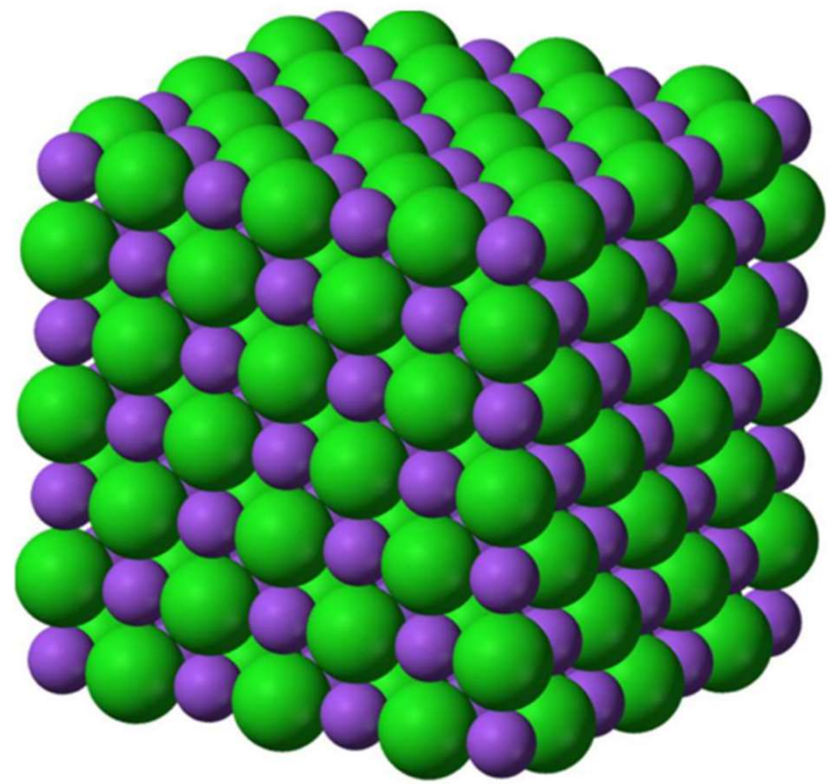
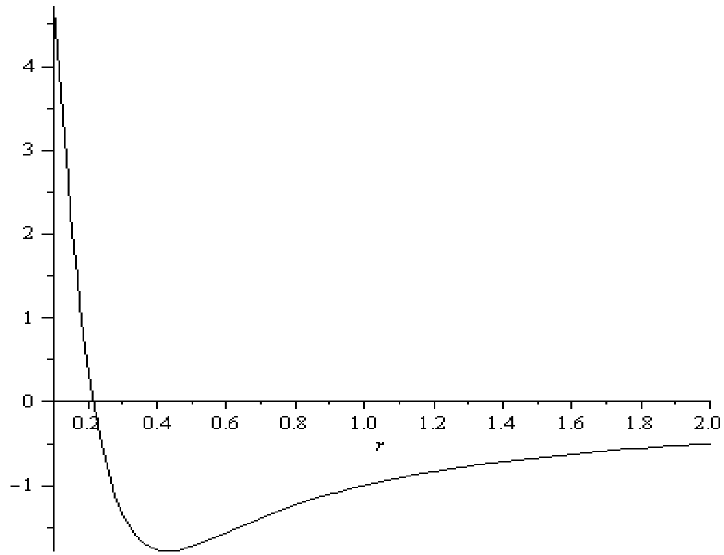
Ionic crystals



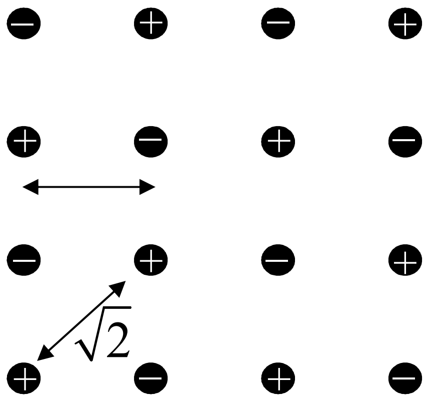
Ionic crystals

Nearest neighbors: $$U_{ij} = \lambda e^{-\frac{r_{ij}}{\rho}} - \frac{e^2}{4\pi\varepsilon_0 r_{ij}}$$



Distant neighbors: $$U_{ij} = \frac{\pm e^2}{4\pi\varepsilon_0 r_{ij}}$$

Ionic crystals



R = nearest neighbor separation

Ernst Madelung

$$U_{\text{ionic}} = -\frac{6e^2}{4\pi\epsilon_0 R} + \frac{8e^2}{4\pi\epsilon_0 \sqrt{2}R} + \frac{6e^2}{4\pi\epsilon_0 2R} + \cdots$$

$$U_{\text{ionic}} = -\frac{e^2}{4\pi\epsilon_0 R}\left(6 - \frac{8}{\sqrt{2}} - 3 + \cdots\right)$$

α Madelung constant

Madelung constant in 1-D

⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖ ⊕ ⊖

$$\alpha = 2\left[1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \tfrac{1}{5} - \cdots\right]$$

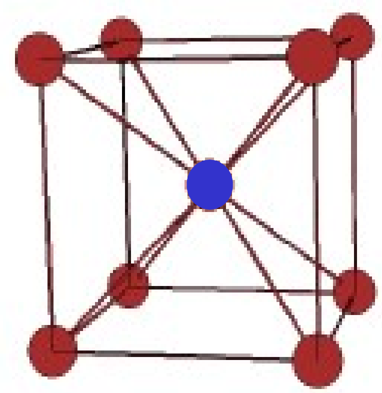
Taylor expansion: $\ln(1+x) = \left[x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \frac{x^5}{5} - \cdots\right]$

$$\ln(2) = \left[1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} + \tfrac{1}{5} - \cdots\right]$$

