Phonons

Thermal properties

1. **Determine the dispersion relation:**

   Write down the equations of motion (masses and springs).

   The solutions to these equations will be

$$A_k \exp\left(i\left(\vec{k}\cdot\vec{a}_1 + \vec{k}\cdot\vec{a}_2 + \vec{k}\cdot\vec{a}_3 - \omega t\right)\right)$$

   Substitute the solutions into the equations of motion to determine the dispersion relation.

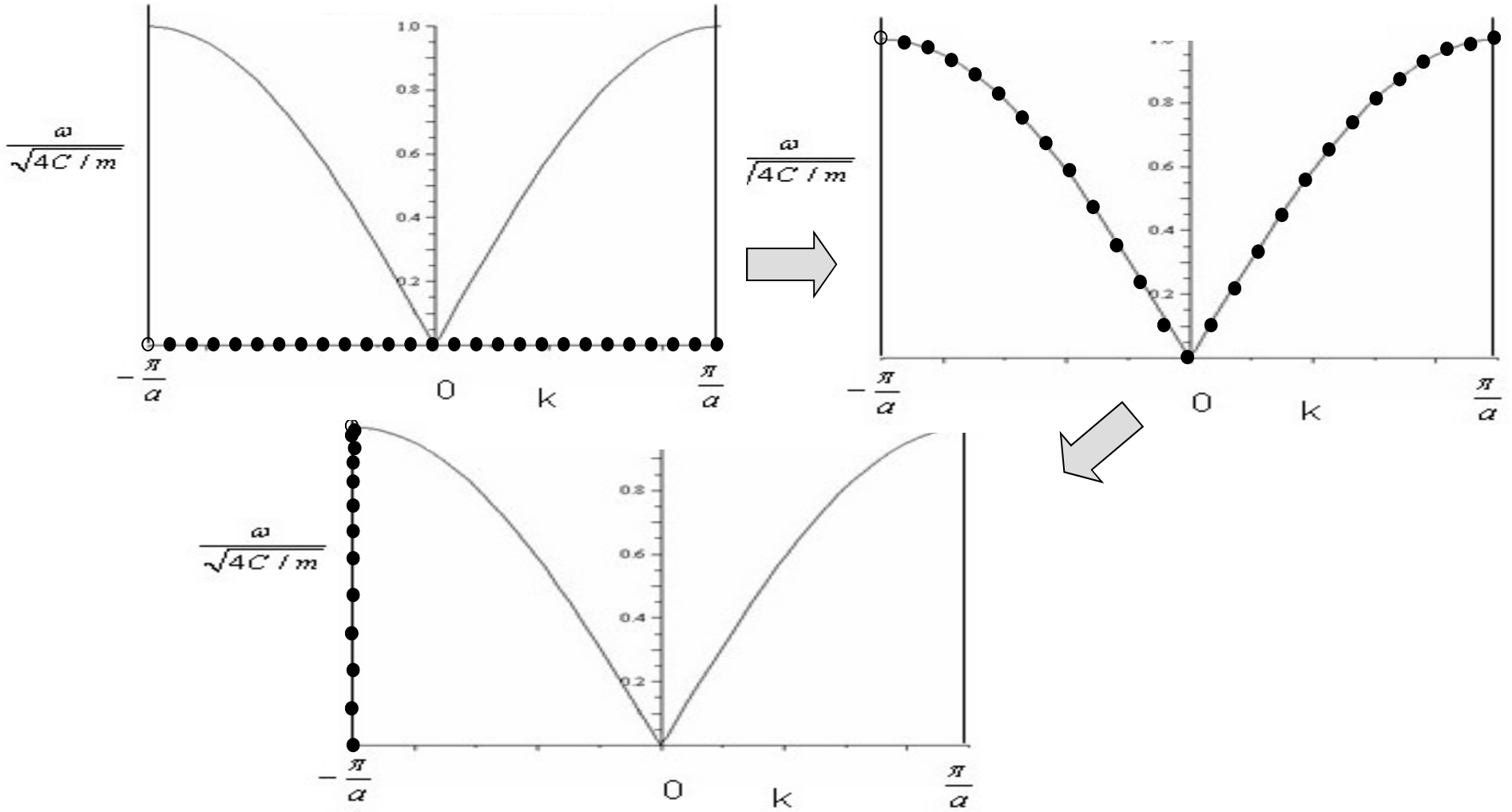
2. **Determine the density of states numerically from the dispersion relation** $D(\omega)$

   For every allowed *k,* find all corresponding values of ω.

Linear Chain - density of states

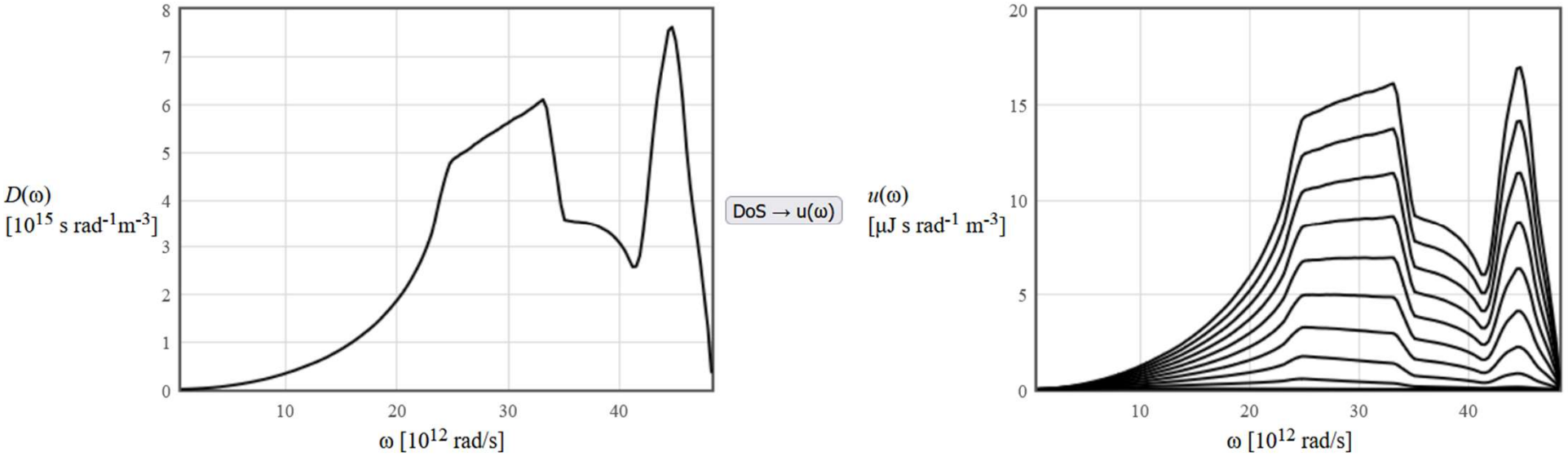
Determine the density of states numerically

$$\omega = \sqrt{\frac{4C}{m}}\left|\sin\left(\frac{ka}{2}\right)\right|$$



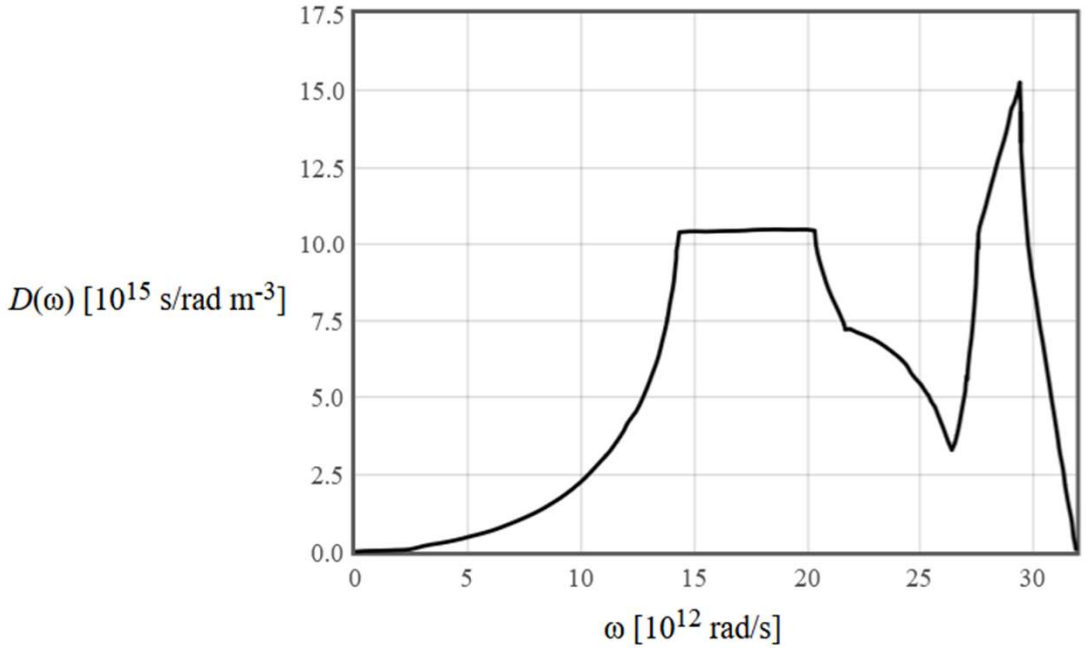
Density of states → energy spectral density

