

8. Bosonic systems

8.1 Bose gas and Bose condensation

■ **Perfect Bose-Einstein gas.** In case of translational invariant ideal boson system with the non-relativistic dispersion law $\varepsilon_\ell = p^2/2m$ in the thermodynamic limit the sum over one-particle states may be replaced by the integral

$$\sum_\ell \cdots = g \sum_{\mathbf{k}} \cdots = \int_0^\infty d\varepsilon \omega_1(\varepsilon) \cdots, \quad (8.1)$$

where $\omega_1(\varepsilon) = C_1 V \sqrt{\varepsilon}$ and

$$C_1 = 2\pi g \left(\frac{2m}{h^2} \right)^{\frac{3}{2}}. \quad (8.2)$$

The particle number, energy and the grand potential are then

$$\bar{N} = C_1 V \int_0^\infty d\varepsilon \sqrt{\varepsilon} \frac{1}{e^{\beta(\varepsilon-\mu)} - 1}, \quad (8.3)$$

$$E = C_1 V \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1}, \quad (8.4)$$

$$\Omega = C_1 V T \int_0^\infty d\varepsilon \sqrt{\varepsilon} \ln \left[1 - e^{-\beta(\varepsilon-\mu)} \right] = -\frac{2}{3} C_1 V \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta(\varepsilon-\mu)} - 1}. \quad (8.5)$$

In the limit of dilute gas ($n = N/V \rightarrow 0$, when also $z = e^{\beta\mu} \rightarrow 0$) these quantities coincide with those of the Maxwell–Boltzmann ideal gas so that in this region the ideal Bose gas obeys the equation of state of the classical ideal gas.

Corrections to the MB limit may be conveniently obtained, when the functions (8.3), (8.4) and (8.5) are expressed as series in the fugacity z . Consider, for instance, the integral for the grand potential:

$$\Omega = -\frac{2}{3} C_1 V \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} z^{-1} - 1} = -\frac{2}{3} C_1 V \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2} z e^{-\beta\varepsilon}}{1 - e^{-\beta\varepsilon} z}.$$

The denominator of the integrand gives rise to geometric series, and having changed the order of integration and summation we arrive at readily calculable integrals of the form

$$\int_0^\infty d\varepsilon \varepsilon^{3/2} e^{-\beta\varepsilon(n+1)} = \frac{T^{5/2} \Gamma(5/2)}{(n+1)^{5/2}}.$$

We thus obtain

$$\Omega = -\frac{2}{3} C_1 \Gamma\left(\frac{5}{2}\right) V z T^{5/2} \sum_{n=0}^{\infty} \frac{z^n}{(n+1)^{5/2}}.$$

The series here is one definition of a less known special function, the *polylogarithm* Li_ν :

$$\text{Li}_\nu(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^\nu}. \quad (8.6)$$

From this series of unit radius of convergence we immediately see the connection with the Riemann ζ function:

$$\text{Li}_\nu(1) = \zeta(\nu). \quad (8.7)$$

From the calculation of the integral for the grand potential the following generalization is readily inferred:

$$\text{Li}_\nu(z) = \frac{1}{\Gamma(\nu)} \int_0^\infty dt \frac{t^{\nu-1}}{e^t z^{-1} - 1}, \quad (8.8)$$

which allows for analytic continuation to values $\text{Re } z < 1$. The polylogarithm $\text{Li}_\nu(z)$ has a branching point at $z = 1$, and the corresponding branch cut is usually put on the real axis from $z = 1$ to $z = \infty$.

Thus, the fugacity expansion of the grand potential may be compactly written as

$$\Omega = -\frac{2}{3} C_1 \Gamma\left(\frac{5}{2}\right) V T^{5/2} \text{Li}_{\frac{5}{2}}(z). \quad (8.9)$$

Similarly

$$N = C_1 \Gamma\left(\frac{3}{2}\right) V T^{3/2} \text{Li}_{\frac{3}{2}}(z). \quad (8.10)$$

Quantum corrections to the MB limit of the boson gas may be expressed in more transparent variables by solving for the chemical potential $\mu = \mu(n, T)$ from (8.10) and substituting in (8.9) to write the grand potential as a function of the volume, particle density and the temperature. As a matter of fact, this is the procedure for construction of the virial expansion for the BE gas, since $\Omega = -pV$.