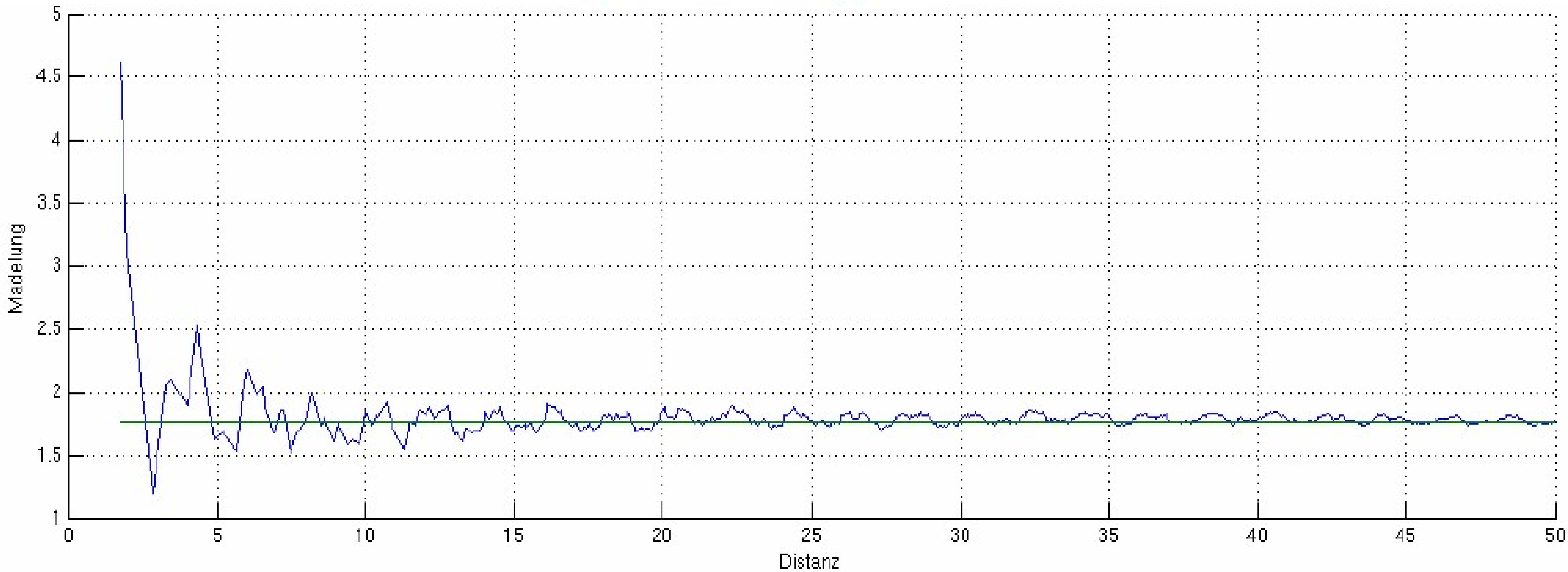
$$\alpha = 2\ln 2 = 1.38629436$$

Calculating the Madelung constant

CsCl
$z = 8$



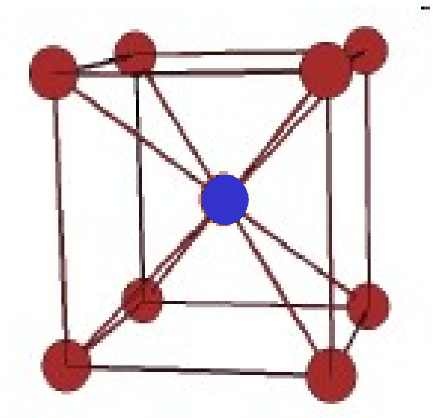
$\alpha = 1.767$



Iterative Bestimmung der Madelung-Konstante für CsCl - Yao Shan und Robert Krisper, 2010