$$u(\omega) = \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2uw.html

Phonon density of states for fcc silver



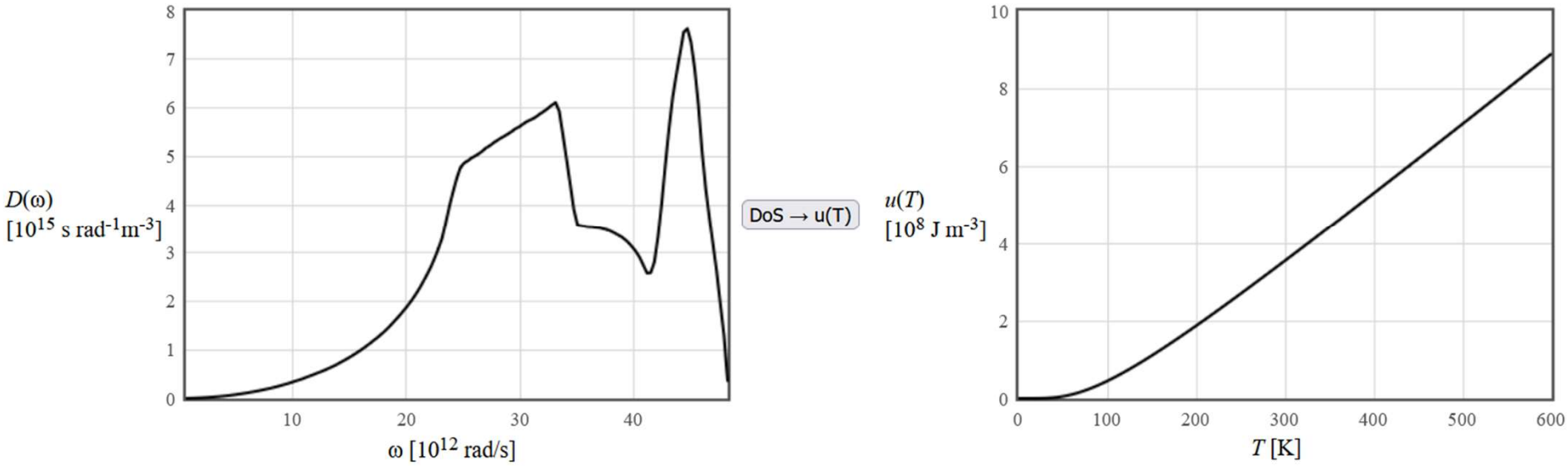
The atomic density is taken to be 5.86×10^{28} m^{-3}. Each atom has three degrees of freedom so the integral over all frequencies is $3\times5.86\times10^{28}$ m^{-3}. The data is from doi: 10.1007/b19988.

T = 296 K

ω [rad/s]	$D(\omega)$ [s $rad^{-1}m^{-3}$]
0.0000	0.0000
5.7327e+10	6.8161e+12
4.0123e+11	2.3856e+13
7.4510e+11	3.0672e+13
1.0890e+12	3.4080e+13
1.4233e+12	4.0897e+13
1.7624e+12	5.1121e+13
2.0967e+12	5.7937e+13
2.4120e+12	7.4977e+13
2.7177e+12	1.2610e+14
3.0379e+12	1.8744e+14
3.3723e+12	2.3516e+14
3.7163e+12	2.7264e+14

Density of states → Internal energy density

$$u(T) = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}\, d\omega$$



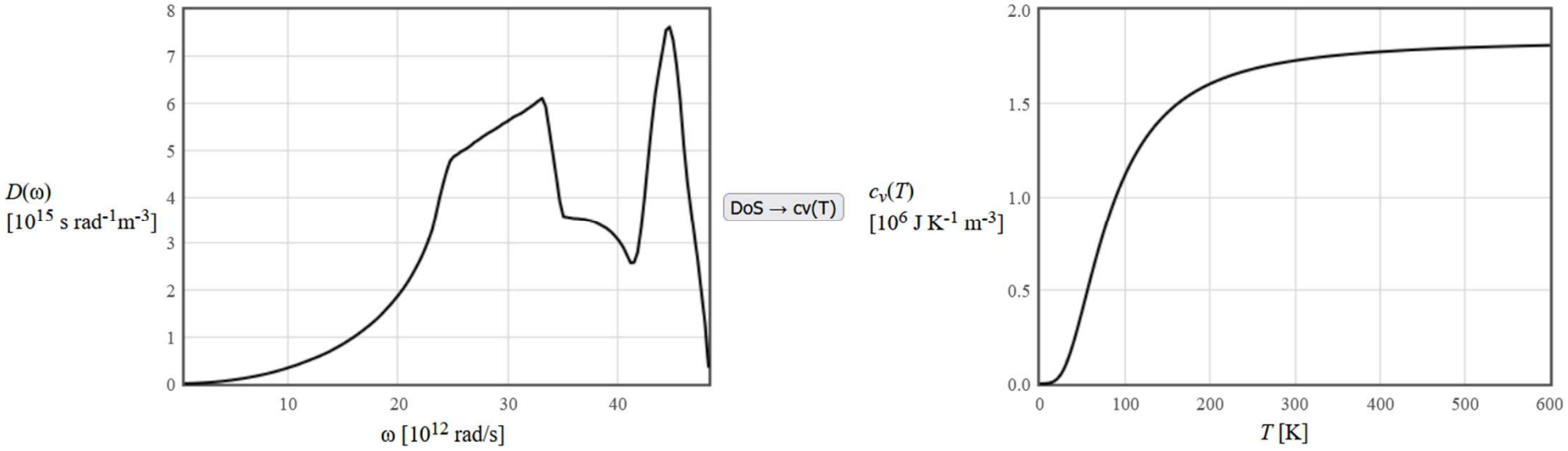
http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2ut.html

Specific Heat

$$c_v = \left(\frac{\partial u}{\partial T}\right)_{N,V}$$

$$c_v = \int \hbar\omega D(\omega) \frac{\partial}{\partial T}\left(\frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\right) d\omega$$

$$c_v = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega) e^{\frac{\hbar\omega}{k_B T}}}{k_B \left(e^{\frac{\hbar\omega}{k_B T}} - 1\right)^2} d\omega$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2cv.html

Heat capacity / specific heat

Heat capacity is the measure of the heat energy required to increase the temperature of an object by a certain temperature interval.

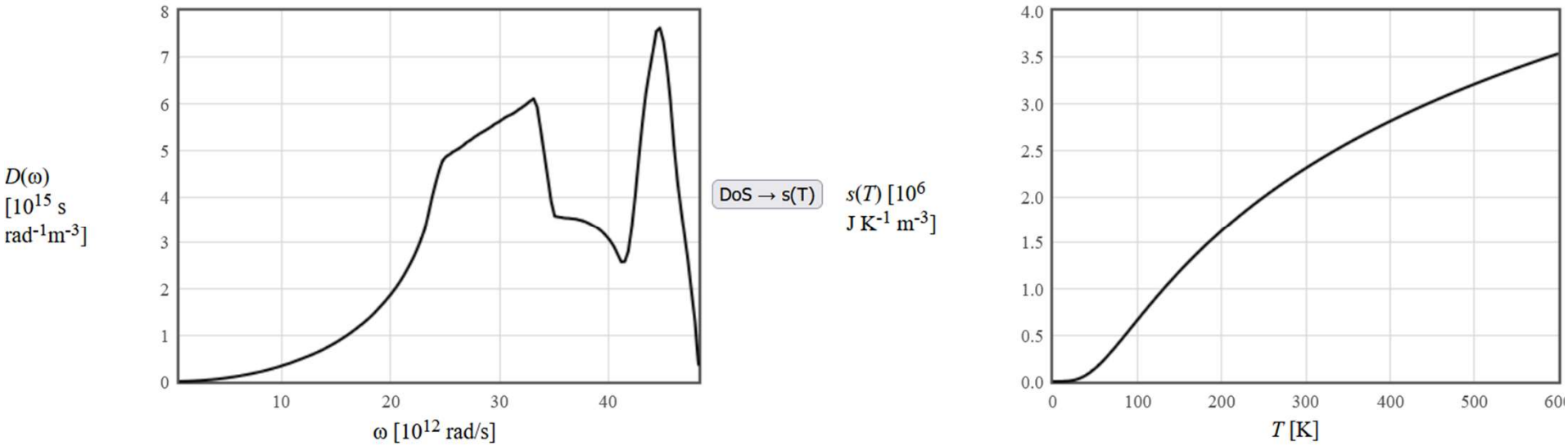
Specific heat is the measure of the heat energy required to increase the temperature of a unit quantity of a substance by a certain temperature interval.

For solids, the heat capacity at constant volume and heat capacity at constant pressure are almost the same.

The heat capacity was historically important for understanding solids.