■ **Bose–Einstein condensation.** In the limit of dense matter properties of the ideal BE gas differ dramatically from those of the classical ideal gas. Since in stable matter $\partial \bar{N} / \partial \mu > 0$ and $\mu \leq 0$, the particle number N at given temperature approaches its maximum value in the limit $\mu \rightarrow 0^-$. Denote this maximum value $N_1(T)$:

$$N_1(T) = C_1 V \int_0^\infty d\varepsilon \frac{\sqrt{\varepsilon}}{e^{\beta\varepsilon} - 1} = C_1 V T^{3/2} \Gamma\left(\frac{3}{2}\right) \zeta\left(\frac{3}{2}\right) = \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) C_1 V T^{3/2},$$

where $\zeta(1.5) \approx 2.612$. The maximum particle density is thus

$$n_1(T) = \frac{N_1(T)}{V} = AT^{3/2}; \quad A = \frac{\sqrt{\pi}}{2} \zeta\left(\frac{3}{2}\right) C_1. \quad (8.11)$$

For fixed particle density n direct calculation yields

$$\left(\frac{\partial\mu}{\partial T}\right)_n = -\frac{1}{T} \frac{\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}(\varepsilon - \mu)e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon - \mu)} - 1)^2}}{\int_0^\infty d\varepsilon \frac{\varepsilon^{1/2}e^{\beta(\varepsilon - \mu)}}{(e^{\beta(\varepsilon - \mu)} - 1)^2}} < 0.$$

revealing that the condition $n < n_1(T)$ may be fulfilled only above the *critical temperature* T_c determined by the condition $AT_c^{3/2} = n$ as

$$T_c = \frac{h^2}{2\pi m} \left(\frac{n}{g\zeta\left(\frac{3}{2}\right)} \right)^{\frac{2}{3}}. \quad (8.12)$$

When the temperature is further lowered, the chemical potential cannot grow any more. In the region $T < T_c$ the *Bose condensation* takes place meaning that a macroscopic portion of the particles occupies the lowest-energy one-particle state $\varepsilon_0 = 0$. In this region in the sum over one-particle states (8.1) the continuum approximation becomes inapplicable. The lowest-energy state must be left outside the integration as a separate term. The correct rule is

$$\sum_\ell \dots = (\text{term } \ell = 0) + \int_0^\infty d\varepsilon \omega_1(\varepsilon) \dots. \quad (8.13)$$

In a system quantized in a finite volume the energy levels ε_ℓ are discrete and differences between low-lying levels $\propto V^{-2/3}$. When μ approaches the energy $\varepsilon_0 = 0$ from below, the occupation number

$$\bar{n}_0 = \frac{1}{e^{-\beta\mu} - 1} \Rightarrow N_0(T)$$

becomes arbitrarily large. The continuum integral (8.3) represents – up to extensive terms – correctly the number of the excited particles ($\ell \neq 0$), so that in the region $T < T_c$ on $N = N_0 + AVT^{3/2}$. With the use of the result (8.11) we obtain

$$\begin{aligned} \frac{N_1}{V} &= n \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \\ \frac{N_0}{V} &= n \left[1 - \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \right] \end{aligned} \quad (8.14)$$

These functions are illustrated in Fig. 8–1. Bose–Einstein gas is an ex-

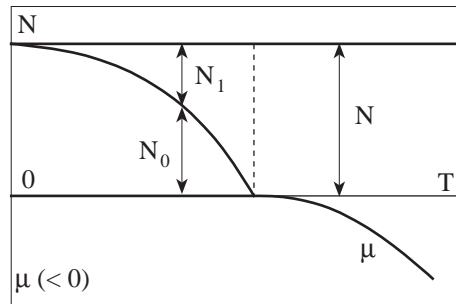


Figure 8–1: Particle numbers and chemical potential of ideal Bose gas as functions of temperature in a fixed volume.

ceptional example of a system, in which the grand canonical ensemble is not statistically equivalent to the canonical ensemble. In the condensate phase the grand-canonical fluctuation of the particle number is macroscopic $\Delta N/N \propto 1$. This is clearly unphysical, so that in principle it would be more correct to use the canonical ensemble. This may practically effected – up to extensive terms – by putting the chemical potential equal to zero in the mean occupation number of the excited states and replacing thereafter the sum over excited states by the continuum integral. Direct contributions of the condensate drop out from the thermodynamic potentials. For instance, the internal energy is determined by the excited particles only

$$E = C_1 V \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{e^{\beta\varepsilon} - 1} = C_1 V T^{5/2} \int_0^\infty dx \frac{x^{3/2}}{e^x - 1} = C_1 V T^{5/2} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right).$$

