Bosonic systems

Bose condensate

Number of particles
The avaerage number of particles is

$$\begin{aligned}\bar{N} &= \langle N\rangle = -\left(\frac{\partial\Omega}{\partial\mu}\right)_T \\ &= \sum_l \frac{1}{e^{\beta(\epsilon_l-\mu)}-1}\end{aligned}$$

or

$$\bar{N} = \sum_l \bar{n}_l.$$

We denote

$$z = e^{\beta\mu} = \text{fugacity},$$

so

$$\bar{n}_l = \frac{1}{e^{\beta\epsilon_l}z^{-1}-1}.$$

Let us consider a free non interacting gas. Then

$$\epsilon_l = \frac{\hbar^2 k_l^2}{2m} = \frac{\boldsymbol{p}_l^2}{2m}.$$

Now

$$1 \le e^{\beta\epsilon_l} < \infty.$$

Since $\bar{n}_l \ge 0$, the fugacity is restricted to lie between

$$0 < z < 1$$

or $\mu < 0$.
We treat the state $\boldsymbol{p} = 0$ separately, since the corresponding occupation number $\bar{n}_0$ can become macroscopic:

$$\bar{n}_0 = \frac{z}{1-z} \rightarrow_{z\to 1} \infty.$$

We write the grand potential as

$$\begin{aligned}\Omega_{\mathrm{BE}} &= k_BT\ln\left[1-e^{\beta\mu}\right] \\ &\quad + k_BT\sum_{\boldsymbol{k}\neq 0}\ln\left[1-e^{\beta\mu}e^{-\beta\frac{\hbar^2k^2}{2m}}\right].\end{aligned}$$

Let us define functions $g_\alpha(z)$ so that

$$g_\alpha(z) = \sum_{n=1}^{\infty}\frac{z^n}{n^\alpha}.$$

Then

$$\Omega_{\mathrm{BE}} = k_BT\ln(1-z) - \frac{Vk_BT}{\lambda_T^3}\,g_{5/2}(z).$$

For the number of particles we get

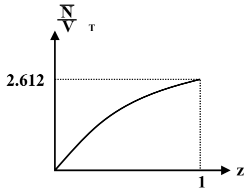
$$\bar{N} = \bar{n}_0 + \frac{V}{\lambda_T^3}\,g_{3/2}(z).$$

When the temperature is high or the density low, the term $\frac{\bar{n}_0}{V}$ is negligible as compared with $\frac{g_{3/2}(z)}{\lambda_T^3}$, i.e.

$$\frac{\bar{N}}{V}\,\lambda_T^3 = g_{3/2}(z).$$

Now $g_{3/2}(z)$ is a positive monotonically increasing function and

$$\begin{aligned}\left(\frac{\bar{N}}{V}\,\lambda_T^3\right)_{z=0} &= g_{3/2}(0) = 0 \\ \left(\frac{\bar{N}}{V}\,\lambda_T^3\right)_{z=1} &= g_{3/2}(1) = \xi(3/2) = 2.612.\end{aligned}$$



Let us choose the density $\rho = \frac{\bar{N}}{V}$ ja T so that

$$\frac{\bar{N}}{V}\,\lambda_T^3 = 2.612,$$

and $z = 1$. If we still increase the density or decrease the temperature the increase of the term $\frac{\bar{N}}{V}\,\lambda_T^3$ must originate from $\frac{\bar{n}_0}{V}\,\lambda_T^3$, since $z \le 1$, i.e.

$$\begin{aligned}\tfrac{\bar{N}}{V}\,\lambda_T^3 &= g_{3/2}(z), &&\text{when } \tfrac{\bar{N}}{V}\,\lambda_T^3 < 2.612 \\ \tfrac{\bar{N}}{V}\,\lambda_T^3 &= \tfrac{\bar{n}_0}{V}\,\lambda_T^3 + g_{3/2}(1), &&\text{when } \tfrac{\bar{N}}{V}\,\lambda_T^3 \ge 2.612.\end{aligned}$$

When

$$\lambda_T^3 \ge 2.612\,\frac{V}{\bar{N}},$$

the state $\boldsymbol{p} = 0$ will be occupied macroscopically forming the *Bose-Einstein condensate.* The formation starts when the temperature is less than the *critical temperature*

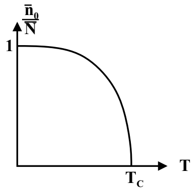
$$T_c = \left(\frac{2\pi\hbar^2}{mk_B}\right)\left(\frac{\rho}{2.612}\right)^{2/3}$$

or the density greater than the *critical density*

$$\rho_c = 2.612\left(\frac{mk_BT}{2\pi\hbar^2}\right)^{3/2}.$$

When $T < T_c$, the relative fraction of the condensate is

$$\frac{\bar{n}_0}{\bar{N}} = 1 - \frac{2.612}{\lambda_T^3}\,\frac{V}{\bar{N}} = 1 - \left(\frac{T}{T_c}\right)^{3/2}.$$

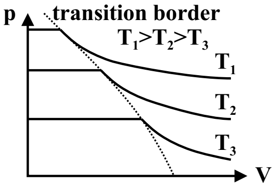


Pressure
With the help of the grand potential the pressure is

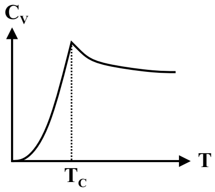
$$\begin{aligned}p &= -\left(\frac{\partial\Omega}{\partial V}\right)_{T,N} = -\frac{\Omega_{\mathrm{BE}}}{V} \\ &= \frac{k_BT}{\lambda_T^3}\,g_{5/2}(z),\end{aligned}$$

so

$$p = \begin{cases} \frac{k_BT}{\lambda_T^3}\, g_{5/2}(z) & \text{above the critical point} \\ \frac{k_BT}{\lambda_T^3}\, g_{5/2}(1) = 1.342\,\frac{k_BT}{\lambda_T^3} & \text{below the critical point.} \end{cases}$$



We are dealing with a 1st order phase transition.

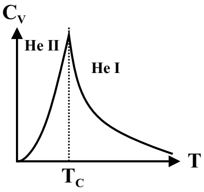


^{4}He liquid

A *second order* phase transition to a *super liquid state* at the temperature $T_c = 2.17$K. The expression given above,

$$T_c = \frac{2\pi\hbar^2}{mk_B}\left(\frac{\rho}{2.612}\right)^{2/3},$$

results $T_c = 3.13$K.



This is called a λ-*transition.*

Two liquid modell

When $T < T_c$, we suppose that ^{4}He is composed of two components: super and normal components. Then

$$\begin{aligned} \rho &= \rho_s + \rho_n \\ \boldsymbol{j} &= \boldsymbol{j}_s + \boldsymbol{j}_n \\ &\vdots \end{aligned}$$

When $T \to 0$, then $\frac{\rho_s}{\rho} \to 1$, but $\frac{\bar{n}_0}{N} \to \sim 0.1$.
This is due to the fact that ^{4}He *is not* an ideal liquid: between ^{4}He atoms there is

- a strong repulsion at short distances,
- an attraction at longer distances.

Black body radiation (photon gas)

The *photon* is a relativistic massles *boson*, whose spin is $S = 1$, so $g = 2S + 1 = 3$. In the vacuum only transversal polarozation exisits, so $g = 2$.