Density of states → entropy density

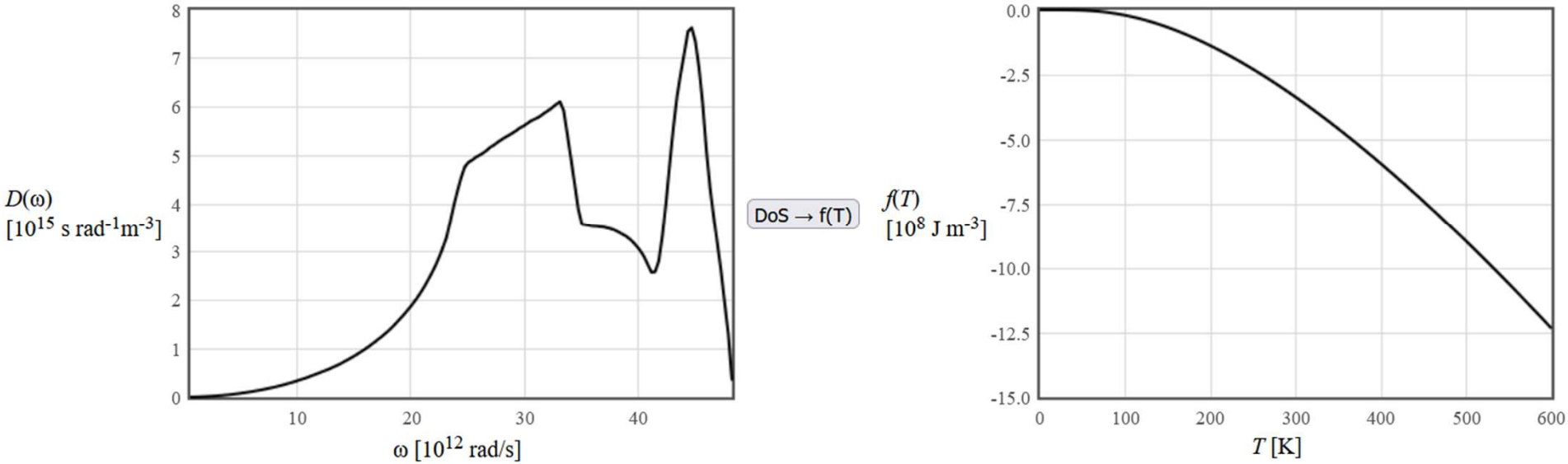
$$s = -\frac{\partial f}{\partial T} = -k_B \int_0^\infty D(\omega) \left(\ln\left(1 - e^{-\hbar\omega / k_B T}\right) + \frac{\hbar\omega}{k_B T \left(1 - e^{\hbar\omega / k_B T}\right)} \right) d\omega$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2s.htmll

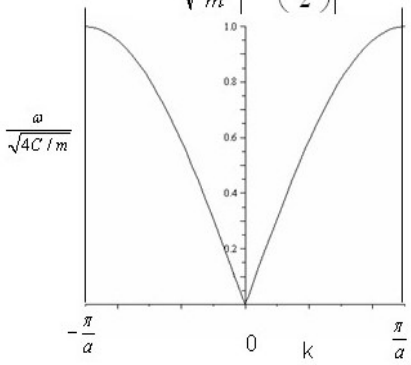
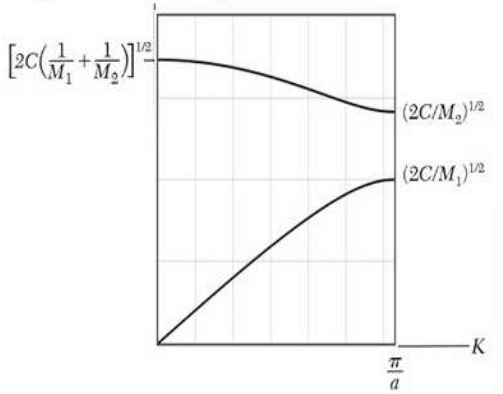
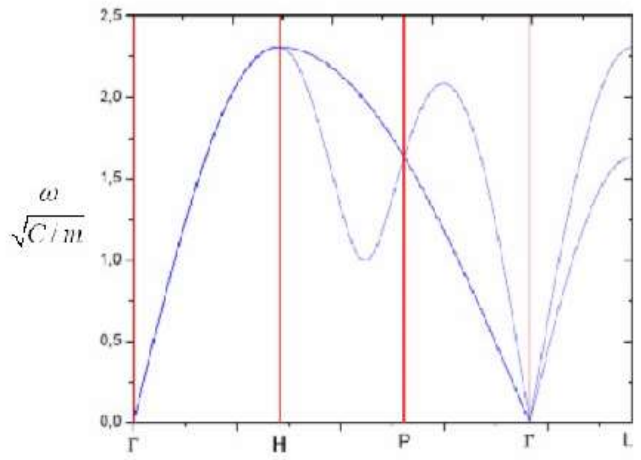
Density of states → Helmholtz free energy density

$$f(T) = k_B T \int_0^{\infty} D(\omega) \ln\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega.$$



http://lampx.tugraz.at/~hadley/ss1/phonons/table/dos2h.html

Phonons

	Linear Chain	Linear chain 2 masses	body centered cubic
	$m\frac{d^2u_s}{dt^2} = C(u_{s+1} - 2u_s + u_{s-1})$	$M_1\frac{d^2u_s}{dt^2} = C(v_{s-1} - 2u_s + v_s)$ $M_2\frac{d^2v_s}{dt^2} = C(u_s - 2v_s + u_{s+1})$	$\frac{d^2u^x_{lmn}}{dt^2} = \frac{C}{\sqrt{3}\,m}[(u^x_{l+1m+1n+1} - u^x_{lmn}) + (u^x_{l-1m+1n+1} - u^x_{lr}$ $+(u^x_{l+1m-1n+1} - u^x_{lmn}) + (u^x_{l+1m+1n-1} - u^x_{lmn}) + (u^x_{l-1m+}$ $+(u^x_{l+1m-1n-1} - u^x_{lmn}) + (u^y_{l+1m+1n+1} - u^y_{lmn}) - (u^y_{l-1m+}$ $+(u^y_{l+1m-1n+1} - u^y_{lmn}) - (u^y_{l+1m+1n-1} - u^y_{lmn}) + (u^y_{l-1m+}$ $+(u^y_{l+1m-1n-1} - u^y_{lmn}) + (u^z_{l+1m+1n+1} - u^z_{lmn}) - (u^z_{l-1m+}$ $+(u^z_{l+1m-1n+1} - u^z_{lmn}) - (u^z_{l+1m+1n-1} - u^z_{lmn}) + (u^z_{l-1m+}$ $-(u^z_{l+1m-1n-1} - u^z_{lmn})]$ And similar expressions for the y and z
Eigenfunction solutions	$u_s = A_k e^{i(ksa - \omega t)}$	$u_s = ue^{i(ksa - \omega t)}$ $v_s = ve^{i(ksa - \omega t)}$	$u^x_{lmn} = u^x_{\vec{k}} e^{i(l\vec{k}\cdot\vec{a_1} + m\vec{k}\cdot\vec{a_2} + n\vec{k}\cdot\vec{a_3})} = u^x_{\vec{k}} e^{i(\frac{(-l-}{}}$ And similar expressions for the y and z
Dispersion relation	$\omega = \sqrt{\frac{4C}{m}}\left\lvert\sin\left(\frac{ka}{2}\right)\right\rvert$ 	$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2\left(\frac{ka}{2}\right)}{M_1M_2}}$  Calculate ω(k)	The dispersic $\begin{bmatrix} 4 - cos(\frac{a}{2}(k_x + k_y + k_z)) - cos(\frac{a}{2}(3k_x - k_y - k_z)) & -cos(\frac{a}{2}(k_x + k_y \\ -cos(\frac{a}{2}(-k_x + 3k_y - k_z)) - cos(\frac{a}{2}(-k_x - k_y + 3k_z)) - \frac{m\omega^2}{\sqrt{3}C} & +cos(\frac{a}{2}(-k_x + 3 \\ -cos(\frac{a}{2}(k_x + k_y + k_z)) + cos(\frac{a}{2}(3k_x - k_y - k_z)) & 4 - cos(\frac{a}{2}(k_x + \\ +cos(\frac{a}{2}(-k_x + 3k_y - k_z)) - cos(\frac{a}{2}(-k_x - k_y + 3k_z)) & -cos(\frac{a}{2}(-k_x + 3 \\ -cos(\frac{a}{2}(k_x + k_y + k_z)) + cos(\frac{a}{2}(3k_x - k_y - k_z)) & -cos(\frac{a}{2}(k_x + k_y \\ -cos(\frac{a}{2}(-k_x + 3k_y - k_z)) + cos(\frac{a}{2}(-k_x - k_y + 3k_z)) & +cos(\frac{a}{2}(-k_x + 3 \end{bmatrix}$ 
Density of states $D(k)$	$D(k) = \frac{1}{\pi}$	$D(k) = \frac{1}{\pi}$	$D(k) = \frac{3k^2}{2\pi^2}$

