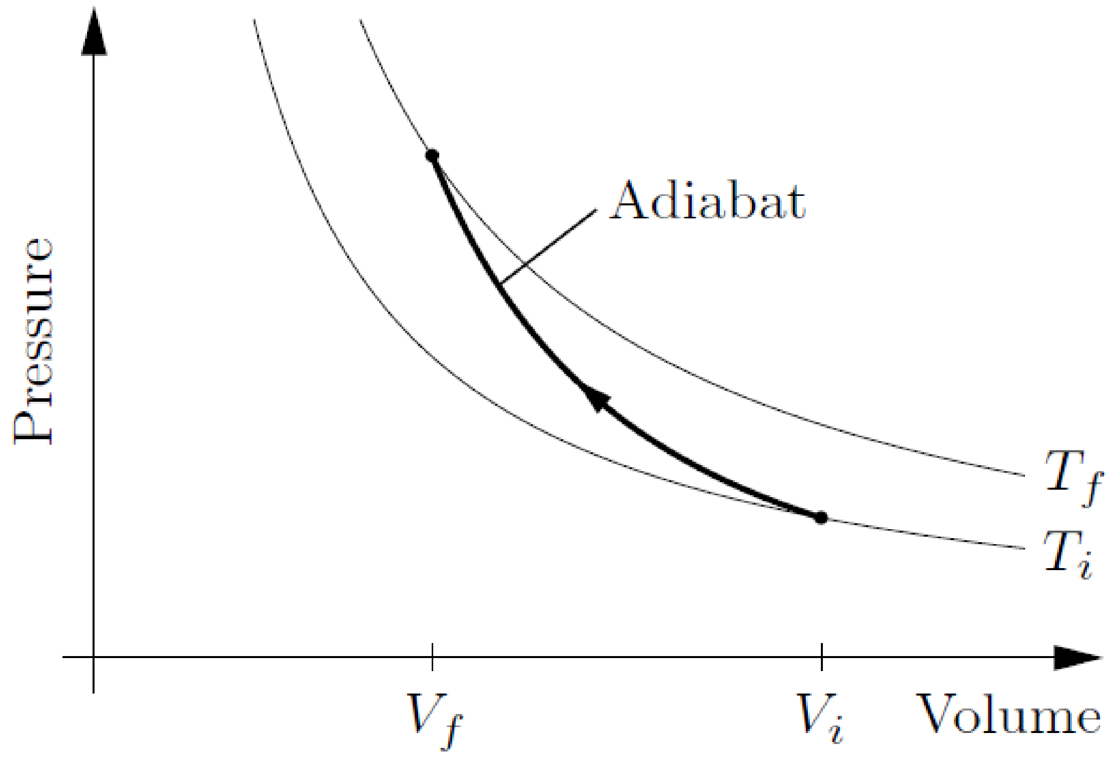
Ideal gas: $PV = NkT$

$$\frac{f}{2}\frac{dT}{T} = -\frac{dV}{V}$$

Integrating both sides:

$$\frac{f}{2}\ln\frac{T_f}{T_i} = -\ln\frac{V_f}{V_i} \qquad V_f\,T_f^{f/2} = V_i\,T_i^{f/2}$$

$$VT^{f/2} = \text{constant} \qquad V^{\gamma}P = \text{constant}$$



pV^{γ}, $TV^{\gamma-1}$, and $Tp^{1/\gamma-1}$ are constants.

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Propagation of sound

Speed of sound c depends on the density ρ of the gas and the adiabatic compression modulus K.

$$K = -V\frac{dp}{dV} = \gamma p \implies$$

$$c = \sqrt{\frac{K}{\rho}} = \sqrt{\frac{\gamma p}{\rho}} = \sqrt{\frac{(f+2)p}{f\rho}}$$

From $\rho = m/V = nM_{\mathrm{mol}}/V$ and $pV = nRT$

$$c_{\mathrm{id}}(T) = \sqrt{\frac{(f+2)RT}{fM_{\mathrm{mol}}}}$$

Kundt's tube experiments

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

K1: contains argon or CO_2 at $T = T_{\mathrm{room}}$
K2: contains air at $T = T_{\mathrm{room}}$
K3: contains air at $T \simeq 70$ °C
K4: contains air at $T \simeq 50$ °C

pV^γ, $TV^{\gamma-1}$, and $Tp^{1/\gamma-1}$ are constants.