The energy of a photon is

$$\begin{aligned} \epsilon(p) &= \sqrt{(m_0c^2)^2 + (pc)^2} \\ &= pc = \hbar kc. \end{aligned}$$

With the help of the frequency f or of the angular velocity ω the energy is

$$\epsilon = \hbar\omega = \hbar 2\pi f = hf.$$

Since the wave length λ is

$$\lambda = \frac{2\pi}{k},$$

we have

$$\begin{aligned} f &= \frac{c}{\lambda} \\ \omega &= ck. \end{aligned}$$

Density of states

Employing the periodic boundary conditions the wave vector is

$$\boldsymbol{k} = \frac{2\pi}{L}\,(n_x, n_y, n_z),$$

so the number of states in the vicinity of $\boldsymbol{k}$ is

$$\begin{aligned} dN_{\boldsymbol{k}} &= g\left(\frac{L}{2\pi}\right)^3 d\boldsymbol{k} \\ &= g\,\frac{V}{(2\pi)^3}\,4\pi k^2 dk. \end{aligned}$$

With the help of the angular velocity this is

$$\begin{aligned} dN_{\boldsymbol{k}} &= dN_\omega = g\,\frac{V}{(2\pi)^3}\,4\pi\,\frac{\omega^2}{c^2}\,\frac{d\omega}{c} \\ &= g\,\frac{V\omega^2 d\omega}{2\pi^2 c^3}. \end{aligned}$$

We denote now

$$dN_\omega = f(\omega)\,d\omega,$$

so

$$f(\omega)\,d\omega = V\,\frac{\omega^2\,d\omega}{\pi^2 c^3}.$$

The sum over quantum states can be replaced by the integration like

$$\sum_l \cdots = \sum_{\boldsymbol{k},\lambda} \cdots = \int_0^\infty d\omega\, f(\omega) \cdots.$$

Here $\boldsymbol{k}$ is the wave vector and

$$\lambda = \begin{cases} L, & \text{left} \\ R, & \text{right} \end{cases}$$

is the polarization.
Photons obey the *Bose-Einstein statistics*
Let's consider n photons each with the angular velocity ω. The total energy of this system is

$$\epsilon_n(\omega) = n\hbar\omega,$$

so the system is equivalent with a *single harmonic* oscillator,

$$E_n = (n + \frac{1}{2})\hbar\omega = n\hbar\omega + \text{0-point motion}.$$

Thus we can consider a system of one harmonic oscillator which is allowed to exchage energy with its surroundings. So we can set $\mu = 0$.
The Hamiltonian of the system is

$$\hat{H} = \sum_{\boldsymbol{k},\lambda} (\hbar c k) a^\dagger_{\boldsymbol{k}\lambda} a_{\boldsymbol{k}\lambda}.$$

According to the Bose-Einstein distribution the occupation of the energy state $\epsilon(\omega)$ is

$$\bar{n}(\omega) = \frac{1}{e^{\beta\hbar\omega} - 1}.$$

The *total energy* is

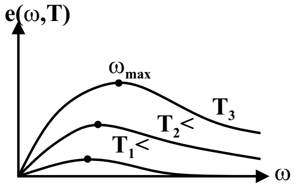
$$E = \int_0^\infty d\omega\, f(\omega)\, \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}.$$

The *energy density* will be

$$\begin{aligned} \frac{E}{V} &= e(T) = \frac{\hbar}{\pi^2 c^3} \int_0^\infty d\omega\, \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \\ &= \int_0^\infty d\omega\, e(\omega, T), \end{aligned}$$

where the energy density at the given angular velocity obeys *Planck's law of radiation*

$$e(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega} - 1)}.$$



We can see that the maximum of the intensity follows the *Wien displacement law*

$$\omega_{\max} = \text{constant} \times T.$$

At the long wave length limit, $\lambda \gg \frac{hc}{k_B T}$ or $\omega \ll \frac{k_B T}{\hbar}$, the energy density obeys the *Rayleigh-Jeans law*

$$e(\omega, T) = \text{vakio} \times \omega^2 T.$$

At a given temperature the energy density will be

$$\begin{aligned} e(T) &= \int_0^\infty d\omega\, \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega} - 1)} \\ &= \frac{\hbar}{\pi^2 c^3} \frac{1}{(\beta\hbar)^4} \int_0^\infty dx\, \frac{x^3}{e^x - 1} \\ &= \frac{k_B^4 T^4}{\pi^2 c^3 \hbar^3} \frac{\pi^4}{15}. \end{aligned}$$

Thus the energy density obeys the *Stefan-Boltzmann law*

$$e(T) = \frac{4}{c}\sigma T^4,$$

where σ is the *Stefan-Boltzmann constant*

$$\sigma = \frac{\pi^2 k_B^4}{60\hbar^3 c^2} = 5.67 \cdot 10^{-8} \frac{\text{W}}{\text{m}^2\text{K}^4}.$$

Now

$$\Omega = F - \mu N = F,$$

since $\mu = 0$. Thus the free energy is

$$\begin{aligned} F &= k_B T \int_0^\infty d\omega\, f(\omega) \ln\left[1 - e^{-\beta\hbar\omega}\right] \\ &= \frac{V}{\pi^2 c^3} k_B T \int_0^\infty d\omega\, \omega^2 \ln\left[1 - e^{-\beta\hbar\omega}\right] \\ &= \frac{V k_B T}{\pi^2 c^3 (\beta\hbar)^3} \int_0^\infty dx\, x^2 \ln\left[1 - e^{-x}\right] \\ &= -V \frac{k_B^4 T^4}{\pi^2 c^3 \hbar^3} \frac{\pi^4}{45}, \end{aligned}$$

or

$$F = -\frac{4}{3}\frac{\sigma}{c} V T^4 = -\frac{1}{3} E.$$

Here

$$E = e(T) V$$

is the total energy.
The *entropy* is

$$S = -\frac{\partial F}{\partial T}$$

or

$$S = \frac{16}{3}\frac{\sigma}{c} V T^3.$$

The *pressure* is

$$p = -\frac{\partial F}{\partial V}$$

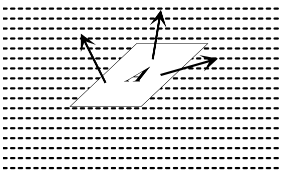
or

$$p = \frac{4}{3}\frac{\sigma}{c} T^4.$$

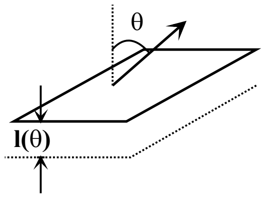
We see that the photon gas satisfies the relation

$$pV = \frac{1}{3} E.$$

Radiation of a black surface



We can think that the emitting surface is a hole on a hollow container filled with isotropic black body radiation. The radiation power can be determined by counting the number of photons escaping through the hole per time interval.



In the time interval τ the photons escaping into the directionθ originate from the region whose depth is

$$\ell(\theta) = c\tau\cos\theta.$$

The total energy of photons landing into the space angle element $d\Omega$ at the direction θ is

$$e(T)Ac\tau\cos\theta\,\frac{d\Omega}{4\pi}.$$

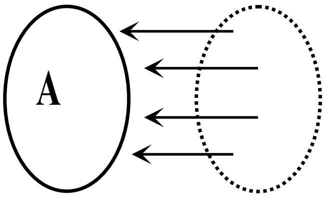
Thus the total energy of the radiation is

$$\begin{aligned} E_{\text{rad}} &= e(T)Ac\tau\int_{\theta=0}^{\pi/2}\cos\theta\,\frac{d\Omega}{4\pi} \\ &= e(T)Ac\tau\,\frac{1}{2}\int_0^{\pi/2} d\theta\,\sin\theta\cos\theta \\ &= \frac{1}{4}Ae(T)c\tau. \end{aligned}$$

The radiation power per unit area is

$$\begin{aligned} P &= \frac{E_{\text{rad}}}{A\tau} = \frac{1}{4}ce(T) \\ &= \sigma T^4. \end{aligned}$$

Absorption and intensity of radiation



When the radiation arrives from a given direction its intensity is

$$\begin{aligned} I &= \frac{E}{A\tau} = \frac{Ac\tau e(T)}{A\tau} \\ &= ce(T) \end{aligned}$$

or

$$I = 4\sigma T^4.$$

The absorption power to a *perpendicular* surface is IA.

Phonons

Classical harmonic lattice

We let the ions of a crystal to oscillate in the vicinity of their equilibrium position. We suppose that

1. At the average equilibrium position the crystal is a Bravais lattice. With every point $\boldsymbol{R}$ of the lattice we can thus associate an atom. The vector $\boldsymbol{R}$, however, reperents only the average position of the ion.
2. Typical deviations from the equilibrium positions are small as compared with the interatomic distances.