Thermal properties

internal energy density $u = \int_0^\infty u(\omega) d\omega = \int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \quad \left[\ \mathrm{J/m^3}\ \right]$

specific heat $c_v = \frac{du}{dT} = \int \left(\frac{\hbar\omega}{T}\right)^2 \frac{D(\omega)\exp\left(\frac{\hbar\omega}{k_B T}\right)}{k_B\left(\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1\right)^2} d\omega \quad [\mathrm{J\ K^{-1}\ m^{-3}}]$

entropy density $s(T) = \int \frac{c_v}{T} dT = \frac{1}{T}\int_0^\infty \frac{\hbar\omega D(\omega)}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} d\omega \quad [\mathrm{J\ K^{-1}\ m^{-3}}]$

Helmholtz free energy density

$$f(T) = u - Ts = k_B T \int_0^\infty D(\omega) \ln\left(1 - \exp\left(\frac{-\hbar\omega}{k_B T}\right)\right) d\omega \quad \left[\mathrm{J/m^3}\right]$$

Quartz

α-Quartz
trigonal
2.65 g/cm^3

573°C ⟹

β-Quartz
hexagonal
2.53 g/cm3

870°C ⟹

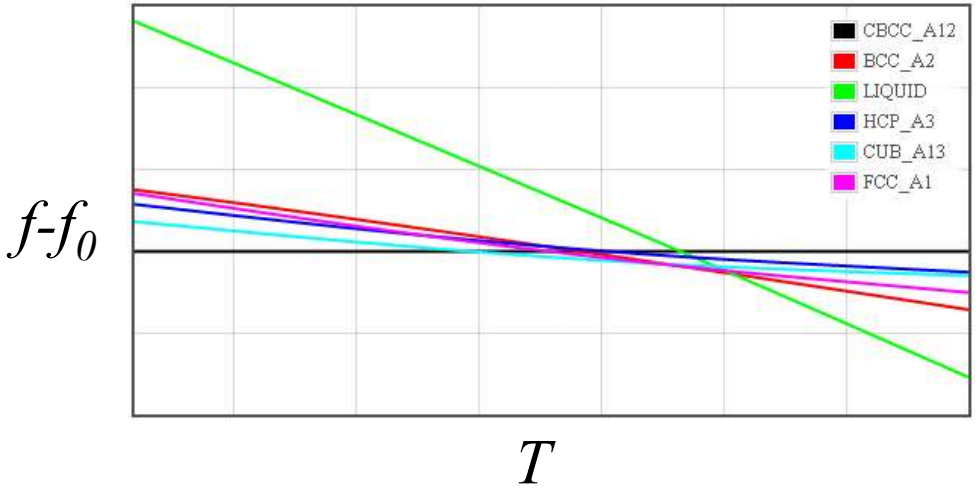
β-Tridymite
hexagonal
2.25 g/cm^3

1470°C ⇓

β-Cristobalite
cubic
2.20 g/cm3

1705°C ⟸

Silica Melt



$GaPO_4$

Material Constants

$GaPO_4$ (gallium phosphate) is a high temperature piezoelectric crystal, with superior sensing properties without any pyroelectric characteristics.
This crystal has been used in technical applications such as pressure sensors since 1994.

GENERAL DATA

Point group	32 (D_3) (quartz-homeotype)
Lattice constants (25°C)	a = 4.901 Å, c = 11.048 Å
Density (25°C)	3570 kg/m^3

PIEZOELECTRIC CONSTANTS

	25°C	500°C	700°C	950°C
d_{11}[a,b] [pC/N]	4.5	4.5	4.5	4.1[c]
d_{14}[a] [pC/N]	1.9	1.6	1.4[c]	1.0[c]

$$d = \begin{pmatrix} d_{11} & -d_{11} & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & -d_{14} & -2d_{11} \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

THERMAL EXPANSION COEFFICIENTS

at $T_0 = 25°C, -253°C < T < 900°C$

	$\alpha_{ii}(T_0)$ [$10^{-6}K^{-1}$]	$T\alpha_{ii}^{(1)}$ [$10^{-9}K^{-2}$]	$T\alpha_{ii}^{(2)}$ [$10^{-12}K^{-3}$]	$T\alpha_{ii}^{(3)}$ [$10^{-15}K^{-4}$]
α_{11}	12.78	10.6	- 16.1	12.3
α_{33}	3.69	5.0	- 5.4	3.6

$$\alpha = \begin{pmatrix} \alpha_{11} & 0 & 0 \\ 0 & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix}$$

$$\alpha_{ii}(T) = \alpha_{ii}(T_0) + \sum_{n=1}^{3} \left[T\alpha_{ii}^{(n)} \cdot (T - T_0)^n \right]$$

THERMAL CONDUCTIVITY

	50°C	70°C	100°C	130°C	150°C	180°C	200°C
λ_{11}[W m^{-1}K^{-1}]	4.21	3.96	3.68	3.28	3.07	2.85	2.71
λ_{33}[W m^{-1}K^{-1}]	6.66	6.14	5.66	5.00	4.78	4.27	4.02

$$\lambda = \begin{pmatrix} \lambda_{11} & 0 & 0 \\ 0 & \lambda_{11} & 0 \\ 0 & 0 & \lambda_{33} \end{pmatrix}$$

ELECTRIC RESISTIVITY

	25°C	200°C	300°C	500°C	700°C	900°C
ρ[Ωm]	> 10^{15}	> 10^{13}	> 10^{11}	> 10^{9}	> 10^{7}	> 10^{5}

ELASTIC CONSTANTS at $T_0 = 25°C$, $-50°C < T < 700°C$

	c_{ij} [GPa]	$Tc_{ij}^{(1)}$ [10^{-6} K^{-1}]	$Tc_{ij}^{(2)}$ [10^{-9} K^{-2}]	$Tc_{ij}^{(3)}$ [10^{-12} K^{-3}]
c_{11}^E	66.58	- 44.1	- 28.5	- 59.4
c_{12}^E	21.81	- 226.7	- 70.8	- 205.7
c_{13}^E	24.87	- 57.6	41.3	- 109.9
$c_{14}^{E\,b}$	3.91	507.2	280.6	- 99.9
c_{33}^E	102.13	- 127.5	- 18.3	- 134.8
c_{44}^E	37.66	- 0.4	- 43.8	- 37.1
c_{66}^E	22.38	44.9	- 7.9	11.9

$$c = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & c_{14} \\ 0 & 0 & 0 & 0 & c_{14} & \frac{(c_{11}-c_{12})}{2} \end{pmatrix}$$

$$c_{ij}(T) = c_{ij}(T_0)\left[1 + \sum_{n=1}^{3} Tc_{ij}^{(n)} \cdot (T - T_0)^n\right]$$

	s_{ij} [$10^{-12}m^2N^{-1}$]	$Ts_{ij}^{(1)}$ [10^{-6} K^{-1}]	$Ts_{ij}^{(2)}$ [10^{-9} K^{-2}]	$Ts_{ij}^{(3)}$ [10^{-12} K^{-3}]
s_{11}^E	17.93	22.4	30.5	62.4
s_{12}^E	- 4.82	- 210.5	- 0.1	- 271.3
s_{13}^E	- 3.19	181.6	78.2	322.2
$s_{14}^{E\,b}$	- 2.36	482.2	315.5	7.9
s_{33}^E	11.35	147.9	14.1	261.5
s_{44}^E	27.04	18.7	54.7	52.0
s_{66}^E	45.51	- 26.9	24.0	- 8.3

$$s = \begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} & 0 & 0 \\ s_{12} & s_{11} & s_{13} & -s_{14} & 0 & 0 \\ s_{13} & s_{13} & s_{33} & 0 & 0 & 0 \\ s_{14} & -s_{14} & 0 & s_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & s_{44} & 2s_{14} \\ 0 & 0 & 0 & 0 & 2s_{14} & 2(s_{11}-s_{12}) \end{pmatrix}$$

$$s_{ij}(T) = s_{ij}(T_0)\left[1 + \sum_{n=1}^{3} Ts_{ij}^{(n)} \cdot (T - T_0)^n\right]$$