$$\gamma = \frac{c_p}{c_V} = \frac{f+2}{f}$$

Kundt's tube experiments

$$\nu_n = an + b, \qquad a = \frac{c}{2L}$$

$T(°C) \approx 25 - 24 \ln r$

$r = R_t/(10^5\,\Omega)$

K1: contains argon or CO_2 at $T = T_{room}$
K2: contains air at $T = T_{room}$
K3: contains air at $T \simeq 70$ °C
K4: contains air at $T \simeq 50$ °C

$$c_{id}(T) = \sqrt{\frac{(f+2)RT}{f M_{mol}}}$$

Measuring latent heat of melting

$$m[H_m + C_v(T_2 - T_0)] = C_0(T_1 - T_2)$$

- Please notice that C_v and C_0 have different units of $J/(K \cdot kg)$ and J/K, respectively.
- m is mass in kg.
- H_m will be in J/kg.
- For re-calculation of H_m from J/kg to J/mol using molar weight of water of 18.02 g/mol.

Heat capacity experiments

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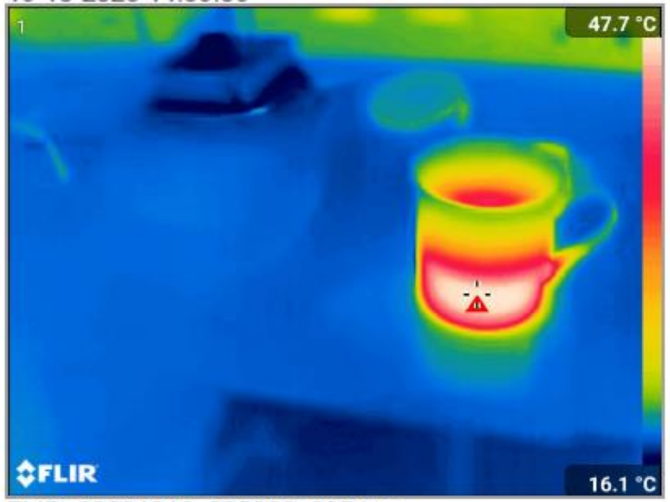

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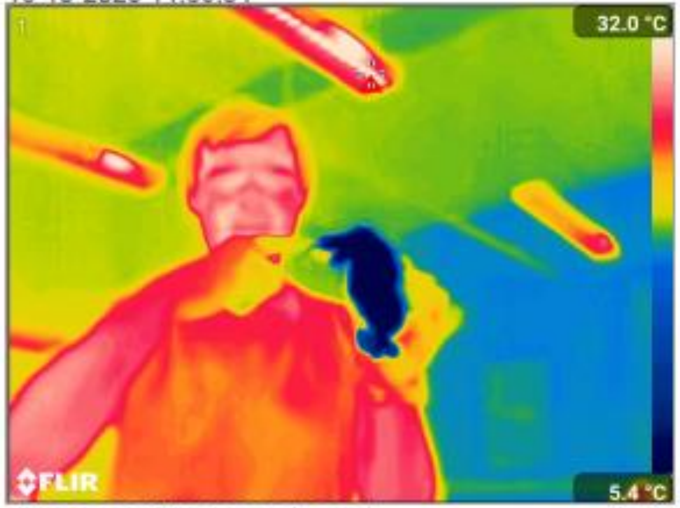