According to the hypothesis 1 the atoms of the crystal can be identified with the Bravais lattice points $\boldsymbol{R}$; e.g. $\boldsymbol{r}(\boldsymbol{R})$ stands for the actual position of the ion associated with the lattice point $\boldsymbol{R}$. If $\boldsymbol{u}(\boldsymbol{R})$ is the deviation of the ion $\boldsymbol{R}$ from its equilibrium then

$$\boldsymbol{r}(\boldsymbol{R}) = \boldsymbol{R} + \boldsymbol{u}(\boldsymbol{R}).$$

Let $\phi(\boldsymbol{r})$ be the potential energy of two ions separated by the distance $\boldsymbol{r}$. The energy of the whole lattice is then

$$\begin{aligned} U &= \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'}\phi(\boldsymbol{r}(\boldsymbol{R}) - \boldsymbol{r}(\boldsymbol{R}')) \\ &= \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'}\phi(\boldsymbol{R} - \boldsymbol{R}' + \boldsymbol{u}(\boldsymbol{R}) - \boldsymbol{u}(\boldsymbol{R}')). \end{aligned}$$

When we use the notation $\boldsymbol{P}(\boldsymbol{R})$ for the momentum of the ion $\boldsymbol{R}$ the total Hamiltonian is

$$H = \sum_{\boldsymbol{R}}\frac{\boldsymbol{P}^2(\boldsymbol{R})}{2m} + U.$$

Harmonic approximation

Since the evaluation of the total potential U starting from the actual pair interactions is hopeless we approximate it resorting to the hypothesis 2 ($\boldsymbol{u}(\boldsymbol{R})$ is small). The first terms in the Taylor series of the potential U are

$$\begin{aligned} U &= \frac{N}{2}\sum_{\boldsymbol{R}}\phi(\boldsymbol{R}) \\ &\quad +\frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'}(\boldsymbol{u}(\boldsymbol{R}) - \boldsymbol{u}(\boldsymbol{R}'))\cdot\nabla\phi(\boldsymbol{R} - \boldsymbol{R}') \\ &\quad +\frac{1}{4}\sum_{\boldsymbol{R}\boldsymbol{R}'}[(\boldsymbol{u}(\boldsymbol{R}) - \boldsymbol{u}(\boldsymbol{R}'))\cdot\nabla]^2\phi(\boldsymbol{R} - \boldsymbol{R}') \\ &\quad +\mathcal{O}(u^3). \end{aligned}$$

In the equilibrium the total force due to other ions affecting the ion $\boldsymbol{R}$ is

$$\boldsymbol{F} = -\sum_{\boldsymbol{R}'}\nabla\phi(\boldsymbol{R} - \boldsymbol{R}').$$

Since we are at a equilibrium this force must be zero. Thus the linear term in the series expansion of U vanishes. Up to the second order we are left with

$$U = U^{\text{eq}} + U^{\text{harm}},$$

where U^{eq} is the potential energy of the equilibrium and

$$\begin{aligned} U^{\text{harm}} &= \frac{1}{4}\sum_{\substack{\boldsymbol{R}\boldsymbol{R}' \\ \mu,\nu=x,y,z}} [u_\mu(\boldsymbol{R}) - u_\mu(\boldsymbol{R}')]\phi_{\mu\nu}(\boldsymbol{R} - \boldsymbol{R}') \\ &\qquad \times[u_\nu(\boldsymbol{R}) - u_\nu(\boldsymbol{R}')] \\ \phi_{\mu\nu}(\boldsymbol{r}) &= \frac{\partial^2\phi(\boldsymbol{r})}{\partial r_\mu\partial r_\nu}. \end{aligned}$$

If we are not interested in the quantities related to the equilibrium of the crystal (total energy, total volume, total compessibility, ...) we can forget the term U^{eq}. The harmonic potential is usually written more generally as

$$U^{\mathrm{harm}} = \frac{1}{2} \sum_{\substack{\boldsymbol{R}\boldsymbol{R}' \\ \mu\nu}} u_\mu(\boldsymbol{R}) D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') u_\nu(\boldsymbol{R}').$$

The former expression can be obtained by setting

$$D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') = \delta_{\boldsymbol{R}\boldsymbol{R}'} \sum_{\boldsymbol{R}''} \phi_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}'') - \phi_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}').$$

The heat capacity of classical lattice
The volume element of the the $3N$ dimensional classical phase space formed by the N ions of the lattice is

$$d\Gamma = \prod_{\boldsymbol{R}} \frac{1}{h}\, d\boldsymbol{u}(\boldsymbol{R})\, d\boldsymbol{P}(\boldsymbol{R}) = \prod_{\boldsymbol{R},\mu} \frac{1}{h}\, du_\mu(\boldsymbol{R}) dP_\mu(\boldsymbol{R})$$

and the canonical partition sum

$$Z = \int d\Gamma\, e^{-\beta H}.$$

The total energy E is then

$$E = \frac{1}{Z} \int d\Gamma\, e^{-\beta H} H = -\frac{\partial}{\partial\beta} \ln Z.$$

When we change variables,

$$\begin{aligned} \boldsymbol{u}(\boldsymbol{R}) &= \beta^{-1/2} \bar{\boldsymbol{u}}(\boldsymbol{R}) \\ \boldsymbol{P}(\boldsymbol{R}) &= \beta^{-1/2} \bar{\boldsymbol{P}}(\boldsymbol{R}), \end{aligned}$$

the partion function can be written as

$$\begin{aligned} Z &= \int d\Gamma \exp\left[-\beta\left(\sum \frac{\boldsymbol{P}(\boldsymbol{R})^2}{2M} + U^{\mathrm{eq}} + U^{\mathrm{harm}}\right)\right] \\ &= e^{-\beta U^{\mathrm{eq}}} \beta^{-3N} \int \prod_{\boldsymbol{R}} \frac{1}{h}\, d\bar{\boldsymbol{u}}(\boldsymbol{R})\, d\bar{\boldsymbol{P}}(\boldsymbol{R}) \times \\ &\exp\left[-\sum \frac{\bar{\boldsymbol{P}}(\boldsymbol{R})^2}{2M} - \frac{1}{2} \sum \bar{u}_\mu(\boldsymbol{R}) D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') \bar{u}_\nu(\boldsymbol{R}')\right] \end{aligned}$$

Since all dependence on the temperature is outside of the integral the energy can be calculated easily

$$\begin{aligned} E &= -\frac{\partial}{\partial\beta} \ln(e^{-\beta U^{\mathrm{eq}}} \beta^{-3N} \times \text{vakio}) \\ &= U^{\mathrm{eq}} + 3N k_B T. \end{aligned}$$

The heat capacity is

$$C_v = \frac{\partial E}{\partial T} = 3N k_B.$$

This expression for heat capacity, due to the lattice vibrations, is known as *Dulong-Petit's law.* Experimentally

- at low temperatures the heat capacity is smaller than the one obtained from the Dulong-Petit law. When we approach the temperature $T = 0$ the heat capacity tends to zero.
- even at higher temperatures the measured heat capacities do not approach the Dulong-Petit limit.

Normal modes of the harmonic crystal
One dimenional Bravais lattice
If the separation of the lattice points in the one dimensional Bravais lattice is a the lattice points are na, n an integer. Every lattice point na is associated with one atom.
We suppose that in this one dimensional lattice only the nearest neighbours interact. Using the notation

$$K = \phi''(x),$$

the harmonic potential of the lattice is

$$U^{\mathrm{harm}} = \frac{1}{2} K \sum_n [u(na) - u((n+1)a)]^2.$$

The classical equations of motion are

$$\begin{aligned} M\ddot{u}(na) &= -\frac{\partial U^{\mathrm{harm}}}{\partial u(na)} \\ &= -K[2u(na) - u((n-1)a) - u((n+1)a)]. \end{aligned}$$

We suppose that the N points of the lattice form a ring, i.e. the deviations satisfy the boundary conditions

$$u((N+1)a) = u(a);\ u(0) = u(Na).$$

We seek solutions of the form

$$u(na,t) \propto e^{i(kna-\omega t)}$$

To satisfy the boundary conditions we must have

$$e^{ikNa} = 1.$$

We see that the allowed values for k are

$$k = \frac{2\pi}{a} \frac{n}{N},\ n \text{ integer}.$$

Substituting the exponential trial into the equation of motion we see that the angular velocity ω must satisfy

$$\omega(k) = \sqrt{\frac{2K(1-\cos ka)}{M}} = 2\sqrt{\frac{K}{M}} |\sin \frac{1}{2} ka|.$$

The solutions represent a wave advancing in the ring with the phase velocity $c = \omega/k$ and with the group velocity $v = \partial\omega/\partial k$. If the wave length is large or the wave vector k small then the disperssion relation

$$\omega = \left(a\sqrt{\frac{K}{M}}\right) k$$

is linear and the phase and group velocities equal.