RELATIVE DIELECTRIC CONSTANTS

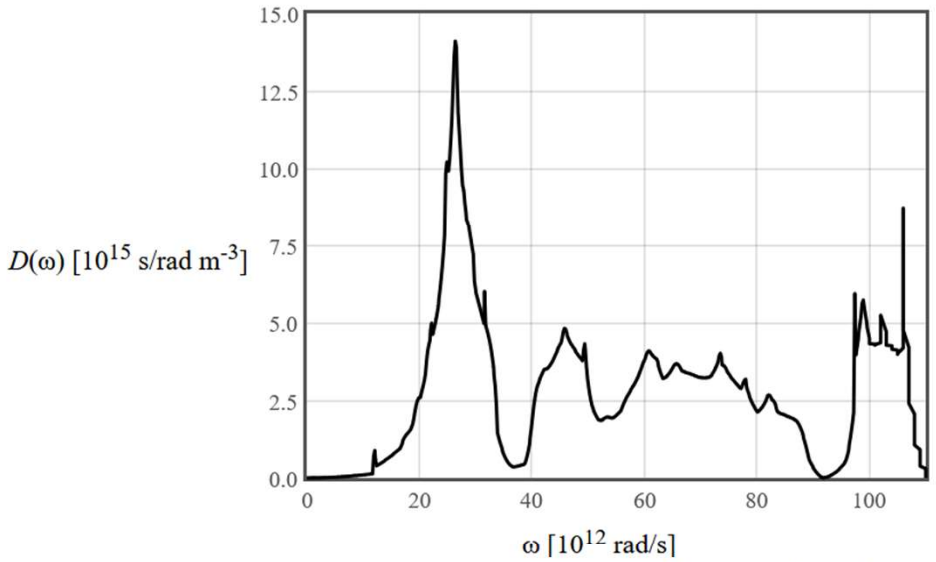
at $T_0 = 25°C$, 1 kHz

ε_{11}^T	6.1	ε_{11}^S	5.8
ε_{33}^T	6.6	ε_{33}^S	6.6

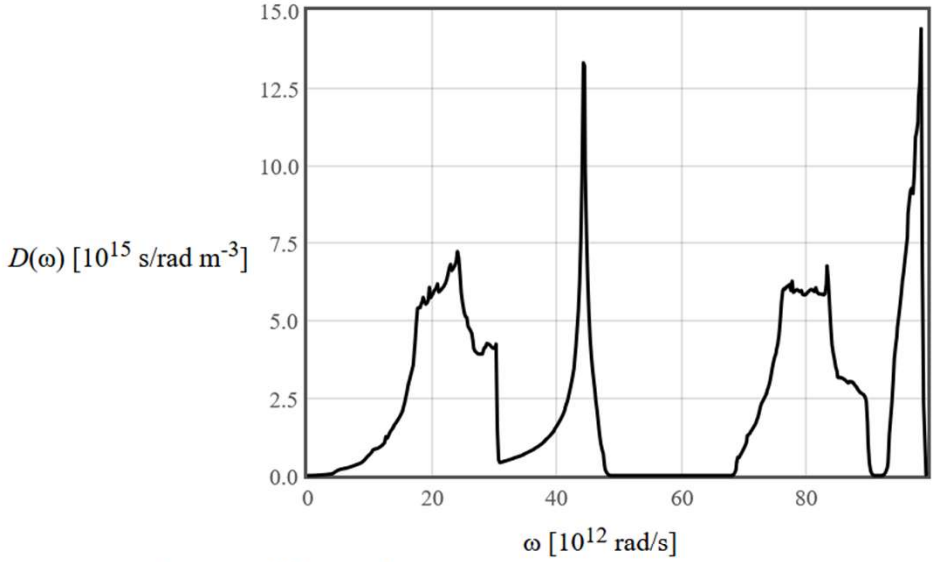
$$\varepsilon = \begin{pmatrix} \varepsilon_{11} & 0 & 0 \\ 0 & \varepsilon_{11} & 0 \\ 0 & 0 & \varepsilon_{33} \end{pmatrix}$$

ZnO

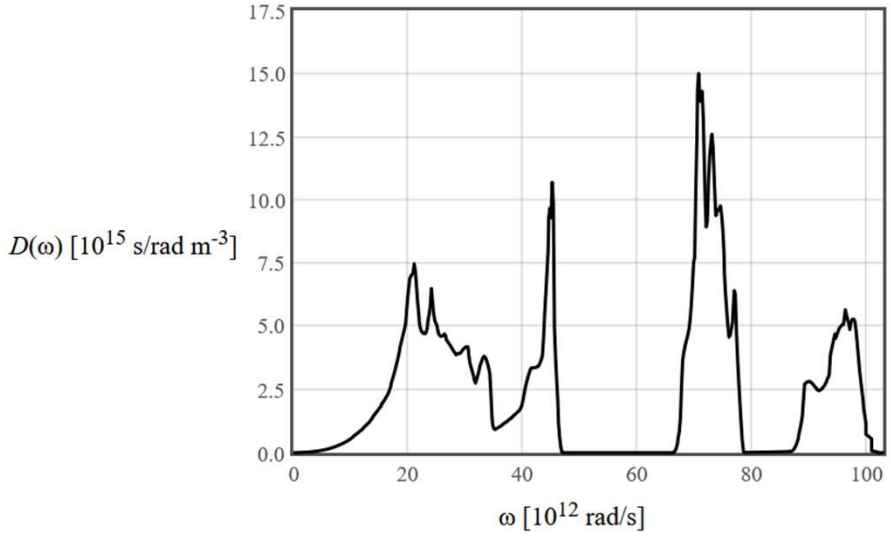
Phonon density of states for ZnO (Rocksalt)



Phonon density of states for ZnO (Zincblende)



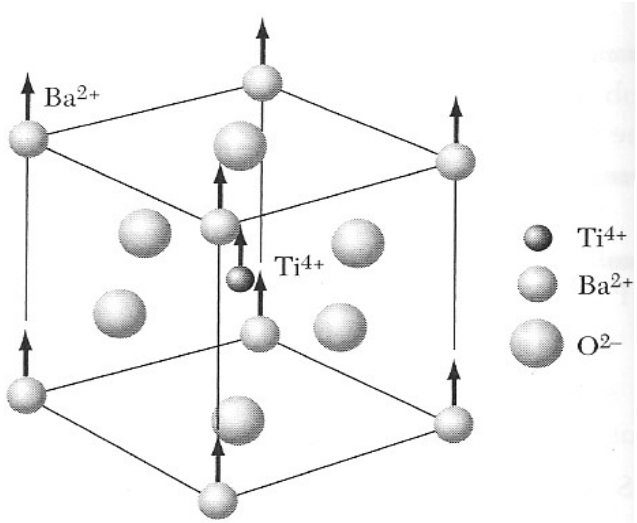
Phonon density of states for ZnO (Wurtzite)



Ferroelectricity

ABX_3

Perovskites

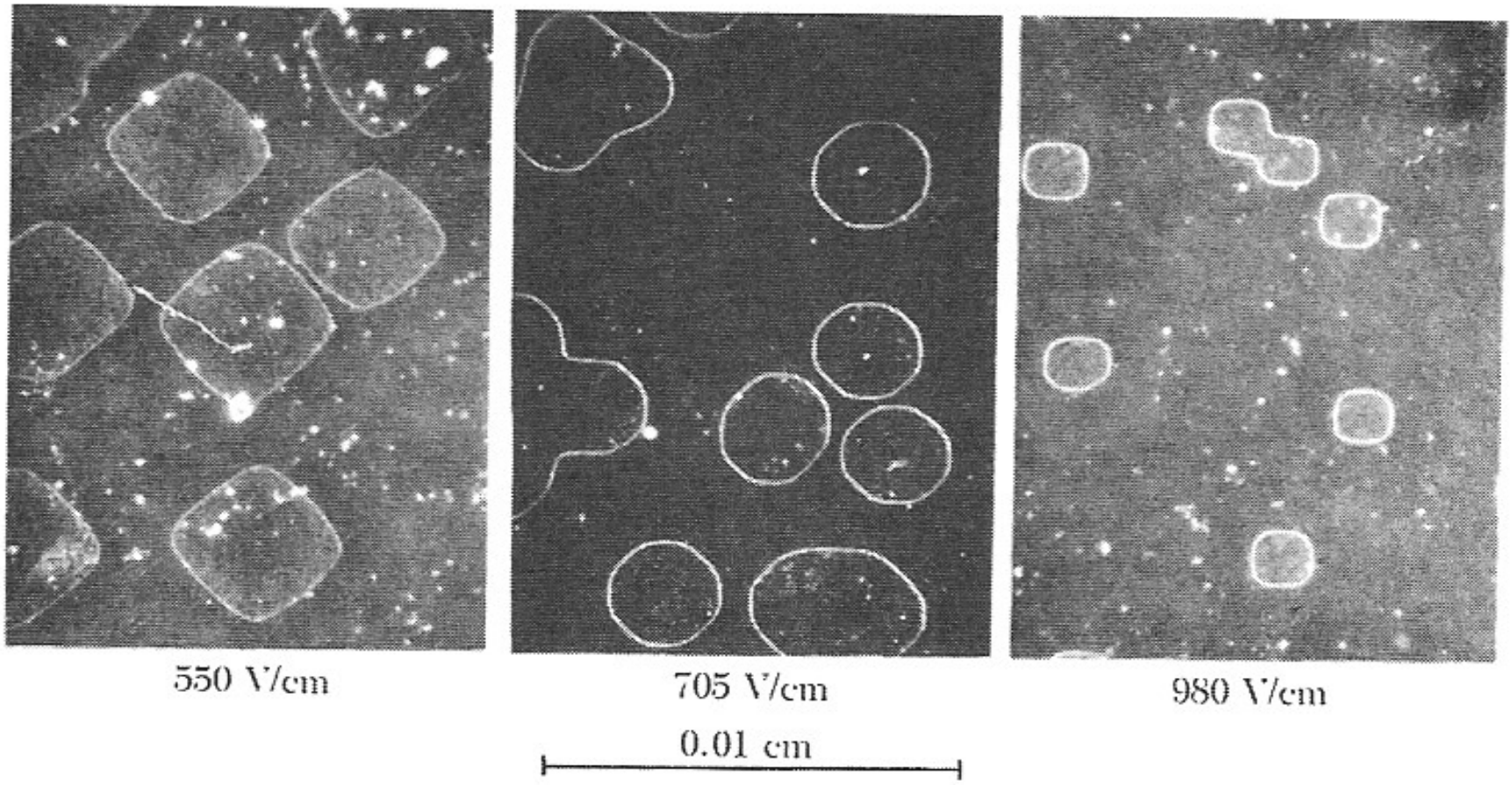


Spontaneous polarization
Analogous to ferromagnetism
Structural phase transition
T_c is transition temperature