From here the heat capacity immediately follows

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{5}{2} C_1 V T^{3/2} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right).$$

Integration of the expression for the heat capacity as the derivative of the entropy allows, together with the normalization due to the third law, to find the entropy as well:

$$S = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{5} C_1 V T^{3/2} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right).$$

Finally, the equation of states follows from the observation that in the extensive approximation $F = \Omega = -\frac{2}{3}E$ and

$$p = -\left(\frac{\partial F}{\partial T}\right)_V = \frac{2}{3} C_1 T^{5/2} \Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right).$$

The pressure is thus independent of the volume! Physically this means that any change in the volume is accompanied by such a change in the number of

particles in the condensate that the pressure remains the same (at constant temperature). For instance, an isothermal compression would lead to the growth of N_0 , but N_1/V would remain constant together as the pressure p . There is no energy, entropy or pressure related to the particles in the condensate state $\varepsilon_0 = 0$. The phase diagrams of the matter in the Vp and Tp planes are depicted in Fig. 8–2. Due to infinite compressibility a part of the Tp plane is completely excluded.

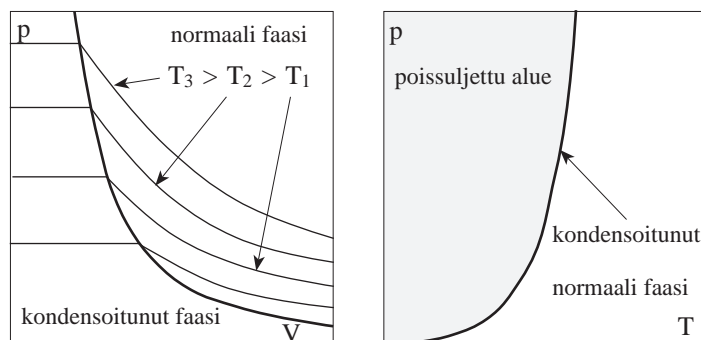


Figure 8–2: Phase diagrams of the ideal Bose gas.

■ **Bose condensation in alkali vapours.** The Bose-Einstein condensation was experimentally observed in 1995 in alkali vapours (^{87}Rb , ^{23}Na , ^7Li) laser cooled below microkelvin temperatures. The cooling took place in magneto-optical traps, in which the potential energy of the magnetic moments of the atoms in a radio-frequency alternating magnetic field may be described by a harmonic potential

$$V(x, y, z) = \frac{1}{2}k_1x^2 + \frac{1}{2}k_2y^2 + \frac{1}{2}k_3z^2. \quad (8.15)$$

The system is thus inhomogeneous and the Bose condensation shows not only in the momentum space but also in the real space.

The genuine Bose condensation requires a continuum spectrum of the one-particle states starting from the ground state. In the boson gas in a box this is achieved in the usual thermodynamic limit: $N, V \rightarrow \infty$ with constant N/V . In the harmonic potential the corresponding limit is $N \rightarrow \infty$, $\omega_i \rightarrow 0$ with $N\omega_1\omega_2\omega_3$ fixed, i.e. the harmonic potential becomes flat. However, differences in the approach to the flat full space lead to physical results different from those obtained in the thermodynamic limit of a gas initially enclosed in a rectangular box, which emphasizes the sensitivity of the thermodynamic limit to the way it is accomplished. For instance, relations (8.14) are replaced by

$$\boxed{\begin{aligned} N_1 &= N \left(\frac{T}{T_c} \right)^3 \\ N_0 &= N \left[1 - \left(\frac{T}{T_c} \right)^3 \right] \end{aligned}} \quad (8.16)$$

with different powers of the temperature.

To see this, let us calculate the density of states of a boson in the harmonic potential (8.15). The eigenvalues of the Hamilton operator are given by

$$\varepsilon_{n_1, n_2, n_3} = \hbar\omega_1 \left(n_1 + \frac{1}{2} \right) + \hbar\omega_2 \left(n_2 + \frac{1}{2} \right) + \hbar\omega_3 \left(n_3 + \frac{1}{2} \right), \quad (8.17)$$

where the $n_i = 0, 1, 2 \dots$ are integers labeling the eigenfunctions. Expectation values are calculated over all values of n_i weighed by the mean occupation number. In the thermodynamic limit it would be desirable to arrive at an integral over the one-particle energies. Let us first introduce the variables

$$u = \hbar\omega_1 n_1, \quad v = \hbar\omega_2 n_2, \quad w = \hbar\omega_3 n_3,$$

for which the difference between adjacent values $\hbar\omega_i$ becomes small in the limit $\omega_i \rightarrow 0$, thus allowing for representation of the sum over n_i as an integral sum:

$$\sum_{n_1, n_2, n_3} = \frac{1}{\hbar^3 \omega_1 \omega_2 \omega_3} \sum_{u, v, w} \Delta u \Delta v \Delta w \longrightarrow \frac{1}{\hbar^3 \omega_1 \omega_2 \omega_3} \int_0^\infty du \int_0^\infty dv \int_0^\infty dw.$$