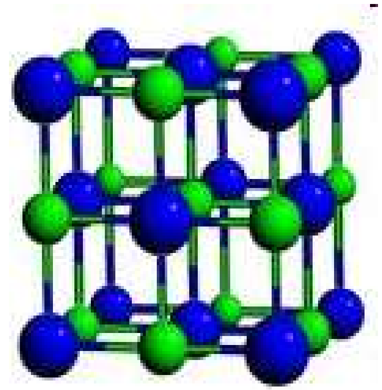
Ionic Crystals

$\alpha = 1.767$



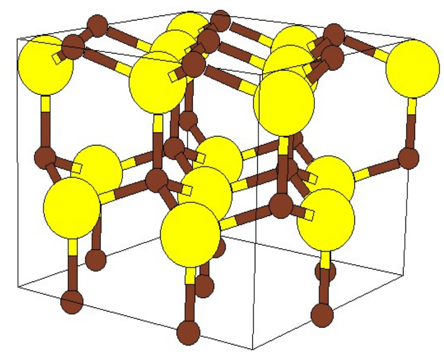
CsCl
$z = 8$

$\alpha = 1.747$



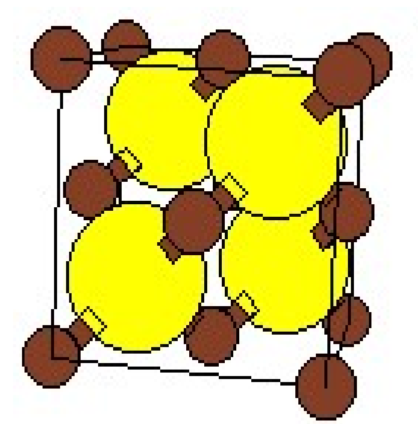
NaCl
$z = 6$

$\alpha = 1.641$



Wurtzite
$z = 4$

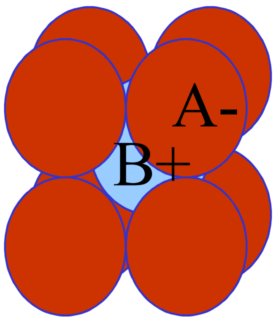
$\alpha = 1.638$



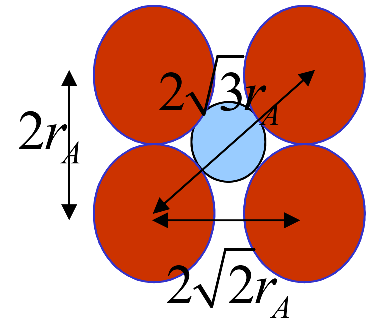
Zincblende
$z = 4$

Ionic radius

CsCl

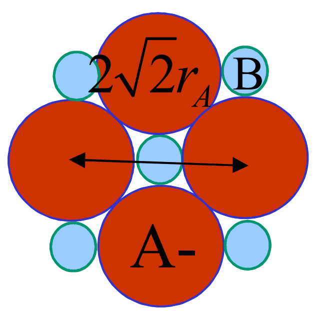


CsCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{3}-1} = 1.366$



CsCl 110 plane

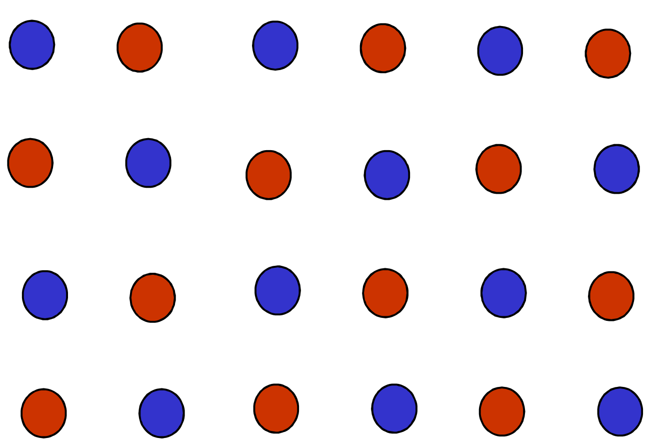
NaCl



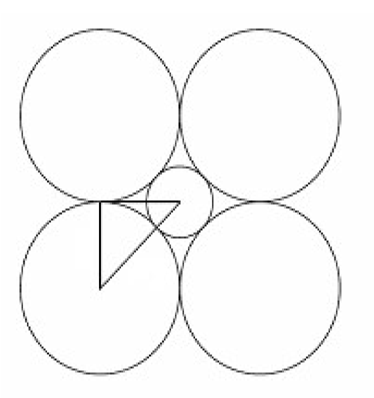
NaCl unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$