Electric field inside the material, is not conducting

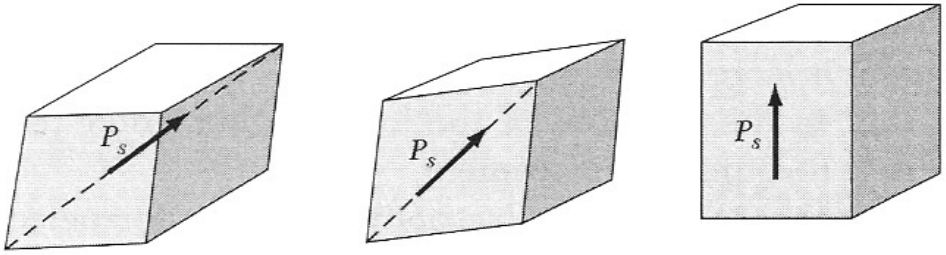
		T_c, in K	P_s, in μC cm^{-2}, at T K	
KDP type	KH_2PO_4	123	4.75	[96]
	KD_2PO_4	213	4.83	[180]
	RbH_2PO_4	147	5.6	[90]
	KH_2AsO_4	97	5.0	[78]
	GeTe	670	—	—
TGS type	Tri-glycine sulfate	322	2.8	[29]
	Tri-glycine selenate	295	3.2	[283]
Perovskites	$BaTiO_3$	408	26.0	[296]
	$KNbO_3$	708	30.0	[523]
	$PbTiO_3$	765	>50	[296]
	$LiTaO_3$	938	50	
	$LiNbO_3$	1480	71	[296]

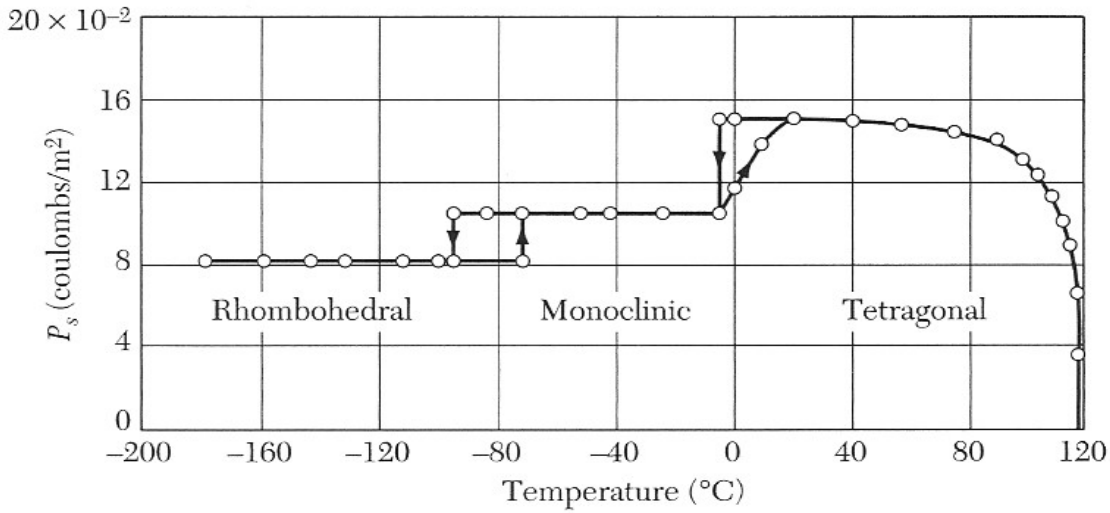
Ferroelectric domains

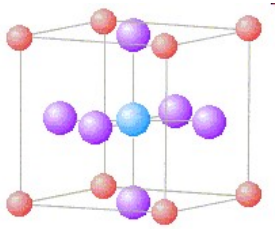


Increasing the electric field polarizes the material.

$BaTiO_3$

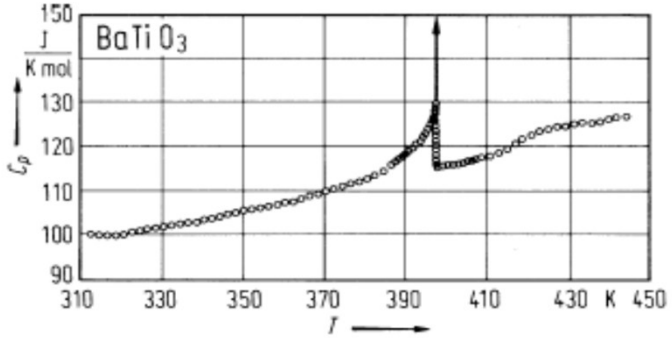






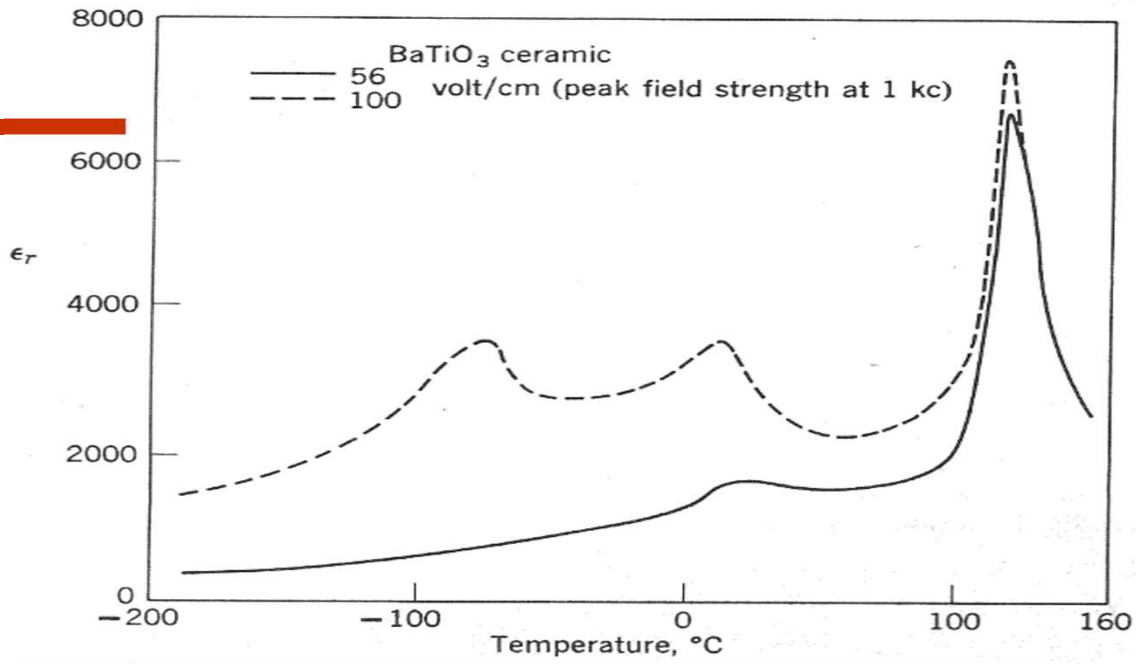
cubic (contains i = > no spontaneous P)