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Heat capacity experiments

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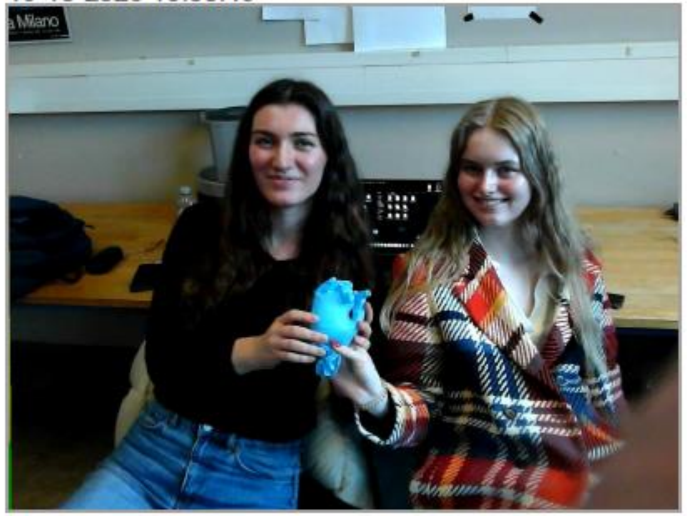

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The **third law** of thermodynamics

$$S = k \ln \Omega$$

$$\boldsymbol{S_{T=0} = 0}$$

At zero temperature, a system should settle into its unique lowest-energy state with Ω = 1 and S = 0.

$$dU = TdS - PdV$$

Heat capacity: $C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V}$.

$$T\frac{\partial S}{\partial T} \equiv \frac{\partial U}{\partial T} \equiv C_V \qquad S(T) = \int_0^T \frac{C_V(T')}{T'}\,dT'$$

Heat capacity goes to zero as T goes to zero: $C_V \to 0 \; as \; T \to 0.$

Einstein solid

Planck constant

h = 6.62607015 × 10^{-34} joule second

$\hbar = h/2\pi$ = 1.054571817 × 10^{-34} J s

$E = \hbar\omega \quad p = \hbar\boldsymbol{k} \quad \boldsymbol{k} = 2\pi/\lambda \quad \omega = 2\pi\nu$

wave vector and wave length

Einstein solid treats a material as system of oscillators (atoms) vibrating at the same frequency ν and quantized energy $\epsilon = h\nu$.

For N oscillators and q energy units, multiplicity of the system is:

$$\Omega = \frac{(N+q-1)!}{(N-1)!\,q!} \approx \frac{(N+q)!}{(N)!\,q!}$$

Stirling's approximation $N! \approx N^N e^{-N}\cancel{\sqrt{2\pi N}}$

$$\Omega(N,q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N$$

$$\boldsymbol{S} = k\ln\Omega = k\left((q+N)\ln(q+N) - q\ln q - N\ln N\right)$$

Heat capacitance of Einstein solid

N′ is number of oscillators

$$\boldsymbol{S} = k \ln\Omega = k\left((\mathrm{q}+\mathrm{N}')\ln(q+\mathrm{N}') - q ln q - \mathrm{N}' ln \mathrm{N}'\right)$$

$$\left(\frac{\partial S}{\partial U}\right)_{\mathrm{N}',V} \equiv \frac{1}{T} \qquad U = \epsilon q \qquad \frac{1}{T} = \frac{k}{\epsilon}\left(\ln(q+\mathrm{N}') - ln q\right) = \frac{k}{\epsilon}\left(\ln\left(1+\frac{\mathrm{N}'}{q}\right)\right)$$