NaCl 100 plane

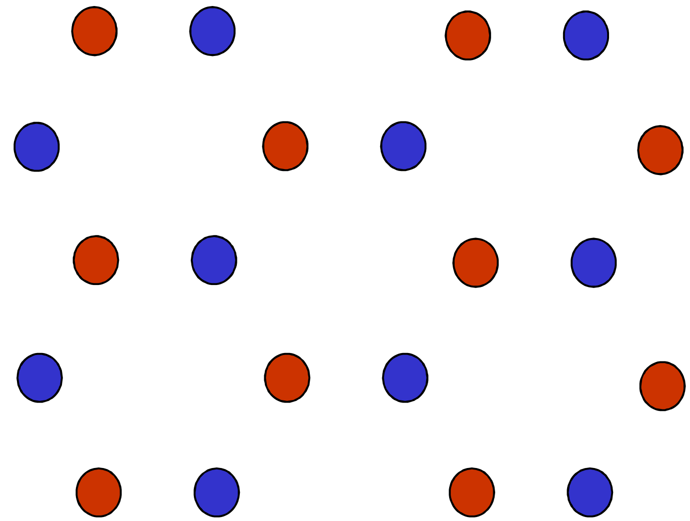
2-D crystals



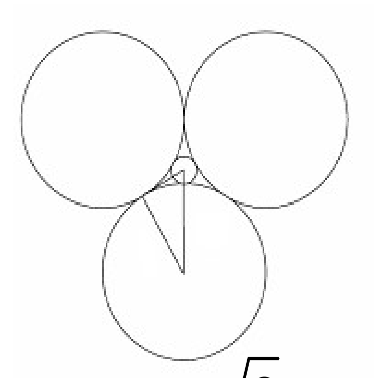
Checkerboard $\alpha = 1.616$



unstable: $\frac{r_A}{r_B} > \frac{1}{\sqrt{2}-1} = 2.41$



Boron nitride $\alpha = 1.542$

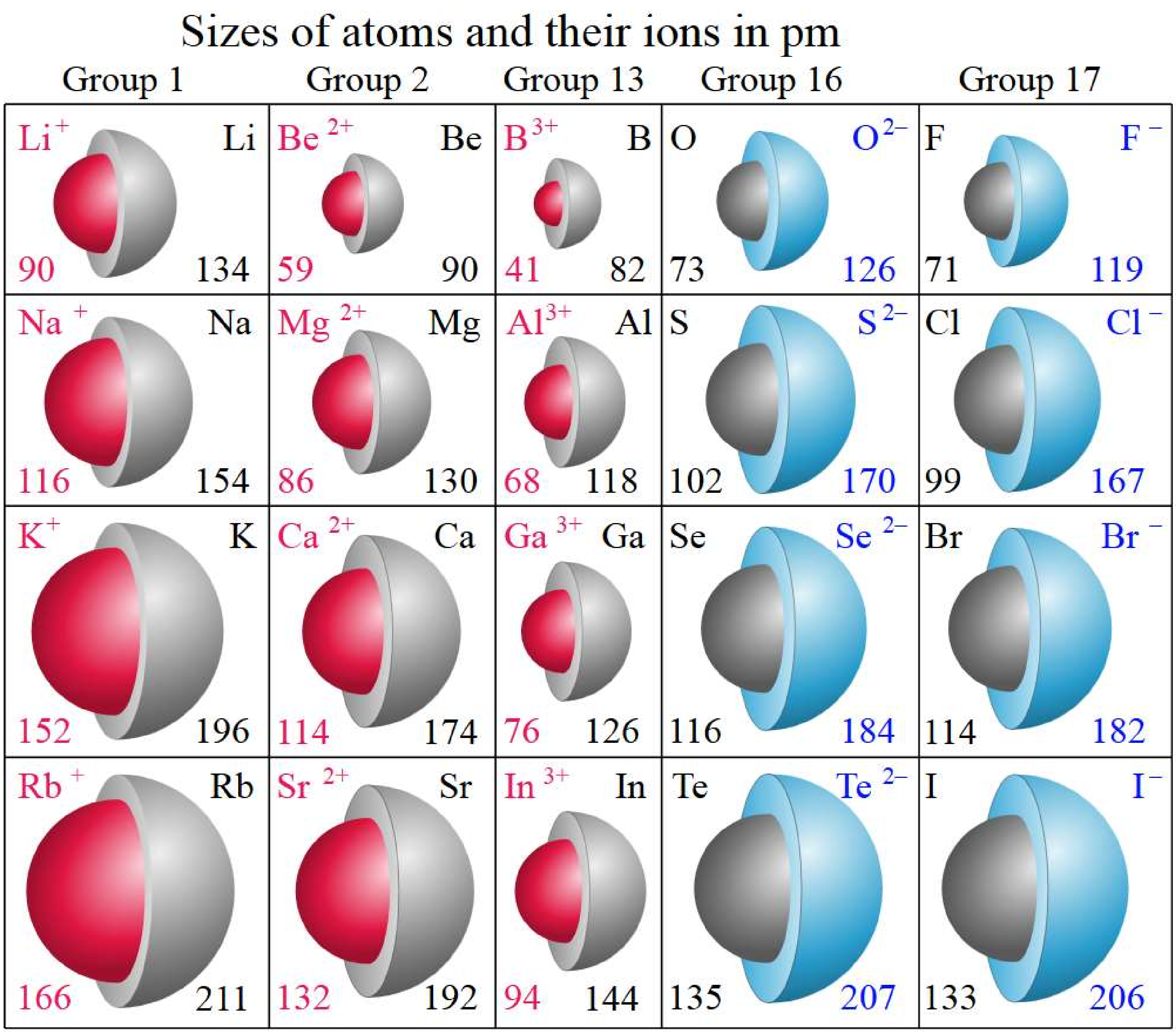


unstable: $\frac{r_A}{r_B} > \frac{\sqrt{3}}{2-\sqrt{3}} = 6.464$

CsCl:

$$\frac{r_A}{r_B} < 1.366$$

$$\frac{r_{Cl}}{r_{Na}} = 1.44$$



https://en.wikipedia.org/wiki/Ionic_radius#/media/File:Atomic_%26_ionic_radii.svg

Fit the constants ρ and λ

$$U_{tot} = N\left(z\lambda e^{-\frac{R}{\rho}} - \frac{\alpha e^2}{4\pi\varepsilon_0 R} \right)$$

$$\frac{dU_{tot}}{dR} = N\left(-\frac{z\lambda e}{\rho}^{-\frac{R}{\rho}} + \frac{\alpha e^2}{4\pi\varepsilon_0 R^2} \right) = 0$$

R_0 is the equilibrium separation

$$R_0^2 e^{-\frac{R_0}{\rho}} = \frac{\alpha e^2 \rho}{4\pi\varepsilon_0 z\lambda}$$

x-ray determination of atomic spacing is accurate to 1 part in 10^5

Elastic constant

Near the minimum, the potential energy is approximately a parabola.

$$U_{tot} \approx \tfrac{1}{2} k \left(R - R_0 \right)^2$$

$$\frac{dU_{tot}}{dR} \approx k \left(R - R_0 \right) = -F$$

$$k = \left. \frac{d^2 U_{tot}}{dR^2} \right|_{R=R_0} = \left(\frac{z \lambda e^{-\frac{R_0}{\rho}}}{\rho^2} - \frac{\alpha e^2}{2\pi \varepsilon_0 R_0^3} \right)$$

spring constant of a bond

From the spring constant, the compressibility can be calculated.

Table 7 Properties of alkali halide crystals with the NaCl structure

All values (except those in square brackets) at room temperature and atmospheric pressure, with no correction for changes in R_0 and U from absolute zero. Values in square brackets at absolute zero temperature and zero pressure, from private communication by L. Brewer.

	Nearest-neighbor separation R_0 in Å	Bulk modulus B, in 10^{11} dyn/cm^2 or 10^{10} N/m^2	Repulsive energy parameter $z\lambda$, in 10^{-8} erg	Repulsive range parameter ρ, in Å	Lattice energy compared to free ions, in kcal/mol: Experimental	Lattice energy compared to free ions, in kcal/mol: Calculated
LiF	2.014	6.71	0.296	0.291	242.3[246.8]	242.2
LiCl	2.570	2.98	0.490	0.330	198.9[201.8]	192.9
LiBr	2.751	2.38	0.591	0.340	189.8	181.0
LiI	3.000	(1.71)	0.599	0.366	177.7	166.1
NaF	2.317	4.65	0.641	0.290	214.4[217.9]	215.2
NaCl	2.820	2.40	1.05	0.321	182.6[185.3]	178.6
NaBr	2.989	1.99	1.33	0.328	173.6[174.3]	169.2
NaI	3.237	1.51	1.58	0.345	163.2[162.3]	156.6
KF	2.674	3.05	1.31	0.298	189.8[194.5]	189.1
KCl	3.147	1.74	2.05	0.326	165.8[169.5]	161.6
KBr	3.298	1.48	2.30	0.336	158.5[159.3]	154.5
KI	3.533	1.17	2.85	0.348	149.9[151.1]	144.5
RbF	2.815	2.62	1.78	0.301	181.4	180.4
RbCl	3.291	1.56	3.19	0.323	159.3	155.4
RbBr	3.445	1.30	3.03	0.338	152.6	148.3
RbI	3.671	1.06	3.99	0.348	144.9	139.6

Data from various tables by M. P. Tosi, Solid State Physics **16**, 1 (1964).

$$B = \frac{1}{V}\frac{dp}{dV} = \frac{1}{\kappa}$$

κ is the compressibility

from Kittel

Photons

The quantization of the electromagnetic field

Wave nature and the particle nature of light

Unification of the laws for electricity and magnetism (described by Maxwell's equations) and light

Quantization of the harmonic oscillator

Planck's radiation law

Serves as a template for the quantization of phonons, magnons, plasmons, electrons, spinons, holons and other quantum particles that inhabit solids.

Maxwell's equations

$$\nabla \cdot \vec{E} = \frac{\rho}{\varepsilon_0}$$

$$\nabla \cdot \vec{B} = 0$$

$$\nabla \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

$$\nabla \times \vec{B} = \mu_0 \vec{J} + \mu_0 \varepsilon_0 \frac{\partial \vec{E}}{\partial t}$$

In vacuum the source terms J and ρ are zero.