The average number of particles, for instance, may be expressed as

$$N = \sum_{n_1, n_2, n_3} g \bar{n}(\varepsilon_{n_1, n_2, n_3}) \longrightarrow \frac{g}{\hbar^3 \omega_1 \omega_2 \omega_3} \int_0^\infty du \int_0^\infty dv \int_0^\infty dw \frac{1}{e^{\beta(u+v+w+\varepsilon_0-\mu)} - 1}, \quad (8.18)$$

where $\varepsilon_0 = \frac{\hbar}{2}(\omega_1 + \omega_2 + \omega_3)$ is the energy of zero-point oscillations. This relation suggests that the thermodynamic limit – in analogy with the gas in the box – corresponds to $N \rightarrow \infty$, $\omega_i \rightarrow 0$ such that the product $N\omega_1\omega_2\omega_3$ is kept constant.

Introduce then the variables $u = x^2$, $v = y^2$, $w = z^2$ in which it is evident that the the integral over one-particle excitation energies may be obtained in the spherical polar coordinates, since the mean occupation number depends on $x^2 + y^2 + z^2 = r^2$ only:

$$N = \frac{8g}{\hbar^3 \omega_1 \omega_2 \omega_3} \int_0^\infty dx \int_0^\infty dy \int_0^\infty dz \frac{xyz}{e^{\beta(x^2+y^2+z^2+\varepsilon_0-\mu)} - 1}.$$

After calculation of the angular integrals and introduction of the excitation energy $\varepsilon' = r^2$ as the new radial integration variable we arrive at the expression

$$N = \frac{g}{2\hbar^3\omega_1\omega_2\omega_3} \int_0^\infty d\varepsilon' \varepsilon'^2 \frac{1}{e^{\beta(\varepsilon'+\varepsilon_0-\mu)} - 1} \quad (8.19)$$

showing that the density of states of the BE gas in the harmonic potential well is

$$\omega_1(\varepsilon) = \frac{g(\varepsilon - \varepsilon_0)^2}{2\hbar^3\omega_1\omega_2\omega_3}. \quad (8.20)$$

The condensation temperature is now determined by the condition $\mu = \varepsilon_0$ as

$$T_c = \hbar \left(\frac{N\omega_1\omega_2\omega_3}{g\zeta(3)} \right)^{\frac{1}{3}}. \quad (8.21)$$

As for the gas in the box, from relations (8.19), (8.21) the temperature dependence of the number of particles is inferred in the form (8.16) quoted above. The thermodynamics of the BE gas in the harmonic well below T_c is also determined by particles above the condensate only. For instance, the internal energy assumes the form

$$E = N_0\varepsilon_0 + \frac{g}{2\hbar^3\omega_1\omega_2\omega_3} \int_0^\infty d\varepsilon' \varepsilon'^2 \frac{\varepsilon' + \varepsilon_0}{e^{\beta\varepsilon'} - 1} = N\varepsilon_0 + \frac{\pi^4 T^4}{30\hbar^3\omega_1\omega_2\omega_3}. \quad (8.22)$$

8.2 Black body radiation

■ **Quantization of the energy of electromagnetic radiation.** Consider a free electromagnetic field with vanishing scalar potential $\phi = 0$ and the vector potential \mathbf{A} subject to the transversality condition $\nabla \cdot \mathbf{A} = 0$. Then the fields are

$$\mathbf{E} = -\frac{\partial \mathbf{A}}{\partial t}, \quad \mathbf{B} = \nabla \times \mathbf{A}, \quad (8.23)$$

and the Maxwell equations give rise to the wave equation for \mathbf{A}

$$\nabla^2 \mathbf{A} - \frac{1}{c^2} \frac{\partial^2 \mathbf{A}}{\partial t^2} = 0.$$