Can be used to make nonvolatile memory

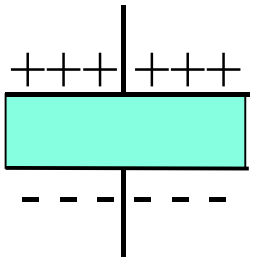


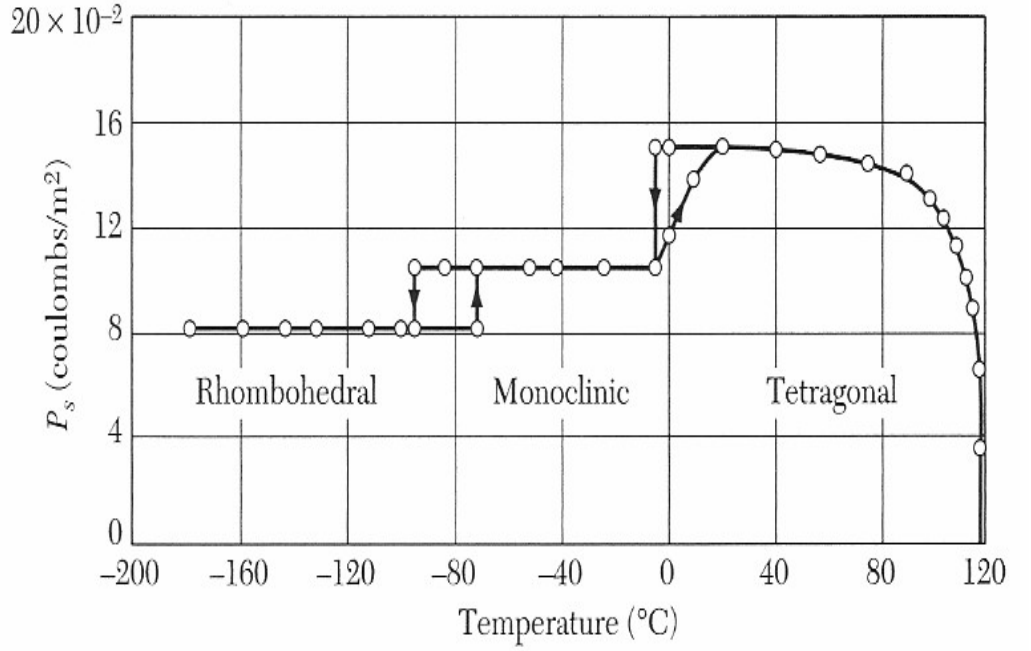
$BaTiO_3$

$$\varepsilon_r = \chi + 1$$



Can be used to make ultracapacitors



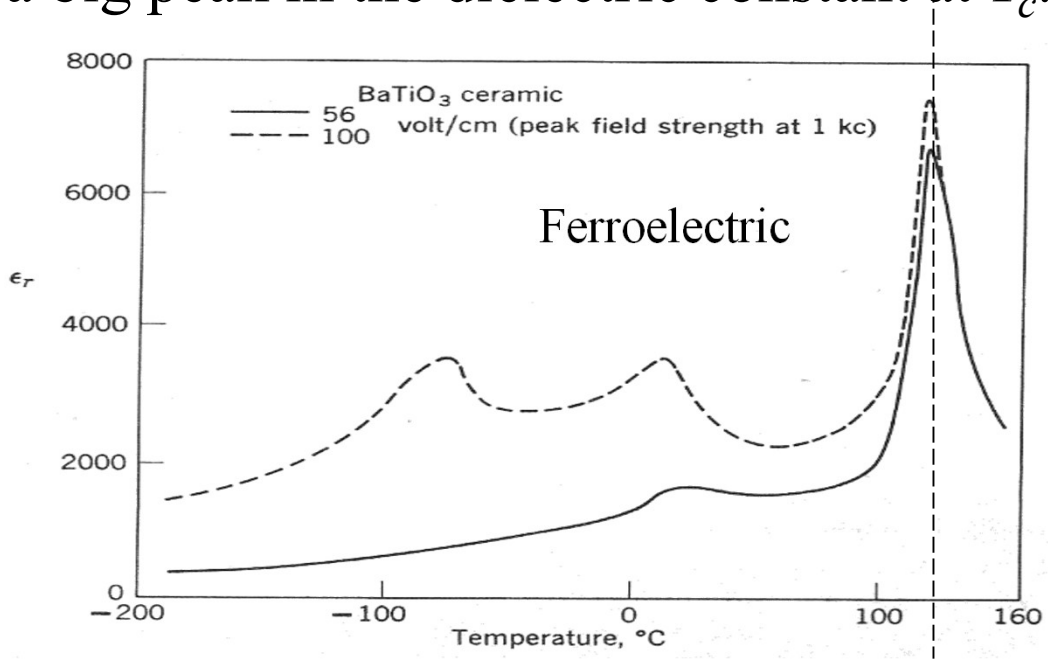


Paraelectric state

Above T_c, $BaTiO_3$ is paraelectric. The susceptibility (and dielectric constant) diverge like a Curie-Weiss law.

$$\chi \propto \frac{1}{T - T_c} \qquad \varepsilon = (1 + \chi)\varepsilon_0$$

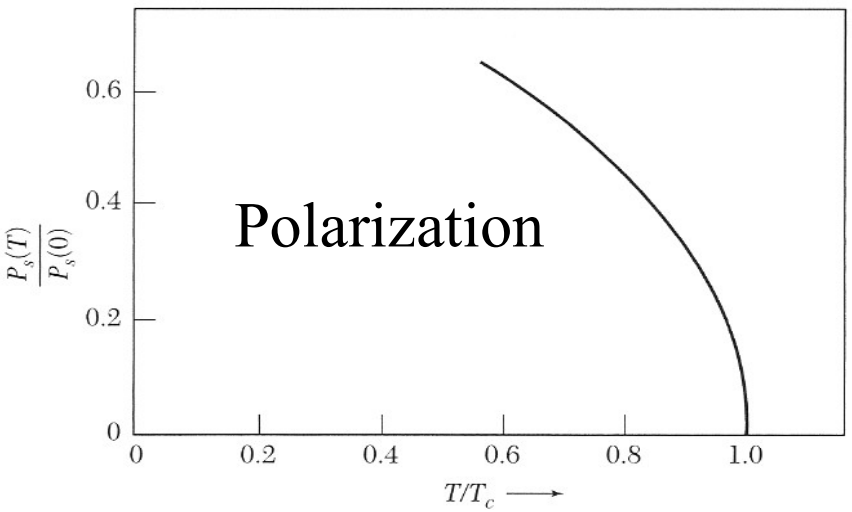
This causes a big peak in the dielectric constant at T_c.

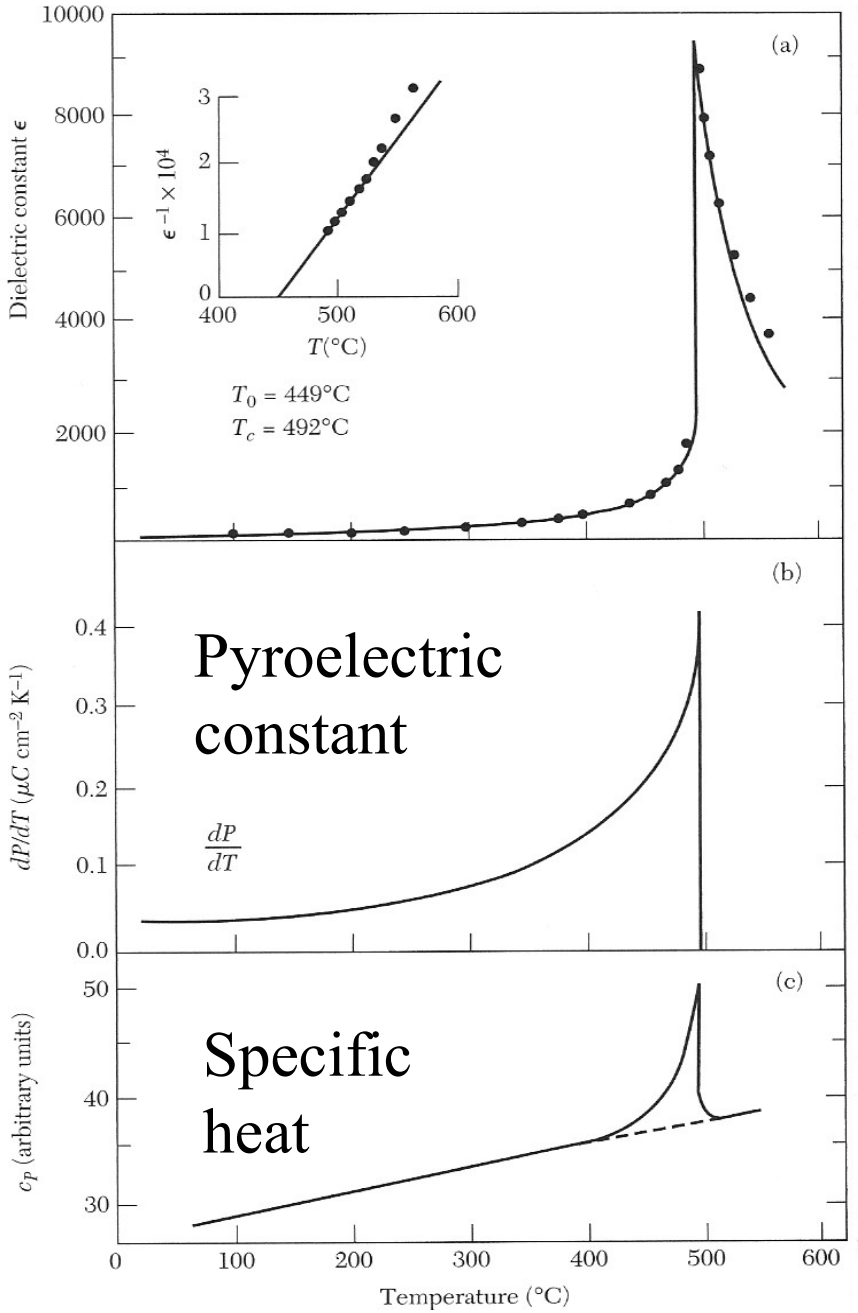


$PbTiO_3$

Dielectric constant

$$\varepsilon \propto \frac{1}{T - T_c}$$





Waves and particles

The eigen function solutions of the wave equation are plane waves. The scattering time is one over the rate for scattering from a given plane wave solution to any other.