The vector potential

$$\vec{B} = \nabla \times \vec{A}$$

$$\vec{E} = -\nabla V - \frac{\partial \vec{A}}{\partial t}$$

Maxwell's equations in terms of A Coulomb gauge $\nabla \cdot \vec{A} = 0$

$$\nabla \cdot \frac{\partial \vec{A}}{\partial t} = 0$$

$$\nabla \cdot \nabla \times \vec{A} = 0$$

$$\nabla \times \frac{\partial \vec{A}}{\partial t} = \frac{\partial}{\partial t} \nabla \times \vec{A}$$

$$\nabla \times \nabla \times \vec{A} = -\mu_0 \varepsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2}$$

The wave equation

$$\nabla \times \nabla \times \vec{A} = -\mu_0 \varepsilon_0 \frac{\partial^2 \vec{A}}{\partial t^2}$$

Using the identity $\nabla \times \nabla \times \vec{A} = \nabla(\nabla \cdot \vec{A}) - \nabla^2 \vec{A}$

$$\boxed{c^2 \nabla^2 \vec{A} = \frac{\partial^2 \vec{A}}{\partial t^2}.}$$

$$c^2 = \frac{1}{\mu_0 \varepsilon_0}$$

normal mode solutions have the form: $\vec{A}(\vec{r},t) = \vec{A}\cos(\vec{k} \cdot \vec{r} - \omega t)$

Normal mode solutions

wave equation: $$c^2\nabla^2\vec{A}=\frac{\partial^2\vec{A}}{\partial t^2}$$

normal mode solution: $$\vec{A}(\vec{r},t)=\vec{A}\cos(\vec{k}\cdot\vec{r}-\omega t)$$ ← Normalschwingungen oder Normalmoden

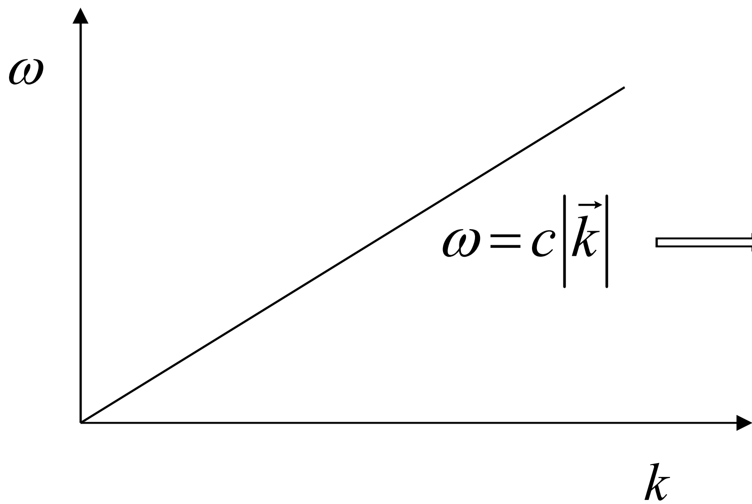
put the solution into the wave equation

$$c^2k^2\vec{A}=\omega^2\vec{A}$$

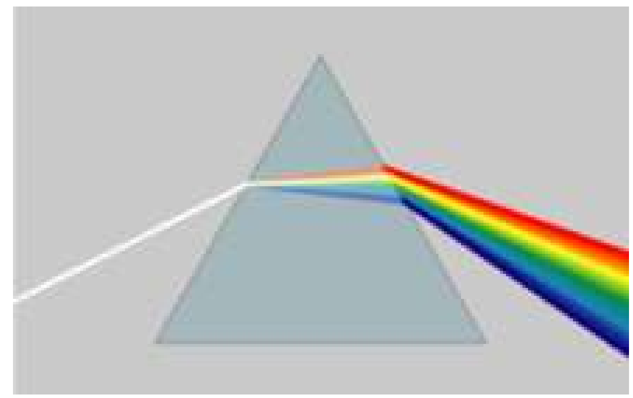
dispersion relation → $$\omega=c\left|\vec{k}\right|$$

$$f=\frac{c}{\lambda}$$

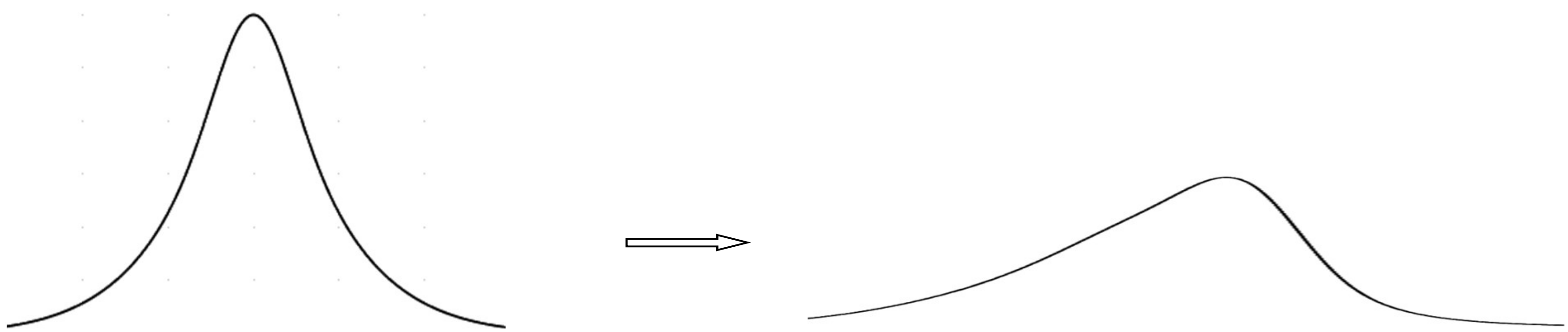
Dispersion relation



$$\omega = c\left|\vec{k}\right| \Longrightarrow f = \frac{c}{\lambda}$$



http://en.wikipedia.org/wiki/Dispersion_%28optics%29



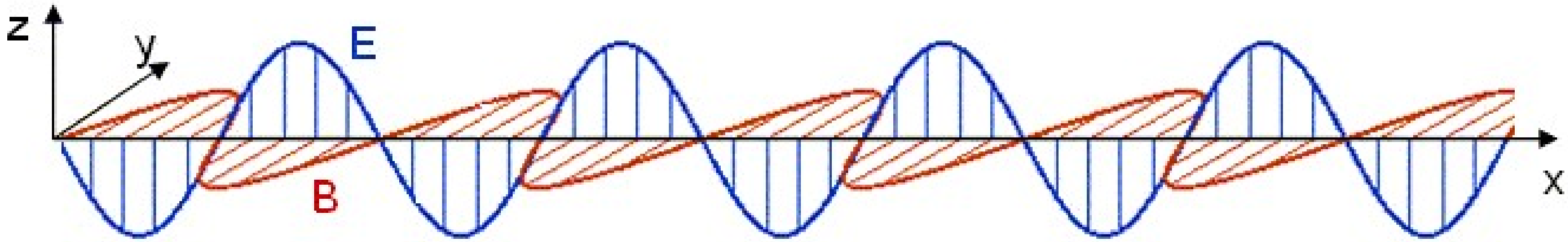
EM waves propagating in the x direction

$$\vec{A} = A_0 \cos(k_x x - \omega t)\hat{z}$$

The electric and magnetic fields are

$$\vec{E} = -\frac{\partial \vec{A}}{\partial t} = -\omega A_0 \sin(k_x x - \omega t)\hat{z}$$

$$\vec{B} = \nabla \times \vec{A} = k_x A_0 \sin(k_x x - \omega t)\hat{y}$$



Quantization (using a trick)