One dimensional lattice with base

We suppose that in the primitive cell there are two atoms. Let the equilibrium positions of the ions to be na and $na+d$, where $d \le a/2$. We denote the deviations of the ions these equlibrium positions by $u_1(na)$ and $u_2(na)$. For the simplicity we suppose that the masses of the atoms are equal. The harmonic interaction due to the nearest neighbours is

$$\begin{aligned} U^{\rm harm} &= \frac{K}{2}\sum_n [u_1(na)-u_2(na)]^2 \\ &+\frac{G}{2}\sum_n [u_2(na)-u_1((n+1)a)]^2, \end{aligned}$$

where K describes the interaction of the ions na and $na+d$, and G the interaction of $na+d$ and $(n+1)a$. The classical equations of motion are

$$\begin{aligned} M\ddot{u}_1(na) &= -\frac{\partial U^{\rm harm}}{\partial u_1(na)} \\ &= -K[u_1(na)-u_2(na)] \\ &\quad -G[u_1(na)-u_2((n-1)a)] \\ M\ddot{u}_2(na) &= -\frac{\partial U^{\rm harm}}{\partial u_2(na)} \\ &= -K[u_2(na)-u_1(na)] \\ &\quad -G[u_2(na)-u_1((n+1)a)]. \end{aligned}$$

Again we look for a solution of the form

$$\begin{aligned} u_1(na) &= \epsilon_1 e^{i(kna-\omega t)} \\ u_2(na) &= \epsilon_2 e^{i(kna-\omega t)}. \end{aligned}$$

Substituting these into the equations of motion we end up with the linear homogenous simultaneous equations

$$\begin{aligned} [M\omega^2-(K+G)]\epsilon_1+(K+Ge^{-ika})\epsilon_2 &= 0 \\ (K+Ge^{ika})\epsilon_1+[M\omega^2-(K+G)]\epsilon_2 &= 0. \end{aligned}$$

This system has a non trivial solution only if the coefficient determinant vanishes. From this we obtain

$$\omega^2 = \frac{K+G}{M} \pm \frac{1}{M}\sqrt{K^2+G^2+2KG\cos ka}.$$

The ration of the amplitudes is

$$\frac{\epsilon_1}{\epsilon_2} = \mp\frac{K+Ge^{ika}}{|K+Ge^{ika}|}.$$

For every allowed wave vector k (counting N) we get *two* solutions. Alltogether the number of the normal modes is now $2N$.

We consider couple of limiting cases.

Case 1. $k \ll \pi/a$

The angular velocities of the modes are now

$$\begin{aligned} \omega &= \sqrt{\frac{2(K+G)}{M}} - \mathcal{O}((ka)^2) \\ \omega &= \sqrt{\frac{KG}{2M(K+G)}}(ka). \end{aligned}$$

Since the latter dispersion relation is linear the corresponding mode is called *acoustic*. In the former mode $\omega = \sqrt{2(K+G)/M}$, when $k=0$. Since at the long wave length limit this mode can couple with electromagnetic radiation it is called the *optical branch*. At the long wave length limit, when $k \approx 0$, the amplitudes satisfy

$$\epsilon_1 = \mp\epsilon_2$$

the upper sign corresponding to the optical mode and the lower sing to the acoustic mode.

Case 2. $k = \pi/a$

At the border of the Brillouin zone the modes are

$$\begin{aligned} \omega &= \sqrt{\frac{2K}{M}}, \text{ optical branch} \\ \omega &= \sqrt{\frac{2G}{M}}, \text{ acoustical branch.} \end{aligned}$$

Correspondingly for the amplitudes

$$\epsilon_1 = \mp\epsilon_2.$$

Case 3. $K \gg G$

The dispersion relations are now

$$\begin{aligned} \omega &= \sqrt{\frac{2K}{M}}\left[1+\mathcal{O}\left(\frac{G}{K}\right)\right] \\ \omega &= \sqrt{\frac{2G}{M}}\sin\frac{1}{2}ka\left[1+\mathcal{O}\left(\frac{G}{K}\right)\right], \end{aligned}$$

and the amplitudes satisfy

$$\epsilon_1 \approx \mp\epsilon_2.$$

The frequency of the optical branch is now independent on the wave vector. Its magnitude corresponds to the vibration frequency of a molecule of two atoms with equal masses and coupled with the spring constant K.

On the other hand, the acoustical branch is the same as in the case of the linear chain.

Case 4. $K = G$

Now we have a Bravais lattice formed by single atoms with the primitive cell length $a/2$.

Three dimensional Bravais lattice of single atoms

Using the matrix notation the harmonic potential can be written more compactly

$$U^{\rm harm} = \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'} \boldsymbol{u}(\boldsymbol{R})\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')\boldsymbol{u}(\boldsymbol{R}').$$

Independent on the interionic forces the matrix $\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')$ obeys certain symmetries:

1. $D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') = D_{\nu\mu}(\boldsymbol{R}'-\boldsymbol{R})$

This property can be verified by exchanging the order of differentiations in the definitions of the elements of $\boldsymbol{D}$:

$$D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') = \left.\frac{\partial^2 U}{\partial u_\mu(\boldsymbol{R})\partial u_\nu(\boldsymbol{R}')}\right|_{\boldsymbol{u}=\boldsymbol{0}}.$$

2. $\boldsymbol{D}(\boldsymbol{R}) = \boldsymbol{D}(-\boldsymbol{R})$

Let's consider a lattice where the displacements from the equilibrium are $\boldsymbol{u}(\boldsymbol{R})$. In the corresponding reversal lattice the displacements are $-\boldsymbol{u}(-\boldsymbol{R})$. Since every Bravais lattice has the inversion symmetry the energies of both lattices must be equal, no matter what the deviations $\boldsymbol{u}(\boldsymbol{R})$ are, i.e.

$$\begin{aligned} U^{\mathrm{harm}} &= \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'} \boldsymbol{u}(\boldsymbol{R})\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')\boldsymbol{u}(\boldsymbol{R}') \\ &= \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'} (-\boldsymbol{u}(-\boldsymbol{R}))\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')(-\boldsymbol{u}(-\boldsymbol{R}')) \\ &= \frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'} \boldsymbol{u}(\boldsymbol{R})\boldsymbol{D}(\boldsymbol{R}'-\boldsymbol{R})\boldsymbol{u}(\boldsymbol{R}'), \end{aligned}$$

for an arbitrary $\boldsymbol{u}(\boldsymbol{R})$. This can be valid only if

$$\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}') = \boldsymbol{D}(\boldsymbol{R}'-\boldsymbol{R}).$$

In addition, according to the symmetry 1, we have

$$D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}') = D_{\nu\mu}(\boldsymbol{R}-\boldsymbol{R}'),$$

so the matrix $\boldsymbol{D}$ is symmetric.