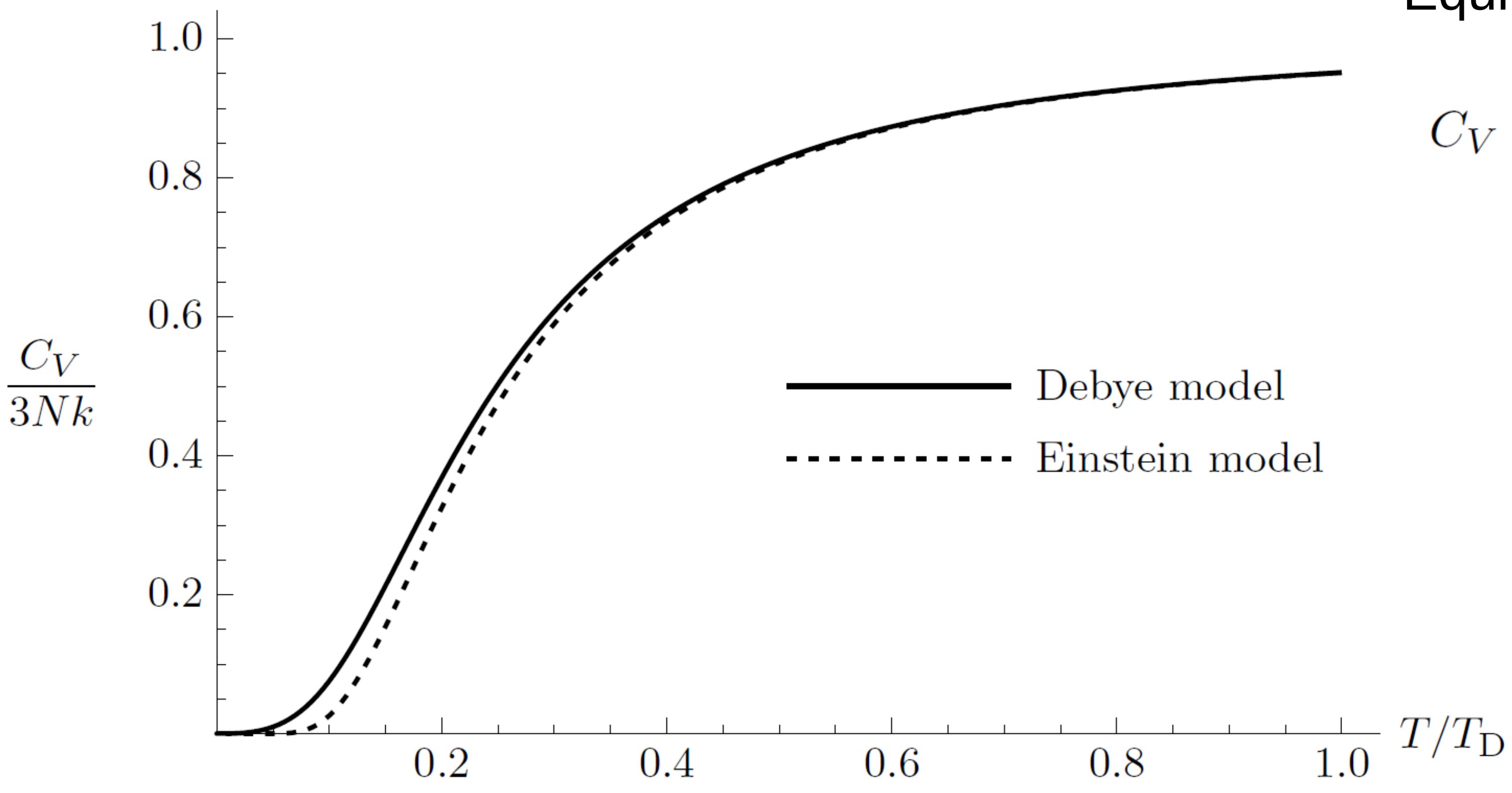
$$q = \mathrm{N}' \cdot \left(e^{\frac{\epsilon}{kT}} - 1\right)^{-1} \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_{\mathrm{N}',V} = \frac{\partial U}{\partial q}\frac{\partial q}{\partial T}$$

N is number of atoms

$$\mathrm{N}' = 3N \qquad C_V = 3Nk\frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(e^{\epsilon/kT}-1)^2}$$

When $kT \gg \epsilon, C_V = 3Nk$ At $kT \ll \epsilon, C_V = 3Nk\frac{(\epsilon/kT)^2}{e^{\epsilon/kT}}$

Einstein model



Equipartition theorem: $U = Nf\frac{1}{2}kT$

$$C_V = \frac{\partial U}{\partial T} = \frac{\partial}{\partial T}\left(\frac{NfkT}{2}\right) = \frac{Nfk}{2}$$

When $kT \gg \epsilon, C_V = 3Nk$

At $kT \ll \epsilon, C_V = 3Nk\frac{(\epsilon/kT)^2}{e^{\epsilon/kT}}$

Heat capacity of photon gas

Total energy density: $$\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15(hc)^3}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aT^3, \qquad a = \frac{8\pi^5 k^4 V}{15(hc)^3}.$$