Phonons are particles. The scattering time is the time before the phonons scatter and randomly change energy and momentum.

$$E = \hbar\omega$$

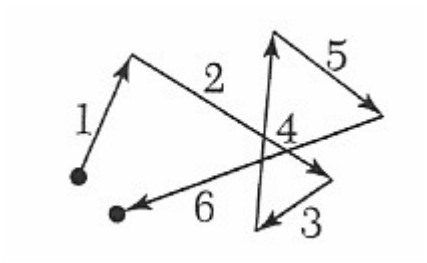
$$\vec{p} = \hbar\vec{k}$$

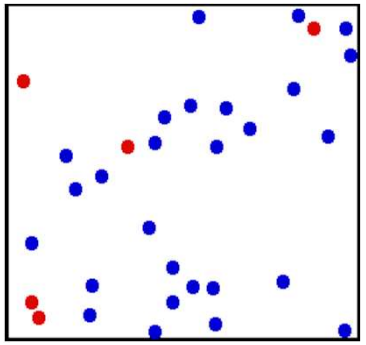
The average time between scattering events is $\tau_{sc} = 1/\Gamma$

Heat transport (Kinetic theory)

Treat phonons as an ideal gas of particles that are confined to the volume of the solid.

Phonons move at the speed of sound. They scatter due to imperfections in the lattice and anharmonic terms in the Hamiltonian.





The average time between scattering events is τ_{sc}

The average distance traveled between scattering events is the mean free path: $\boldsymbol{l} = v\tau_{sc} \sim 10$ nm

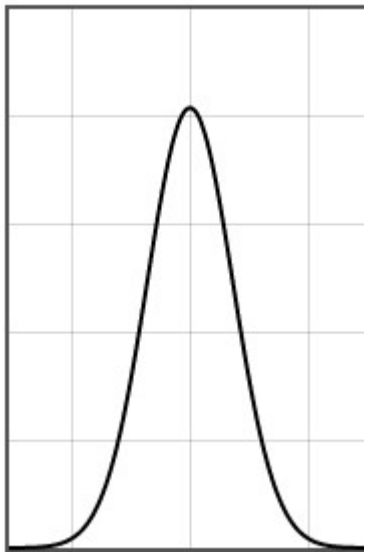
Diffusion equation/ heat equation

$$\frac{dn}{dt} = -D\nabla^2 n$$

Diffusion constant

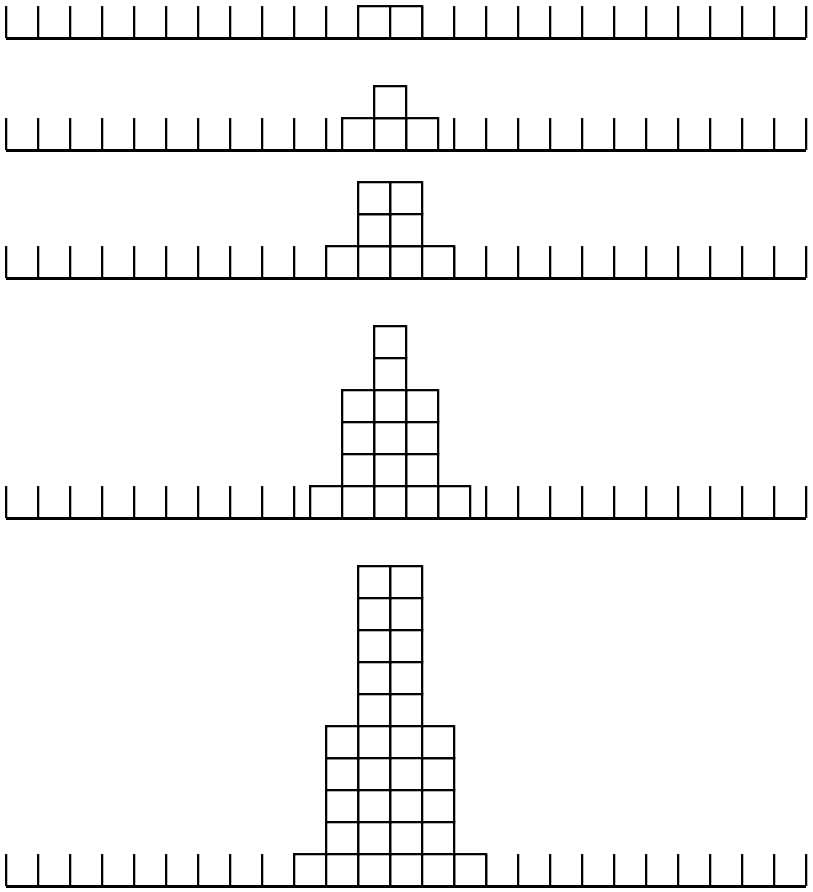
Fick's law $\vec{j} = -D\nabla n$

Continuity equation $\frac{dn}{dt} = \nabla \cdot \vec{j}$

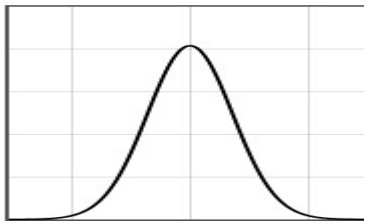


$$n = \frac{1}{\sqrt{4\pi Dt}} \exp\left(\frac{-r^2}{4Dt}\right)$$

Random walk



$$\frac{\Delta n_s}{\Delta t} = n_{s+1} - 2n_s + n_{s-1}$$



$$\exp\left(-x^2\right)$$

Central limit theorem: A function convolved with itself many times forms a Gaussian

Thermal conductivity

$$\vec{j}_U = \bar{E}\vec{j}$$

Average particle energy

$$u = \bar{E}n$$

internal energy density

$$\vec{j}_U = -\bar{E}D\nabla n = -D\nabla u$$

$$\vec{j}_U = -D\frac{du}{dT}\nabla T = -Dc_v\nabla T$$

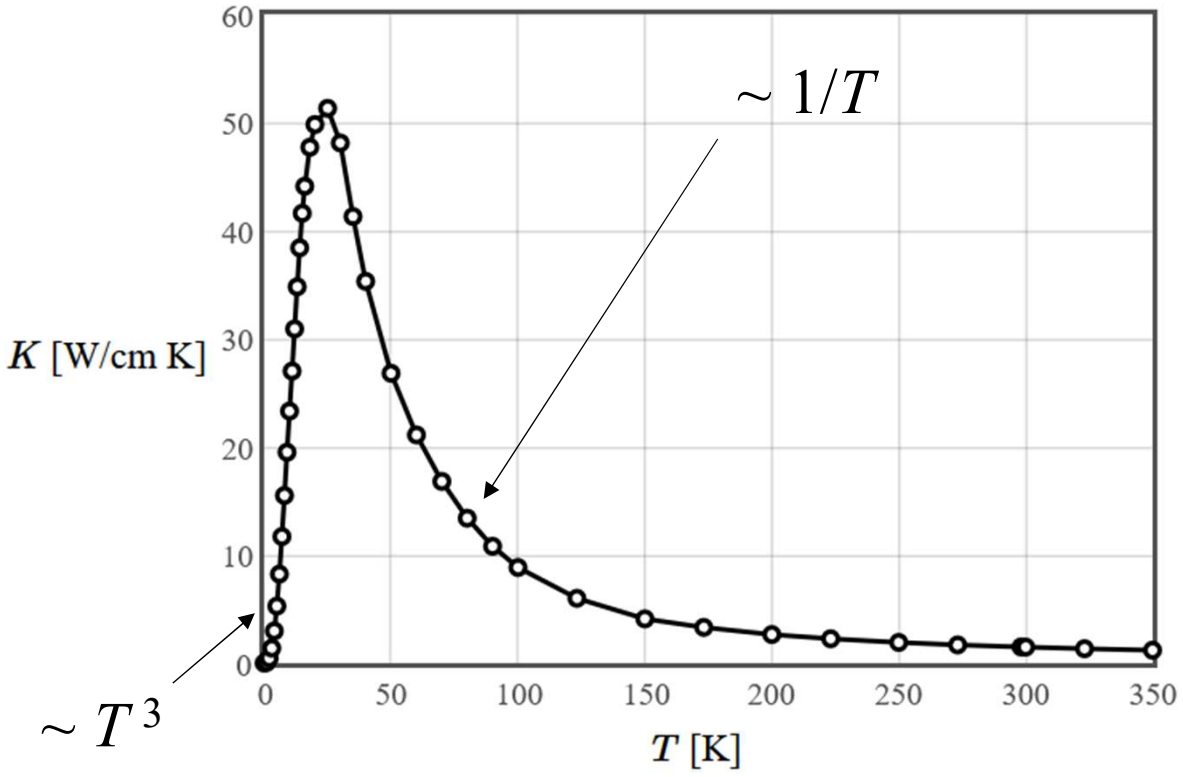
$$\vec{j}_U = -K\nabla T$$

Thermal conductivity

$$K = Dc_v$$

$$K \to 0 \quad \text{as} \quad T \to 0$$

Thermal conductivity $\vec{j}_U = -K\nabla T$



The thermal conductivity of silicon.[1]

Thermal conductivity

$$\vec{j}_U = -K\nabla T$$

Material	**Thermal conductivity W/(m·K)**
Glass	1.1
Concrete, stone	1.7
Ice	2
Sandstone	2.4
Sapphire	35
Stainless steel	12.11 ~ 45.0
Lead	35.3
Aluminum	237
Aluminum alloys	120—180
Gold	318
Copper	401
Silver	429
Diamond	900 - 2320
Graphene	(4840±440) - (5300±480)