Put the system in a box of volume V and express the vector potential as the linear combination of plane waves (normalized to unity in the volume V)

$$\mathbf{A} = \sum_{\mathbf{k}} \left(\mathbf{a}_{\mathbf{k}} \frac{e^{-i\omega t + i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{V}} + \mathbf{a}_{\mathbf{k}}^* \frac{e^{i\omega t - i\mathbf{k} \cdot \mathbf{r}}}{\sqrt{V}} \right), \quad (8.24)$$

where $\mathbf{k} \cdot \mathbf{a}_{\mathbf{k}} = 0$ and $\mathbf{a}_{\mathbf{k}} \propto e^{-i\omega t}$ with the dispersion law $\omega(\mathbf{k}) = c|\mathbf{k}|$. The sum in (8.24) is taken over all integers labeling the components of the wave

vector in the box, where $\mathbf{k} = \left(\frac{2\pi n_1}{L_x}, \frac{2\pi n_2}{L_y}, \frac{2\pi n_3}{L_z} \right)$. Introduce the canonical variables

$$\begin{aligned} \mathbf{Q}_{\mathbf{k}} &= \sqrt{\varepsilon_0} (\mathbf{a}_{\mathbf{k}} e^{-i\omega t} + \mathbf{a}_{\mathbf{k}}^* e^{i\omega t}), \\ \mathbf{P}_{\mathbf{k}} &= \dot{\mathbf{Q}}_{\mathbf{k}} = -i\omega\sqrt{\varepsilon_0} (\mathbf{a}_{\mathbf{k}} e^{-i\omega t} - \mathbf{a}_{\mathbf{k}}^* e^{i\omega t}). \end{aligned} \quad (8.25)$$

Expressing the coefficients of the Fourier expansion of the vector potential in terms of the canonical variables

$$\begin{aligned} \mathbf{a}_{\mathbf{k}} e^{-i\omega t} &= \frac{1}{2\sqrt{\varepsilon_0}} \left(\mathbf{Q}_{\mathbf{k}} + i \frac{\mathbf{P}_{\mathbf{k}}}{\omega} \right) \\ \mathbf{a}_{\mathbf{k}}^* e^{i\omega t} &= \frac{1}{2\sqrt{\varepsilon_0}} \left(\mathbf{Q}_{\mathbf{k}} - i \frac{\mathbf{P}_{\mathbf{k}}}{\omega} \right), \end{aligned} \quad (8.26)$$

substituting in the expression for the Hamilton function of the electromagnetic field becomes

$$H = \int d^3\mathbf{r} \left(\frac{\varepsilon_0 E^2}{2} + \frac{B^2}{2\mu_0} \right),$$

resolving the wave-vector sums with the aid of the identity

$$\int d^3\mathbf{r} e^{i\mathbf{r} \cdot (\mathbf{k} - \mathbf{k}')} = V \delta_{n_1 n'_1} \delta_{n_2 n'_2} \delta_{n_3 n'_3}$$

and the transversality condition $\mathbf{k} \cdot \mathbf{a}_{\mathbf{k}} = 0$ we arrive at the the Hamilton function of the electromagnetic field in the form of the sum of Hamilton functions of independent harmonic oscillators:

$$H = \int d^3\mathbf{r} \left(\frac{\varepsilon_0 E^2}{2} + \frac{B^2}{2\mu_0} \right) = \frac{1}{2} \sum_{\mathbf{k}} (\mathbf{P}_{\mathbf{k}}^2 + \omega^2 \mathbf{Q}_{\mathbf{k}}^2).$$

Due to transversality $\mathbf{k} \cdot \mathbf{a}_{\mathbf{k}} = 0$ the vectors $\mathbf{P}_{\mathbf{k}}$ and $\mathbf{Q}_{\mathbf{k}}$ have only two components corresponding the two independent polarization modes. Therefore, in the box the Hamilton function of the electromagnetic field in the canonical variables may be written as

$$H = \frac{1}{2} \sum_{\mathbf{k}, \lambda} (P_{\mathbf{k}, \lambda}^2 + \omega^2 Q_{\mathbf{k}, \lambda}^2), \quad (8.27)$$

where λ labels the polarization components. This representation suggests quantization with the introduction of the momentum and coordinate operators with the standard commutation rules

$$\left[\hat{P}_{\mathbf{k}, \lambda}, \hat{Q}_{\mathbf{k}', \lambda'} \right] = -i\hbar \delta_{\lambda, \lambda'} \delta_{\mathbf{k}, \mathbf{k}'}. \quad (8.28)$$