Heat capacity of photon gas is proportional to T^3

Comparison of photons and phonons

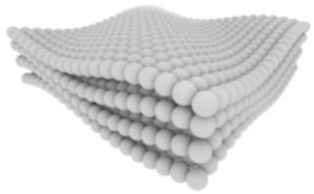
Similarities

- Low-energy excitations of a solid material are not oscillations of a single atom, but collective modes propagating through the material (Peter Debye,1912).
- Oscillations of a solid crystal are similar to oscillations of electromagnetic field in vacuum. Quanta of both waves are bosons with zero chemical potential.

Differences

- Sound waves travel much slower than light waves, at a speed that depends on the stiffness and density of the material.
- Light waves are polarized transversely, whereas sound waves can also be longitudinally polarized.
- The transversely polarized waves are called shear waves, or S-waves, while longitudinally polarized waves are called pressure waves, or P-waves. Instead of two polarizations for electromagnetic waves, sound waves have three polarizations.
- Light waves can have arbitrarily short wavelengths. The wavelength of sound waves is restricted by the atomic spacing.

Heat capacity of phonon gas



Low-energy excitations of a solid material are not oscillations of a single atom, but collective modes propagating through the material (Peter Debye,1912).

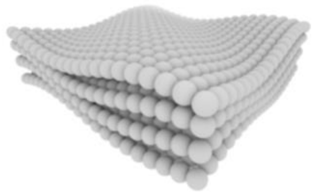
Kelvin: Thermodynamic Temperature | NIST

- Collective quantised motions are called phonons propagating with speed of sound c_s
- There is integer number of wavelengths on each length of the sample
- Smallest wavelength is equal to distance between atoms in solid
- Phonons are bosons with zero chemical potential (as for photons)
- Average number of phonons with energy ϵ is:

$$\bar{n}_{ph} = \frac{1}{e^{\frac{\epsilon}{kT}} - 1}$$

There are many states in the system with energy $\epsilon = pc_s$
To calculate them, it is convenient to use momentum space

Density of phonon states



Kelvin: Thermodynamic Temperature | NIST

Average number of phonons with energy ϵ is:

$$\bar{n}_{ph} = \frac{1}{e^{\frac{\epsilon}{kT}} - 1}$$

Number of states with energy $\epsilon = pc_s$ can be calculated using momentum space p or $\hbar\boldsymbol{k}$

If the sample is cube with dimensions $L \times L \times L$, k is quantised in units of $\frac{2\pi}{L}$ or p in units of $\hbar\boldsymbol{k} = \frac{2\pi\hbar}{L} = \frac{h}{L}$. For cubic lattice, maximum p_{max} is $\frac{h}{a}$, where a is distance between atoms.

The total number of states n at a maximum momentum p is $N = \frac{4\pi}{3}p^3/\left(\frac{h}{L}\right)^3$

Since $\epsilon = pc_s$, total number of states is: $N = \frac{4\pi}{3}p^3/\left(\frac{h}{L}\right)^3 = \frac{4\pi V}{3}\epsilon^3/(hc_s)^3$

In a solid with N primitive cells (with one atom per cell), there are N phonon modes.

The density of states is then: $D(\epsilon) = dN/d\epsilon = V(4\pi\epsilon^2)/(hc_s)^3$

Total energy of solid

Average number of phonons with energy ϵ is:

$$\bar{n}_{ph} = \frac{1}{e^{\frac{\epsilon}{kT}} - 1}$$

Total energy is:

$$U = 3\int_0^{\epsilon_{max}} \bar{n}_{ph}\epsilon d(\epsilon) d\epsilon$$

3 is due to three different polarizations.

$$U = 3\int_0^{\epsilon_{max}} \frac{V(4\pi\epsilon^3 d\epsilon)/(hc_s)^3}{e^{\frac{\epsilon}{kT}} - 1}$$

$$x = \frac{\epsilon}{kT}$$

$$\epsilon_{max} = kT_D$$

$$U = \frac{12\pi V k^4 T^4}{(hc_s)^3}\int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1}$$

Debye temperature

$\epsilon_{max} = kT_D$ $\epsilon = pc_s$

In a solid with N primitive cells (one atom per cell) there are N phonon modes.