3. $\sum_{\boldsymbol{R}} \boldsymbol{D}(\boldsymbol{R}) = \mathbf{o}$

We move every ion $\boldsymbol{R}$ to $\boldsymbol{R}+\boldsymbol{d}$. This is equivalent with translating the whole lattice by the amount $\boldsymbol{d}$. The potential energies of the original and the translated lattices are equal; in particular at the equilibrium 0, i.e.

$$\begin{aligned} 0 &= \sum_{\substack{\boldsymbol{R}\boldsymbol{R}' \\ \mu\nu}} d_\mu D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}')d_\nu \\ &= \sum_{\mu\nu} N d_\mu d_\nu \left(\sum_{\boldsymbol{R}} D_{\mu\nu}(\boldsymbol{R})\right). \end{aligned}$$

Since the vector $\boldsymbol{d}$ is arbitrary we must have

$$\sum_{\boldsymbol{R}} \boldsymbol{D}(\boldsymbol{R}) = \mathbf{o}.$$

The classical equations of motion

$$M\ddot{u}_\mu(\boldsymbol{R}) = -\frac{\partial U^{\mathrm{harm}}}{\partial u_\mu(\boldsymbol{R})} = -\sum_{\boldsymbol{R}'\nu} D_{\mu\nu}(\boldsymbol{R}-\boldsymbol{R}')u_\nu(\boldsymbol{R}'),$$

or in the matrix notation

$$M\ddot{\boldsymbol{u}}(\boldsymbol{R}) = -\sum_{\boldsymbol{R}'} \boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')\boldsymbol{u}(\boldsymbol{R}')$$

form a system of $3N$ equations. Again we seek solutions of the form

$$\boldsymbol{u}(\boldsymbol{R},t) = \boldsymbol{\epsilon} e^{i(\boldsymbol{k}\cdot\boldsymbol{R}-\omega t)}.$$

Here the *polarisation vector* $\boldsymbol{\epsilon}$ tells us the direction of the motion of the ions. Furthermore we require that for every primitive vector $\boldsymbol{a}_i$ the solutions satisfy the Born-von Karman boundary conditions

$$\boldsymbol{u}(\boldsymbol{R}+N_i\boldsymbol{a}_i) = \boldsymbol{u}(\boldsymbol{R}),$$

when the total number of primitive cells is $N = N_1N_2N_3$. These conditions can be satisfied only if the wave vector $\boldsymbol{k}$ is of form

$$\boldsymbol{k} = \frac{n_1}{N_1}\boldsymbol{b}_1 + \frac{n_2}{N_2}\boldsymbol{b}_2 + \frac{n_3}{N_3}\boldsymbol{b}_3.$$

Here $\boldsymbol{b}_i$ are vectors in the reciprocal lattice and n_i integers.

We see that we get different solution only if $\boldsymbol{k}$ is restricted into the 1st Brillouin zone, i.e. there are exactly N allowed values for the wave vector.

We substtitute the trial into the equations of motion and end up with

$$M\omega^2\boldsymbol{\epsilon} = \boldsymbol{D}(\boldsymbol{k})\boldsymbol{\epsilon}, \qquad (*)$$

where

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

is so called *dynamical matrix.* For every allowed $\boldsymbol{k}$ we have as the solution of $(*)$ three eigen values and vectors. The number of normal modes is therefore $3N$.

Employing symmetry properties of $\boldsymbol{D}(\boldsymbol{R})$ we can rewrite the dynamical matrix as

$$\begin{aligned} \boldsymbol{D}(\boldsymbol{k}) &= \frac{1}{2}\sum_{\boldsymbol{R}} \boldsymbol{D}(\boldsymbol{R})[e^{-i\boldsymbol{k}\cdot\boldsymbol{R}} + e^{i\boldsymbol{k}\cdot\boldsymbol{R}} - 2] \\ &= \sum_{\boldsymbol{R}} \boldsymbol{D}(\boldsymbol{R})[\cos(\boldsymbol{k}\cdot\boldsymbol{R}) - 1]. \end{aligned}$$

Thus the dynamical matrix is

$$\boldsymbol{D}(\boldsymbol{k}) = -2\sum_{\boldsymbol{R}} \boldsymbol{D}(\boldsymbol{R})\sin^2(\frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{R}).$$

We see that $\boldsymbol{D}(\boldsymbol{k})$ is a real and symmetric function of $\boldsymbol{k}$. Since $\boldsymbol{D}(\boldsymbol{R})$ is symmetric $\boldsymbol{D}(\boldsymbol{k})$ is also symmetric. We rewrite the equation $(*)$ as

$$\boldsymbol{D}(\boldsymbol{k})\boldsymbol{\epsilon}_s(\boldsymbol{k}) = \lambda_s(\boldsymbol{k})\boldsymbol{\epsilon}_s(\boldsymbol{k}).$$

As the eigen values of a real and symmetric matrix $\lambda_s(\boldsymbol{k})$ are real and the eigenvectors $\boldsymbol{\epsilon}_s(\boldsymbol{k})$ can be orthonormalized, i.e.

$$\boldsymbol{\epsilon}_s(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_{s'}(\boldsymbol{k}) = \delta_{ss'},\ \ s,s' = 1,2,3.$$

The polarizations of three normal modes are $\boldsymbol{\epsilon}_s(\boldsymbol{k})$ and the angular velocities correspondingly

$$\omega_s(\boldsymbol{k}) = \sqrt{\frac{\lambda_s(\boldsymbol{k})}{M}}.$$

Let us suppose now that the mutual interaction of the ions decreases rapidly with the increasing separation. Strictly speaking we suppose that

$$\lim_{\boldsymbol{R}\to\infty} \boldsymbol{D}(\boldsymbol{R}) = \mathcal{O}(R^{-5}).$$

Then, at long wave length, i.e. when $\boldsymbol{k}\approx\mathbf{o}$, we have

$$\sin^2(\frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{R}) \approx (\frac{1}{2}\boldsymbol{k}\cdot\boldsymbol{R})^2$$

and

$$\boldsymbol{D}(\boldsymbol{k}) \approx -\frac{k^2}{2}\sum_{\boldsymbol{R}}(\hat{\boldsymbol{k}}\cdot\boldsymbol{R})^2\boldsymbol{D}(\boldsymbol{R}).$$

Let $c_s(\hat{\boldsymbol{k}})^2$ be the eigenvalues of the matrix

$$-\frac{1}{2M}\sum_{\boldsymbol{R}}(\hat{\boldsymbol{k}}\cdot\boldsymbol{R})^2\boldsymbol{D}(\boldsymbol{R}).$$

We see that at small wave vectors the frequency is

$$\omega_s(\boldsymbol{k}) = c_s(\hat{\boldsymbol{k}})k.$$

Thus the dispersion of all three modes is a linear function of k so all three modes are acoustical. In general $c_s(\hat{\boldsymbol{k}})$, together with $\omega_s(\boldsymbol{k})$, depend also on the direction $\hat{\boldsymbol{k}}$ of the propagation in addition to the mode s.

Three dimensional lattice with base

We proceed exactly like in the case the one dimensional lattice with base. We suppose that there are p ions in the primitive cell. Every ion in the primitive cell adds one degree of freedom so the total number of modes at a given wave vector $\boldsymbol{k}$ is $3p$. The corresponding frequences are $\omega_s^i(\boldsymbol{k})$, where now $s = 1, 2, 3$ and $i = 1, 2, \ldots, p$. The corresponding displacements are

$$\boldsymbol{u}_s^i(\boldsymbol{R}, t) = \boldsymbol{\epsilon}_s^i(\boldsymbol{k})e^{i(\boldsymbol{k}\cdot\boldsymbol{R}-\omega_s^i(\boldsymbol{k})t)}.$$

The polarizations are no more orthogonal but satisfy

$$\sum_{i=1}^{p}\boldsymbol{\epsilon}_s^{i\,*}(\boldsymbol{k})\cdot\boldsymbol{\epsilon}_{s'}^i(\boldsymbol{k}) = \delta_{ss'}.$$

Analogically with one dimensional lattice 3 of the modes are now acoustical and the rest $3(p-1)$ modes optical.