The wave equation for a single mode.

$$-c^2\left(k_x^2+k_y^2+k_z^2\right)\vec{A}(\vec{k},t)=\frac{\partial^2\vec{A}(\vec{k},t)}{\partial t^2}$$

The equation for a single mode is mathematically equivalent to:

$$-\kappa x = m\frac{\partial^2 x}{\partial t^2}$$

$\kappa \leftrightarrow c^2k^2$, $m \leftrightarrow 1$

Quantization

Classical mathematical equivalence $\rightarrow$ quantum mathematical equivalence

$$E = \hbar\omega\left(j + \tfrac{1}{2}\right) \qquad\qquad j = 0, 1, 2\ldots$$

$$\omega = \sqrt{\frac{\kappa}{m}}$$

Rewriting this in terms of the electromagnetic field variables:

$$\kappa \leftrightarrow c^2k^2 \text{ , } m \leftrightarrow 1$$

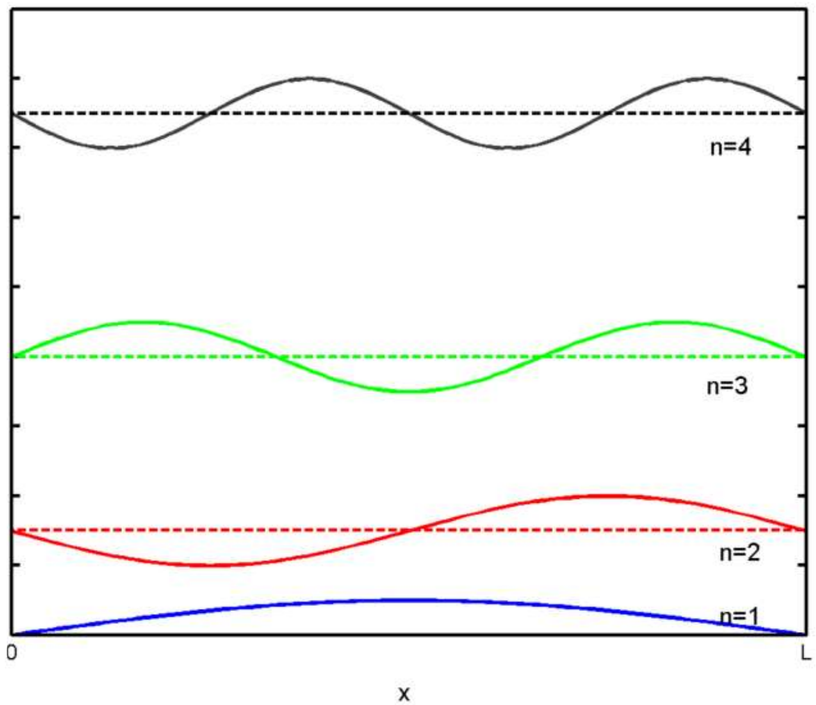
$$E = \hbar\omega\left(j + \tfrac{1}{2}\right) \qquad\qquad j = 0, 1, 2\ldots$$