Calculating number of modes:

The total number of states N at maximum momentum p_{max} is $N = \frac{4\pi}{3} {p_{max}}^3 / \left(\frac{h}{L}\right)^3$. Number of states as function of maximum energy is then:

$$N = \frac{4\pi}{3}(\epsilon_{max})^3 / \left(\frac{hc_s}{L}\right)^3$$

$$N = \frac{4\pi}{3}(\epsilon_{max})^3 / \left(\frac{2\pi\hbar c_s}{L}\right)^3 = \frac{V}{6\pi^2}(\epsilon_{max})^3 / (\hbar c_s)^3$$

$$\epsilon_{max} = \hbar c_s \left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}} \qquad T_D = \frac{\hbar c_s}{k}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}}$$

T_D of different materials

Aluminum	428K	Iron	470K
Cadmium	209K	Lead	105K
Chromium	630K	Manganese	410K
Copper	343.5K	Nickel	450K
Gold	165K	Platinum	240K
Silicon	645K	Tungsten	400K
Silver	225K	Zinc	327K
Tantalum	240K	Carbon	2230K
Tin(white)	200K	Ice	192K
Titanium	420K		

Total energy

$$U = \frac{12\pi V k^4 T^4}{(hc_s)^3} \int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1} \qquad T_D = \frac{\hbar c_s}{k}\left(\frac{6\pi^2 N}{V}\right)^{\frac{1}{3}} \Rightarrow V = 6\pi^2 N \left(\frac{\hbar c_s}{T_D k}\right)^3$$

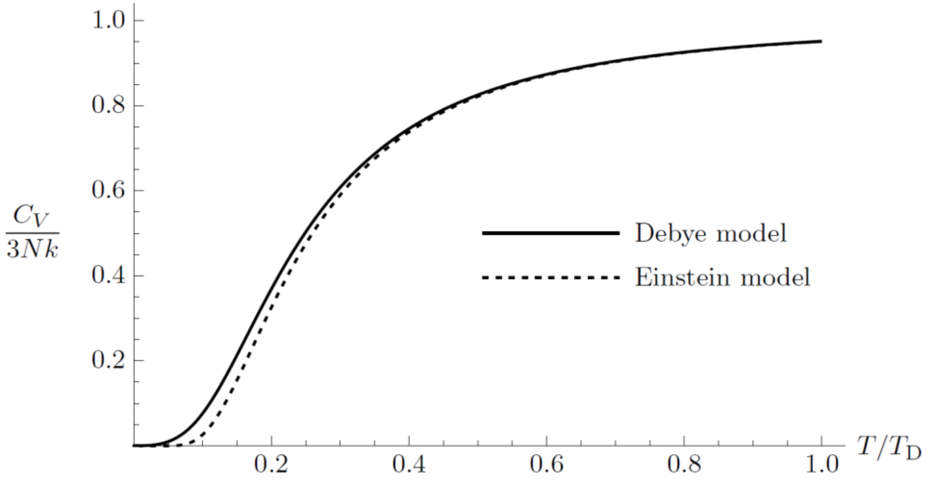
The total number of states N up to maximum energy:

$$U = 6\pi^2 N \left(\frac{\hbar c_s}{T_D k}\right)^3 \frac{12\pi k^4 T^4}{\underset{\substack{\Uparrow \\ 2\pi\hbar}}{(hc_s)^3}} \int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1} = \frac{9NkT^4}{(T_D)^3} \int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1}$$

$$U = \frac{9NkT^4}{T_{\mathrm{D}}^3} \int_0^{T_{\mathrm{D}}/T} \frac{x^3}{e^x - 1} dx. \qquad \text{D.V.S} \quad (7.112)$$