Quantum mechanical treatment

Let us consider the harmonic Hamiltonian

$$\begin{aligned} H^{\text{harm}} &= \sum_{\boldsymbol{R}}\frac{1}{2M}P(\boldsymbol{R})^2 \\ &\quad +\frac{1}{2}\sum_{\boldsymbol{R}\boldsymbol{R}'}\boldsymbol{u}(\boldsymbol{R})\boldsymbol{D}(\boldsymbol{R}-\boldsymbol{R}')\boldsymbol{u}(\boldsymbol{R}') \end{aligned}$$

describing the lattice. Let $\omega_s(\boldsymbol{k})$ and $\boldsymbol{\epsilon}_s(\boldsymbol{k})$ be the frequences and polarizations in the corresponding classical lattice. We define the operator $a_{\boldsymbol{k}s}$ so that

$$\begin{aligned} a_{\boldsymbol{k}s} &= \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}}e^{-i\boldsymbol{k}\cdot\boldsymbol{R}}\boldsymbol{\epsilon}_s(\boldsymbol{k})\cdot \\ &\quad \left[\sqrt{\frac{M\omega_s(\boldsymbol{k})}{2\hbar}}\boldsymbol{u}(\boldsymbol{R}) + i\sqrt{\frac{1}{2\hbar M\omega_s(\boldsymbol{k})}}\boldsymbol{P}(\boldsymbol{R})\right]. \end{aligned}$$

The Hermitean conjugate $a_{\boldsymbol{k}s}^\dagger$ of the operator $a_{\boldsymbol{k}s}$ is

$$\begin{aligned} a_{\boldsymbol{k}s}^\dagger &= \frac{1}{\sqrt{N}}\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}}\boldsymbol{\epsilon}_s(\boldsymbol{k})\cdot \\ &\quad \left[\sqrt{\frac{M\omega_s(\boldsymbol{k})}{2\hbar}}\boldsymbol{u}(\boldsymbol{R}) - i\sqrt{\frac{1}{2\hbar M\omega_s(\boldsymbol{k})}}\boldsymbol{P}(\boldsymbol{R})\right]. \end{aligned}$$

The operator $a_{\boldsymbol{k}s}^\dagger$ is called the phonon creation operator and $a_{\boldsymbol{k}s}$ the phonon destruction operator.
We employ the canonical commutation relations for the position and momentum

$$\begin{aligned} [u_\mu(\boldsymbol{R}), P_\nu(\boldsymbol{R}')] &= i\hbar\delta_{\mu\nu}\delta_{\boldsymbol{R}\boldsymbol{R}'} \\ [u_\mu(\boldsymbol{R}), u_\nu(\boldsymbol{R}')] &= [P_\mu(\boldsymbol{R}), P_\nu(\boldsymbol{R}')] = 0, \end{aligned}$$

the identities

$$\sum_{\boldsymbol{R}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = \begin{cases} 0, & \boldsymbol{k}\text{ is not a reciprocal vector} \\ N, & \boldsymbol{k}\text{ is a reciprocal vector} \end{cases}$$

and

$$\sum_{\boldsymbol{k}}e^{i\boldsymbol{k}\cdot\boldsymbol{R}} = 0,\ \boldsymbol{R}\neq 0$$

together with the property of an orthogonal vector set

$$\sum_{s=1}^{3}[\boldsymbol{\epsilon}_s(\boldsymbol{k})]_\mu[\boldsymbol{\epsilon}_s(\boldsymbol{k})]_\nu = \delta_{\mu\nu}.$$

One can straightforwardly show that the creation and annihilation operators obey the commutation relations

$$\begin{aligned} [a_{\boldsymbol{k}s}, a_{\boldsymbol{k}'s'}^\dagger] &= \delta_{\boldsymbol{k}\boldsymbol{k}'}\delta_{ss'} \\ [a_{\boldsymbol{k}s}, a_{\boldsymbol{k}'s'}] &= [a_{\boldsymbol{k}s}^\dagger, a_{\boldsymbol{k}'s'}^\dagger] = 0. \end{aligned}$$

With the help of the creation and destruction operators the operators $\boldsymbol{u}(\boldsymbol{R})$ and $\boldsymbol{P}(\boldsymbol{R})$ can be written as

$$\begin{aligned} \boldsymbol{u}(\boldsymbol{R}) &= \frac{1}{\sqrt{N}}\sum_{\boldsymbol{k}s}\sqrt{\frac{\hbar}{2M\omega_s(\boldsymbol{k})}}(a_{\boldsymbol{k}s} + a_{-\boldsymbol{k}s}^\dagger)\times \\ &\quad \boldsymbol{\epsilon}_s(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{R}} \\ \boldsymbol{P}(\boldsymbol{R}) &= \frac{-i}{\sqrt{N}}\sum_{\boldsymbol{k}s}\sqrt{\frac{\hbar M\omega_s(\boldsymbol{k})}{2}}(a_{\boldsymbol{k}s} - a_{-\boldsymbol{k}s}^\dagger)\times \\ &\quad \boldsymbol{\epsilon}_s(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{R}}. \end{aligned}$$

The Hamiltonian is now

$$H = \sum_{\boldsymbol{k}s}\hbar\omega_s(\boldsymbol{k})(a_{\boldsymbol{k}s}^\dagger a_{\boldsymbol{k}s} + \frac{1}{2}).$$

This is simply the Hamiltonian of the system of $3N$ independent harmonic oscillators whose energies are correspondingly

$$E = \sum_{\boldsymbol{k}s}(n_{\boldsymbol{k}s} + \frac{1}{2})\hbar\omega_s(\boldsymbol{k}).$$

Here $n_{\boldsymbol{k}s}$ the eigenvalues of the occupation number operator $\hat{n}_{\boldsymbol{k}s} = a_{\boldsymbol{k}s}^\dagger a_{\boldsymbol{k}s}$, i.e. $n_{\boldsymbol{k}s} = 0, 1, 2, \ldots$.

Einstein's model

Let us suppose that every ion of the crystal moves in a similar potential well. Then

$$H = \sum_{\boldsymbol{k}s}\hbar\omega_E(a_{\boldsymbol{k}s}^\dagger a_{\boldsymbol{k}s} + \frac{1}{2}),$$

where the parameter

$$\omega_E \equiv \frac{k_BT_E}{\hbar}$$

is the *Einstein frequency* common for all $3N$ oscillators and T_E the corresponding *Einstein temperature.*
The partition function of one single harmonic oscillator is

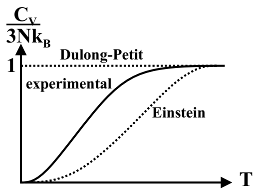
$$\begin{aligned} Z_{\mathrm{harm}}(\omega) &= \operatorname{Tr} e^{-\beta\hbar\omega(a^\dagger a+\frac{1}{2})} = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+\frac{1}{2})} \\ &= e^{-\frac{1}{2}\beta\hbar\omega}\sum_n \left(e^{-\beta\hbar\omega}\right)^n = \frac{e^{-\frac{1}{2}\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}} \\ &= \frac{1}{2\sinh(\frac{1}{2}\beta\hbar\omega)}. \end{aligned}$$

Since the number of modes is $3N$ the canonical partition function is

$$\begin{aligned} Z &= \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{3N}=1}^{\infty} e^{-\beta\hbar\omega_E\sum_{j=1}^{3N}(n_j+\frac{1}{2})} \\ &= \prod_{j=1}^{3N}\sum_{n=0}^{\infty} e^{-\beta\hbar\omega_E(n+\frac{1}{2})} = Z_{\mathrm{harm}}^{3N}(\omega_E) \\ &= \left[2\sinh\left(\frac{T_E}{2T}\right)\right]^{-3N}. \end{aligned}$$

The heat capacity is

$$\begin{aligned} C_V &= \frac{\partial E}{\partial T} = -\frac{\partial}{\partial T}\frac{\partial}{\partial \beta}\ln Z = \frac{\partial}{\partial T}\left(k_BT^2\frac{\partial \ln Z}{\partial T}\right) \\ &= k_BT\frac{\partial^2}{\partial T^2}T\ln Z = 3Nk_B\,\frac{(T_E/2T)^2}{\sinh^2(T_E/2T)}. \end{aligned}$$



Debye's model

To get the exact solution we should evaluate the partition function

$$\begin{aligned} Z &= \operatorname{Tr} e^{-\beta\sum_{\boldsymbol{k}s}\hbar\omega_s(\boldsymbol{k})(a^\dagger_{\boldsymbol{k}s}a_{\boldsymbol{k}s}+\frac{1}{2})} \\ &= \sum_{\{n_{\boldsymbol{k}s}=0\}}^{\infty} e^{-\beta\sum_{\boldsymbol{k}s}\hbar\omega_s(\boldsymbol{k})(n_{\boldsymbol{k}s}+\frac{1}{2})}, \end{aligned}$$

which in turn would require the knowledge of of the disperions $\omega_s(\boldsymbol{k})$. In practice we have to be satisfied with, normally quite realistic, *Debye's model*:

- At low temperatures only the contribution of the low energetic phonons is prominent, so
  - we take into account only the acoustic modes: 2 tranversal and 1 longitudinal.
  - we take only the phonons associated with small k, so we can employ the linear dispersions

$$\begin{aligned} \omega_l(k) &= c_lk \\ \omega_t(k) &= c_tk. \end{aligned}$$

- We cut the spectra at the *Debye frequency*

$$\omega_D \equiv \frac{k_BT_D}{\hbar},$$

  where T_D is the corresponding *Debye temperature.*

In each mode j the density of states is

$$dN_j = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk = \frac{V}{2\pi^2c_j^3}\,\omega^2 d\omega.$$

Thus the total density is

$$dN = \frac{V}{2\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)\omega^2 d\omega.$$

Since the total number of modes is

$$3N = \int_{\omega=0}^{\omega_D} dN = \frac{V}{6\pi^2}\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)\omega_D^3$$

we get as the Debye temperature

$$\omega_D^3 = \frac{N}{V}\,18\pi^2\left(\frac{2}{c_t^3}+\frac{1}{c_l^3}\right)^{-1}$$

and correspondingly as the state density

$$dN(\omega) = \frac{9N}{\omega_D^3}\,\omega^2 d\omega \quad (\omega < \omega_D).$$

The canonical partition function is

$$\begin{aligned} Z &= \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_{3N}=0}^{\infty} e^{-\beta\sum_{\boldsymbol{k}s}\hbar\omega_s(\boldsymbol{k})(n_{\boldsymbol{k}s}+\frac{1}{2})} \\ &= \prod_{\boldsymbol{k}s}\frac{e^{-\frac{1}{2}\beta\hbar\omega_s(\boldsymbol{k})}}{1-e^{-\beta\hbar\omega_s(\boldsymbol{k})}}, \end{aligned}$$

from which we can derive as the free energy

$$F = \underbrace{\sum_{\boldsymbol{k}s}\frac{1}{2}\hbar\omega_s(\boldsymbol{k})}_{\text{0-point energy}} + k_BT\sum_{\boldsymbol{k}s}\ln\left[1-e^{-\beta\hbar\omega_s(\boldsymbol{k})}\right]$$

or

$$F = F_0 + k_BT\,\frac{9N}{\omega_D^3}\int_0^{\infty} d\omega\,\omega^2\ln\left(1-e^{-\beta\hbar\omega}\right).$$

Since $S = -\frac{\partial F}{\partial T}$ and $C_V = T\frac{\partial S}{\partial T}$, is $C_V = -T\frac{\partial^2 F}{\partial T^2}$, so we have

$$C_V = 3Nk_Bf_D\left(\frac{T_D}{T}\right).$$

Here

$$f_D(x) = \frac{3}{x^3}\int_0^x dy\,\frac{y^4e^y}{(e^y-1)^2}$$

is the so called *Debye function.*
Typical Debye temperatures

	T_D
Au	170
Cu	315
Fe	420
Cr	460
B	1250
C (diamond)	1860

Note The higher T_D the stiffer, harder crystal.
Behaviour of C_V:
$T \to \infty$
Since

$$f_D(x) \underset{x\to 0}{\to} \frac{3}{x^3}\int_0^x dy\, y^2 = 1,$$

we have

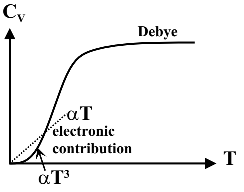
$$C_V \to 3Nk_B,$$

or we end up with the Dulong-Petit heat capacity.
$T \to 0$
Since

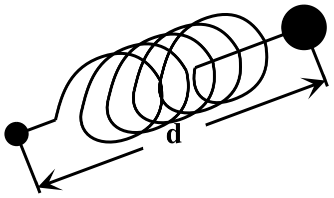
$$f_D(x) \underset{x\to\infty}{\to} \frac{3}{x^3}\int_0^\infty dy\, \frac{y^4 e^y}{(e^y-1)^2} = \frac{\text{constant}}{x^3},$$

we get

$$C_V(T) \to \text{vakio} \times T^3 = \frac{12\pi^4}{5} Nk_B \left(\frac{T}{T_D}\right)^3 .$$



Diatomic ideal gas



We classify molecules of two atoms to

- homopolar molecules (identical atoms), e.g. H_2, N_2, O_2, …, and
- heteropolar molecules (different atoms), e.g. CO, NO, HCl, …

When the density of the gas is low the intermolecular interactions are minimal and the ideal gas equation of state holds. The internal degrees of freedom, however, change the thermal properties (like C_V).
When we suppose that the modes corresponding to the internal degrees of freedom are independent on each other, we can write the total Hamiltonian of the molecule as the sum

$$H \approx H^{\text{tr}} + H^{\text{rot}} + H^{\text{vibr}} + H^{\text{el}} + H^{\text{ydin}}.$$

Here

$H^{\text{tr}} = \frac{\boldsymbol{p}^2}{2m}$ = kinetic energy
m = mass of molecule

$H^{\text{rot}} = \frac{\boldsymbol{L}^2}{2I}$ = rotational energy
$\boldsymbol{L}$ = angular momentum
I = moment of inertia

$$I = \sum_i m_i x_i^2 = \frac{m_1 m_2}{m_1+m_2} d^2$$

Example H_2-molecule
$d = 0.75$Å
$L = \hbar\sqrt{l(l+1)}, \quad l = 0,1,2,\ldots$
$\frac{\hbar^2}{2Ik_B} = 85.41$K
eigenvalues
$\frac{\hbar^2}{2I} l(l+1)$
are $(2l+1)$-fold degenerated

$H^{\text{vibr}} = \hbar\omega_v(\hat{n} + \frac{1}{2})$ = vibration energy
The vibrational degrees of freedom of the separation d of nuclei correspond at small amplitudes to a linear harmonic oscillator.
$\hat{n} = a^\dagger a = 0,1,2,\ldots$
Each energy level is non degenerate

H^{el} = electronic energies

- jumping of electrons from an orbital to another
- ionization
- energies $\gtrsim 1$eV $\approx k_B 10^4$K
- in normal circumstances these degrees of freedom are frozen and can be neglected.

H^{nucl} = energies corresponding to nucleonic degrees of freedom
In normal circumstances only the nuclear spins are interesting. The spin degeneracy is
$g_y = (2I_1+1)(2I_2+1)$,
where I_1 and I_2 are the spins of the nuclei

Energy terms do not couple appreciably, i.e. the energy E_i of the state i is

$$E_i \approx E_{\mathrm{tr}} + E_{\mathrm{rot}} + E_{\mathrm{vibr}},$$

so the partition sum of one molecule is

$$\begin{aligned} Z_1 &= \sum_{\boldsymbol{p}} \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} g_y (2l+1) \times \\ & \quad e^{-\beta \frac{p^2}{2m} - \beta \frac{\hbar^2}{2I} l(l+1) - \beta \hbar \omega_v (n+\frac{1}{2})} \\ &= Z^{\mathrm{tr}} Z^{\mathrm{rot}} Z^{\mathrm{vibr}} Z^{\mathrm{nucl}}, \end{aligned}$$

i.e. the state sum can be factorized.
Above

$$\begin{aligned} Z^{\mathrm{tr}} &= \sum_{\boldsymbol{p}} e^{-\beta \frac{p^2}{2m}} = \frac{V}{\lambda_T^3} \\ & \quad \lambda_T = \sqrt{\frac{h^2}{2\pi m k_B T}} \\ Z^{\mathrm{rot}} &= \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \\ & \quad T_r = \frac{\hbar^2}{2 I k_B} \\ Z^{\mathrm{vibr}} &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega_v (n+\frac{1}{2})} \\ &= \left[2 \sinh \frac{T_v}{2T} \right]^{-1} \\ & \quad T_v = \frac{\hbar \omega_v}{k_B} \\ Z^{\mathrm{nucl}} &= g_y = (2I_1+1)(2I_2+1). \end{aligned}$$