Dispersion relation $\rightarrow$ $\omega = c\left|\vec{k}\right|$

j is the number of photons in that mode

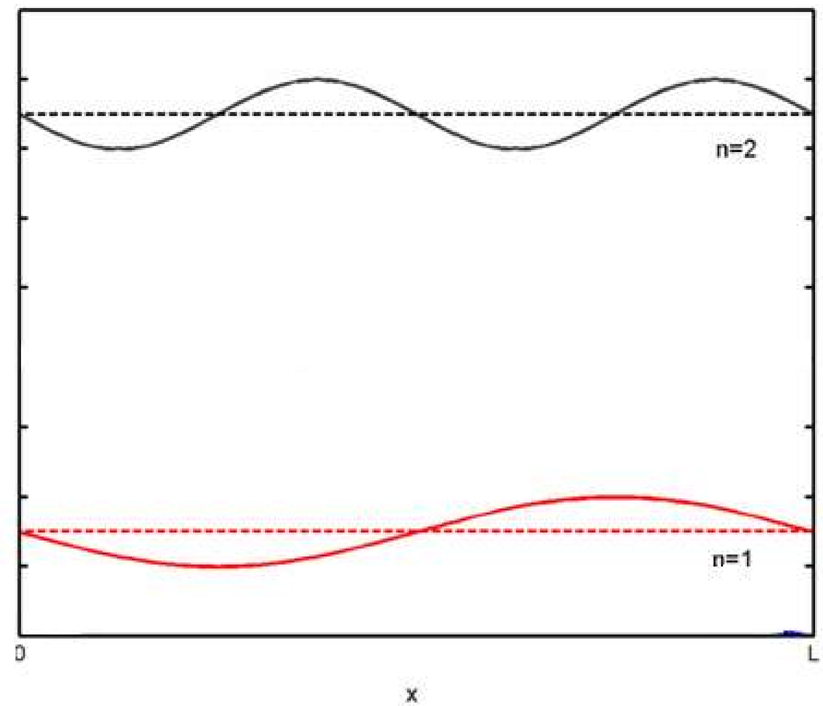
Boundary conditions

fixed boundary conditions



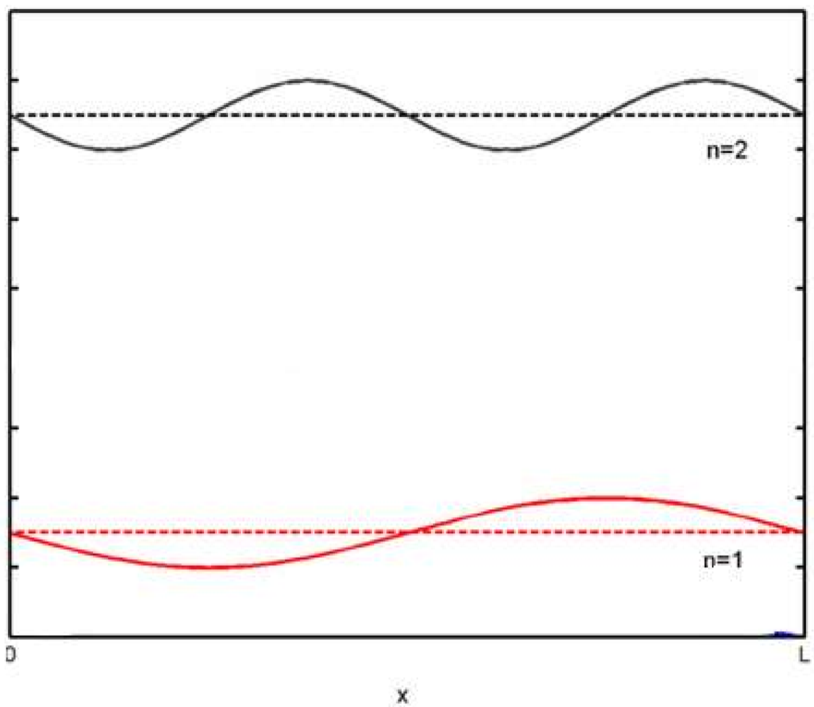
$$k = \frac{2\pi}{\lambda} = \frac{n\pi}{L}$$

periodic boundary conditions



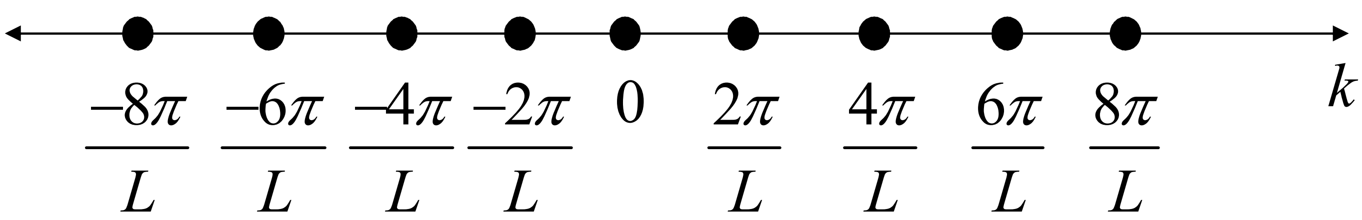
$$k = \pm\frac{2\pi}{\lambda} = \pm\frac{2n\pi}{L}$$