Heat capacity: general expression

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



$$U = \frac{9NkT^4}{(T_D)^3}\int_0^{\frac{T_D}{T}} \frac{x^3 dx}{e^x - 1}$$

$$N = \frac{4\pi V}{3(hc_s)^3}(kT_D)^3$$

$$D(\epsilon) = dN/d\epsilon = V(4\pi\epsilon^2)/(hc_s)^3$$

$$U = 3\int_0^{\epsilon_{max}} \frac{\epsilon V(4\pi\epsilon^2)/(hc_s)^3 d\epsilon}{e^{\frac{\epsilon}{kT}} - 1}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3\int_0^{\epsilon_{max}} \frac{\epsilon V(4\pi\epsilon^2 d\epsilon)/(hc_s)^3 e^{\frac{\epsilon}{kT}}\epsilon}{\left(e^{\frac{\epsilon}{kT}} - 1\right)^2 kT^2}$$

$$V = 6\pi^2 N\left(\frac{\hbar c_s}{T_D k}\right)^3$$

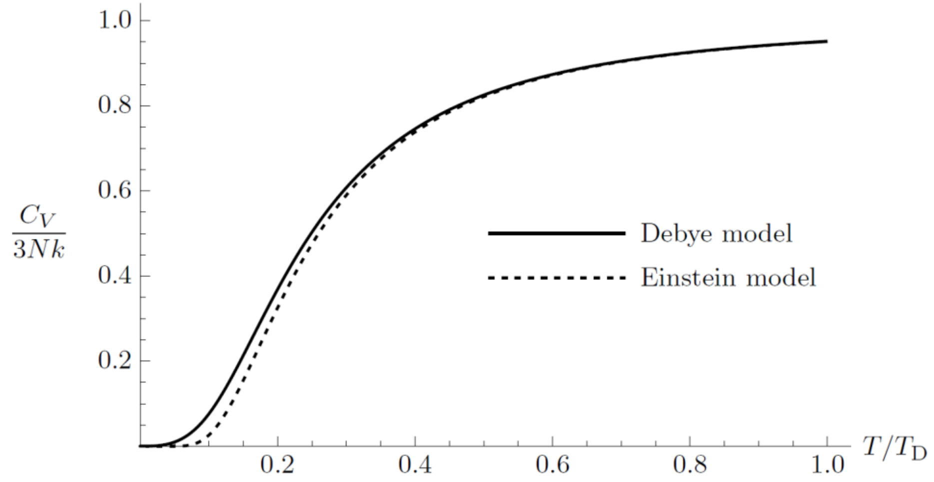
$$C_V = 9Nk\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2}\, dx$$

D.V.S

Heat capacity: limits of high and low temperatures

$$k = 1.381\ 10^{-23}\ J/K$$

$$C_V = 9Nk\left(\frac{T}{T_\mathrm{D}}\right)^3 \int_0^{T_\mathrm{D}/T} \frac{x^4\, e^x}{(e^x-1)^2}\, dx$$



$$x = \frac{\epsilon}{kT}$$

When $kT \gg \epsilon,\ e^x \approx 1 + x$

$$C_V = 9Nk\left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} x^2\, dx = 9Nk\left(\frac{T}{T_D}\right)^3 \frac{1}{3}\left(\frac{T_D}{T}\right)^3 = 3Nk$$

When $kT \ll \epsilon,\ e^x - 1 \approx e^x$

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

$$C_V = 9Nk\left(\frac{T}{T_D}\right)^3 \int_0^{\infty} \frac{x^4}{e^x}\, dx = 9Nk\left(\frac{T}{T_D}\right)^3 \frac{4\pi^4}{15}$$