Approximatively (neglecting the multiple occupation of states) the state sum of N molecules is

$$Z_N = \frac{1}{N!} Z_1^N,$$

where $1/N!$ takes care of the identity of molecules. We associate this factor with the tranlational sum.
The free energy

$$F = -k_B T \ln Z_N$$

can be divided into terms

$$\begin{aligned} F^{\mathrm{tr}} &= -k_B T \ln \left[\frac{1}{N!} \left(Z^{\mathrm{tr}} \right)^N \right] \\ &= -k_B T \ln \left[\frac{1}{N!} V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2} N} \right] \\ &= -k_B T N \left[\ln \frac{V}{N} + 1 + \frac{3}{2} \ln k_B T + \frac{3}{2} \ln \frac{2\pi m}{h^2} \right] \\ F^{\mathrm{rot}} &= -N k_B T \ln \left\{ \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \right\} \\ F^{\mathrm{vibr}} &= N k_B T \ln \left[2 \sinh \frac{T_v}{2T} \right] \\ F_{\mathrm{nucl}} &= -N k_B T \ln g_y . \end{aligned}$$

The internal energy is

$$\begin{aligned} U &= F + TS = F - T \frac{\partial F}{\partial T} \\ &= -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right), \end{aligned}$$

so the internal energy corresponding to tranlational degrees of freedom is

$$U^{\mathrm{tr}} = -T^2 \frac{\partial}{\partial T} \left(\frac{F^{\mathrm{tr}}}{T} \right) = N \frac{3}{2} k_B T$$

and

$$C_V^{\mathrm{tr}} = \frac{3}{2} N k_B$$

so we end up with the ideal gas result.
Since only F^{tr} depends on volume V the pressure is

$$p = -\frac{\partial F}{\partial V} = -\frac{\partial F^{\mathrm{tr}}}{\partial V} = \frac{N k_B T}{V},$$

i.e. we end up with the ideal gas equation of state

$$pV = N k_B T.$$

Rotation
Typical rotational temperatures

Gas	T_r
H_2	85.4
N_2	2.9
NO	2.4
HCl	15.2
Cl_2	0.36

We see that $T_r \ll$ the room temperature.
$T \ll T_r$
Now

$$Z^{\mathrm{rot}} = \sum_{l=0}^{\infty} (2l+1) e^{-\frac{T_r}{T} l(l+1)} \approx 1 + 3 e^{-2 \frac{T_r}{T}},$$

so the corresponding free energy is

$$F^{\mathrm{rot}} \approx -3 N k_B T e^{-2 \frac{T_r}{T}}$$

and the internal energy

$$U^{\mathrm{rot}} = -T^2 \frac{\partial}{\partial T} \left(\frac{F^{\mathrm{rot}}}{T} \right) \approx 6 N k_B T_r e^{-2 \frac{T_r}{T}}.$$

Rotations contribute to the heat capacity like

$$C_V^{\mathrm{rot}} \approx 12 N k_B \left(\frac{T_r}{T} \right)^2 e^{-2 \frac{T_r}{T}} \underset{T \to 0}{\longrightarrow} 0.$$

$T \gg T_r$
Now

$$\begin{aligned} Z^{\mathrm{rot}} &\approx \int_0^{\infty} dl \, (2l+1) e^{-\frac{T_r}{T} l(l+1)} \\ &= -\frac{T}{T_r} \Big/_{0}^{\infty} e^{-\frac{T_r}{T} l(l+1)} = \frac{T}{T_r}, \end{aligned}$$

so the free energy is

$$F^{\text{rot}} \approx -Nk_BT\ln\frac{T}{T_r}$$

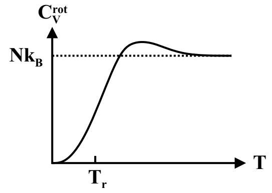
and the internal energy

$$U^{\text{rot}} \approx Nk_BT.$$

The contribution to the heat capacity is

$$C_V^{\text{rot}} \approx Nk_B = f^{\text{rot}}\frac{1}{2}Nk_B,$$

or in the limit $T \gg T_r$ there are $f^{\text{rot}} = 2$ rotational degrees of freedom.
Precisely:



Vibration
Typical vibrational temperatures:

Gas	T_v
H_2	6100
N_2	3340
NO	2690
O_2	2230
HCl	4140

We see that $T_v \gg$ the room temperature.
$T \ll T_v$
The free energy is

$$\begin{aligned} F^{\text{vibr}} &= Nk_BT\ln\left[e^{\frac{T_v}{2T}}(1-e^{-\frac{T_v}{T}})\right] \\ &\approx \frac{1}{2}Nk_BT_v - Nk_BTe^{-\frac{T_v}{T}}, \end{aligned}$$

so

$$C_V^{\text{vibr}} \approx Nk_B\left(\frac{T_v}{T}\right)^2 e^{-\frac{T_v}{T}}.$$

$T \gg T_v$
Now the free energy is

$$F^{\text{vibr}} \approx Nk_BT\ln\frac{T_v}{T}$$

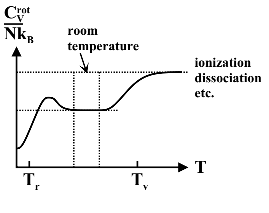
and the internal energy correspondingly

$$U^{\text{vibr}} \approx Nk_BT,$$

so the heat capacity is

$$C_V^{\text{vibr}} \approx Nk_B.$$

We see that in the limit $T \gg T_v$ two degrees of freedom are associated with vibrations like always with harmonic oscillators ($E = \langle T\rangle + \langle V\rangle = 2\langle T\rangle$).



Rotation of homopolar molecules
The symmetries due to the identity of nuclei must be taken into account.
Example H_2-gas:
The nuclear spins are

$$I_1 = I_2 = \frac{1}{2},$$

so the total spin of the molecule is

$$I = 0, 1.$$

We consider these two cases:

$\uparrow\uparrow$	$\uparrow\downarrow$
$I = 1$	$I = 0$
$I_z = -1, 0, 1$	$I_z = 0$
triplet	singlet
orthohydrogen	parahydrogen
spin wavefunctions symmetric:	spin wave function antisymmetric:
$\lvert 1\,1\rangle = \lvert\uparrow\uparrow\rangle$ $\lvert 1\,0\rangle = \frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow\rangle + \lvert\downarrow\uparrow\rangle)$ $\lvert 1\,{-1}\rangle = \lvert\downarrow\downarrow\rangle$	$\lvert 0\,0\rangle = \frac{1}{\sqrt{2}}(\lvert\uparrow\downarrow\rangle - \lvert\downarrow\uparrow\rangle)$
Space wave function antisymmetric:	Space wave function symmetric:
$(-1)^l = -1$	$(-1)^l = 1$

The corresponding partition functions are

$$\begin{aligned} Z_{\text{ortho}} &= \sum_{l=1,3,5,\ldots}(2l+1)e^{-\frac{T_r}{T}\,l(l+1)} \\ Z_{\text{para}} &= \sum_{l=0,2,4,\ldots}(2l+1)e^{-\frac{T_r}{T}\,l(l+1)} \end{aligned}$$

and the partition function associated with rotation is

$$Z^{\text{rot}} = 3Z_{\text{ortho}} + Z_{\text{para}}.$$

When $T \gg T_r$ collisions cause conversions between ortho and para states so the system is in an equilibrium. In addition $Z_{\text{orto}} \approx Z_{\text{para}}$, so all 4 spin states are equally probable.
When $T \lesssim T_r$ the gas may remain as an *metastable mixture* of ortho and para hydrogens. In the mixture the ratio of the spin populations is 3 : 1. Then we must use the partion sum

$$Z_N^{\text{rot}} = Z_{\text{orto}}^{\frac{3N}{4}} Z_{\text{para}}^{\frac{N}{4}}.$$

The internal energy is now

$$U^{\text{rot}} = \frac{3}{4}U^{\text{orto}} + \frac{1}{4}U^{\text{para}}$$

and the heat capacity correspondingly

$$C^{\text{rot}} = \frac{3}{4}C^{\text{orto}} + \frac{1}{4}C^{\text{para}}.$$