Counting the normal modes

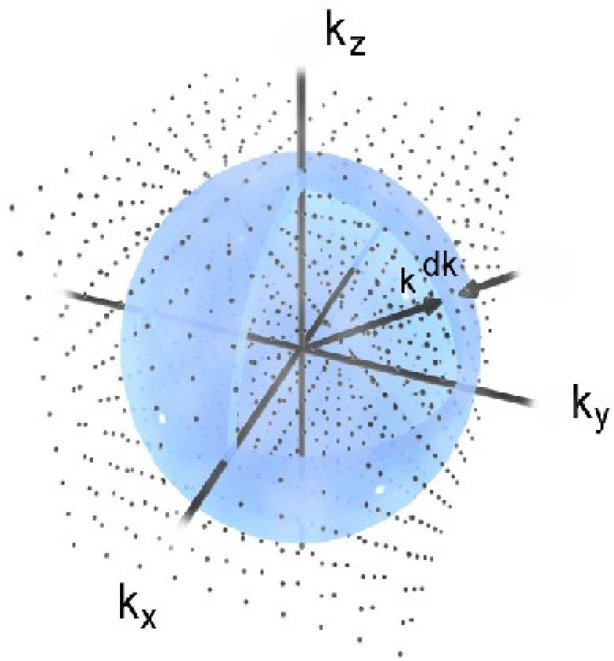


periodic boundary conditions

$$k = \pm \frac{2\pi}{\lambda} = \pm \frac{2n\pi}{L}$$



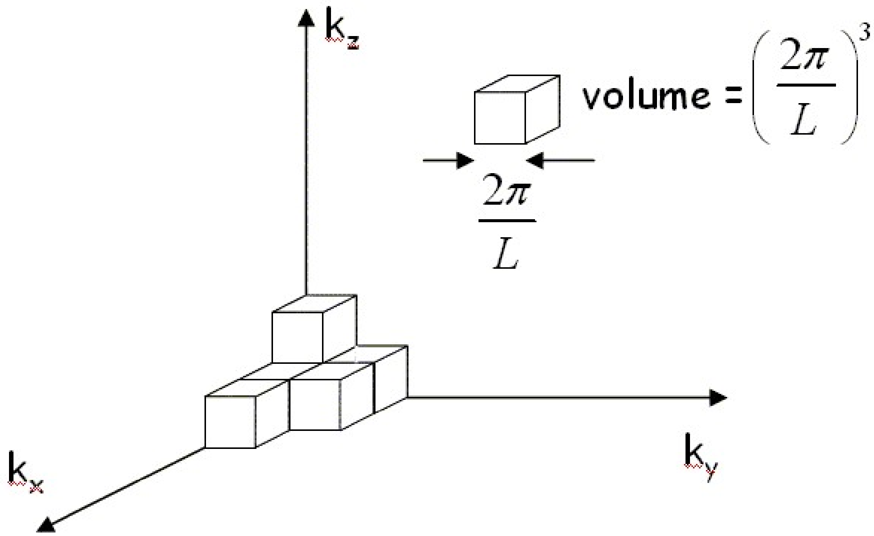
Density of states



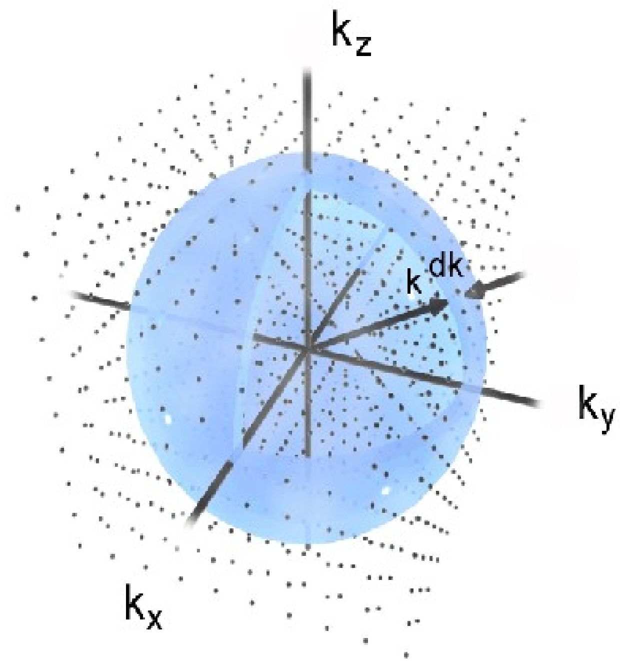
$$k_x, k_y, k_z = \ldots, \frac{-4\pi}{L}, \frac{-2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \ldots$$

All states in the same shell have the same frequency.

Density of states



$$k_x, k_y, k_z = \ldots, \frac{-4\pi}{L}, \frac{-2\pi}{L}, 0, \frac{2\pi}{L}, \frac{4\pi}{L}, \ldots$$



Number of states between k and $k+dk$ for a box of size L^3. =

$$2\frac{4\pi k^2 dk}{\left(\frac{2\pi}{L}\right)^3} = \frac{k^2 L^3}{\pi^2} dk = L^3 D(k) dk$$

polarizations

$D(k) = k^2/\pi^2$ = density of states/m^3

Density of states

The number of states per unit volume with a wavenumber between k and $k + dk$ is,

$$D(k)dk = \frac{k^2}{\pi^2}dk$$

$$\omega = ck \qquad \lambda = 2\pi/k$$

$$d\omega = c\,dk \qquad d\lambda = -2\pi/k^2 dk$$

The number of states per unit volume with a frequency between ω and $\omega + d\omega$ is,

$$D(\omega)d\omega = D(k)dk = \frac{\omega^2}{c^3\pi^2}d\omega.$$

The number of states per unit volume with a wavelength between λ and $\lambda + d\lambda$ is,

$$D(\lambda)d\lambda = D(k)dk = \frac{8\pi}{\lambda^4}d\lambda$$

Photons are Bosons

The mean number of bosons is given by the Bose-Einstein factor.

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

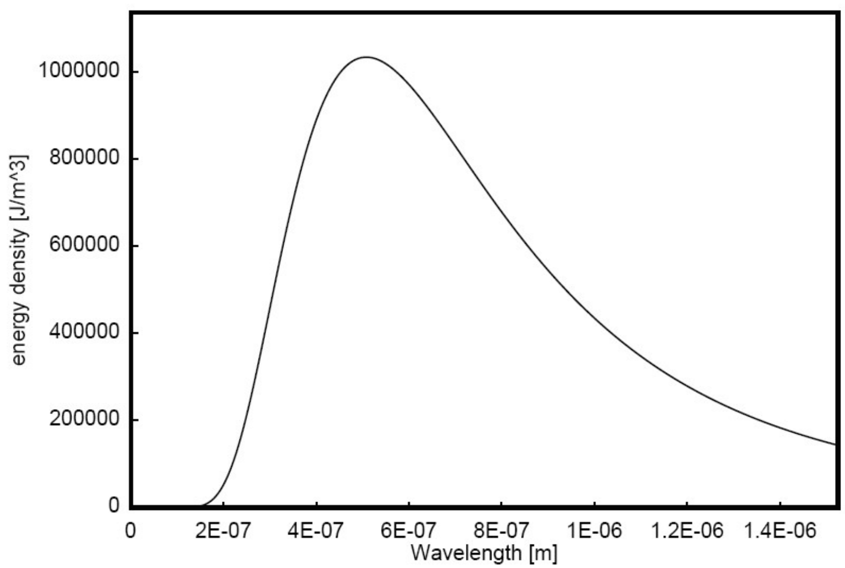
Planck's radiation law

The energy density between λ and λ + $d\lambda$ is the energy $E = hf = hc/\lambda$ of a mode times the density of modes, times the mean number of photons in that mode.

$$\frac{hc}{\lambda}\cdot\frac{8\pi}{\lambda^4}\cdot\frac{1}{e^{hc/\lambda k_B T}-1}\,d\lambda$$

E ; $D(\lambda)$; Bose - Einstein factor

$$u(\lambda)=\frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda k_B T}-1}\,d\lambda \quad \text{J/m}^3$$



Planck's radiation law, Wien's law

Planck's radiation law is often expressed in terms of the intensity

$$I(\lambda) = \frac{2\pi hc^2}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} d\lambda \quad \mathrm{W/m^2}$$

Differentiate to find the position of the peak

Wien's law: $\lambda_{\mathrm{max}} T = 0.0028977$ m K

Stefan - Boltzmann law

Integrate intensity over all wavelengths

$$I = \int_0^\infty \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda k_B T} - 1} d\lambda = \frac{2\pi^5 k_B^4 T^4}{15 h^3 c^2} = \sigma T^4 \quad \mathrm{W/m^2}$$

$$\sigma = 5.67051 \times 10^{-8} \quad \mathrm{W\ m^{-2}\ K^{-4}}$$

Integrating the energy spectral density over all wavelengths

$$u = \frac{4\sigma T^4}{c} \quad \mathrm{J/m^3}$$

Thermodynamic quantities

Specific heat: $c_v = \left(\frac{\partial u}{\partial T}\right)_V = \frac{16\sigma T^3}{c}$ J K^{-1} m^{-3}

entropy: $s = \int \frac{c_v}{T} dT = \frac{16\sigma T^3}{3c}$ J K^{-1} m^{-3}

$$f = u - Ts$$

Helmholtz free energy: $f = \frac{-4\sigma T^4}{3c}$ J/m^3

Thermodynamic quantities

Radiation Pressure: $$P = -\frac{\partial F}{\partial V} = \frac{4\sigma V T^4}{3c} = \frac{4\sigma T^4}{3c} \quad \mathrm{N/m^2}$$

Momentum of a photon: $$\vec{p} = \hbar \vec{k}$$