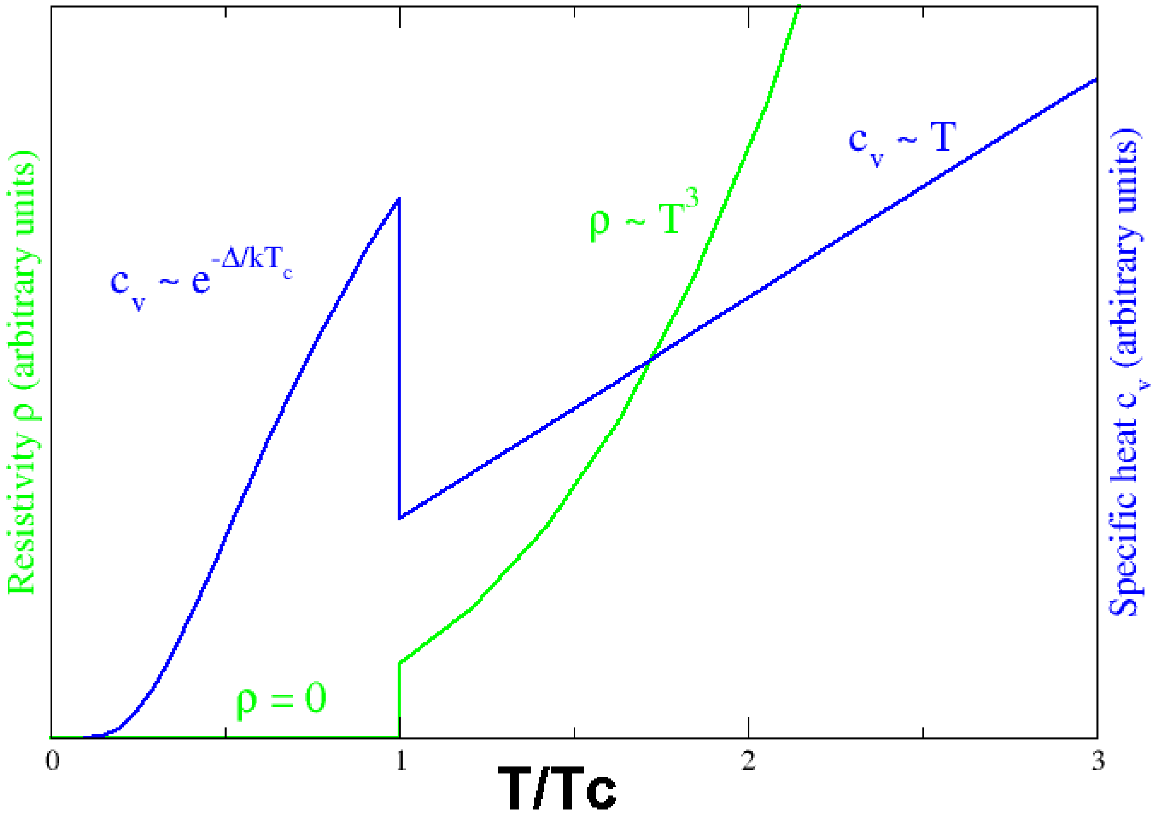
$$U = \frac{9NkT^4}{(T_D)^3}\int_0^{\infty} \frac{x^3 dx}{e^x - 1} = \frac{9NkT^4}{(T_D)^3}\frac{\pi^4}{15}$$

Bose-Einstein condensation and superconductivity

- Superconductivity is the result of Bose-Einstein condensation taking place when fermions form bosons being united into Cooper pairs.
- As a result, electron gas acquires property of superfluidity dropping resistance to absolute zero.
- Superconductors have unique quantum properties allowing multiple uses in modern technology.

Fermi gas: $$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2 N k^2 T}{2\epsilon_F}$$

Superconductor:



Created by Alison Chaiken https://commons.wikimedia.org/wiki/File:Cvandrhovst.png

Quantum superconducting brain

https://www.epfl.ch/campus/spiritual-care/wp-content/uploads/2018/10/quantum-mind.jpg

Summary

- Heat capacity is important parameter in both classical thermodynamics and quantum statistics.
- Heat capacity of solids is defined by quantised collective oscillations of crystal lattice named phonons.
- The wavelength of phonons is restricted by the distance between atoms. The frequency of phonons is inversely proportional to the wavelength and proportional to speed of sound.
- Debye temperature provides temperature scale for the heat capacity. It is maximal energy of phonons divided by the Boltzmann constant.
- Heat capacity of solids is proportional to T^3 at low temperatures and approaches to $3Nk$ at high temperatures.