Due to the orthogonality of plane waves with different wave vectors the Hamilton operator assumes exactly the same form as the Hamilton function with canonical variables replaced by operators:

$$\hat{H} = \frac{1}{2} \sum_{\mathbf{k}, \lambda} \left(\hat{P}_{\mathbf{k}, \lambda}^2 + \omega^2 \hat{Q}_{\mathbf{k}, \lambda}^2 \right). \quad (8.29)$$

The energy eigenvalues are thus

$$E = \sum_{\mathbf{k}, \lambda} \hbar \omega \left(n_{\mathbf{k}, \lambda} + \frac{1}{2} \right), \quad (8.30)$$

where $n_{\mathbf{k}, \lambda} = 0, 1, 2, \dots$ for each set \mathbf{k}, λ . Similarly, the expression for the momentum of the electromagnetic field

$$\mathbf{P} = \varepsilon_0 \int d^3 \mathbf{r} \mathbf{E} \times \mathbf{B}$$

in terms of the canonical variables (8.25) gives rise to the momentum operator in the form

$$\hat{\mathbf{P}} = \frac{1}{2} \sum_{\mathbf{k}, \lambda} \frac{\mathbf{k}}{ck} \left(\hat{P}_{\mathbf{k}, \lambda}^2 + \omega^2 \hat{Q}_{\mathbf{k}, \lambda}^2 \right), \quad (8.31)$$

whose eigenvalues are also expressed with the aid of the occupation numbers $n_{\mathbf{k}, \lambda}$ as

$$\mathbf{P} = \sum_{\mathbf{k}, \lambda} \hbar \mathbf{k} \left(n_{\mathbf{k}, \lambda} + \frac{1}{2} \right). \quad (8.32)$$

The representations (8.30) and (8.32) allow for the interpretation of the excitations of the quantized electromagnetic field as *photons* of energy $\varepsilon = \hbar \omega$ and momentum $\mathbf{p} = \hbar \mathbf{k}$ with the dispersion law $\varepsilon = cp$. The quantity $n_{\mathbf{k}, \lambda}$ then is the number of photons of frequency ω , direction of propagation \mathbf{k}/k and polarization state λ . Note that this involves a new physical interpretation of the excited states of the harmonic oscillator, each of which now represents $n_{\mathbf{k}, \lambda}$ *particles* with the energy $\varepsilon = \hbar \omega$, momentum $\mathbf{p} = \hbar \mathbf{k}$ and the polarization vector \mathbf{e}_λ .

Since the occupation number $n_{\mathbf{k}, \lambda} = 0, 1, 2, \dots$ may be any non-negative integer, the photons obey Bose-Einstein statistics. The polarization state is a degree of freedom corresponding to spin, whose value is actually 1, but the longitudinal component is absent in the radiation field and the spin degeneracy factor is $g = 2$. In the description of radiation the zero-frequency energy and momentum are usually subtracted from expressions (8.30) and (8.32) and deferred to the definition of the "vacuum".

The energy of photons may be arbitrarily small, therefore it is not possible to fix their number or even its average as the condition for the construction of a statistical ensemble. Rather, the number of photons is determined as an equilibrium condition for the free energy as $\frac{\partial F}{\partial N} = \mu = 0$. Therefore, the mean "occupation number" of the photons corresponding to an oscillator mode is

$$\bar{n}(\omega) = \frac{1}{e^{\beta \hbar \omega} - 1}. \quad (8.33)$$

This is the *Planck distribution*.. The density of states is often determined with respect to the angular frequency. In the thermodynamic limit the sum

over wave vector components is first replaced by the integral over the wave-vector space with account of the isotropy of the mean occupation number $dN_{\mathbf{k}} = g(L/2\pi)^3 d^3 \mathbf{k} = gV/(2\pi^2) k^2 dk$. When the condition $dN_{\mathbf{k}} = dN_{\omega} = f(\omega)d\omega$ is then imposed, the density of states with respect to ω is found as:

$$\sum_{\ell} \cdots = \int_0^{\infty} d\omega f(\omega) \cdots; \quad f(\omega)d\omega = V \frac{\omega^2}{\pi^2 c^3} d\omega \quad (8.34)$$

The full energy density of the radiation field now assumes the form

$$\mathcal{E}(T) \equiv \frac{E}{V} = \int_0^{\infty} d\omega \mathcal{E}(\omega, T), \quad (8.35)$$

where the spectral energy density $\mathcal{E}(\omega, T)$ is given by the *Planck radiation law*

$$\mathcal{E}(\omega, T) = \frac{\hbar \omega^3}{\pi^2 c^3 (e^{\beta \hbar \omega} - 1)}. \quad (8.36)$$

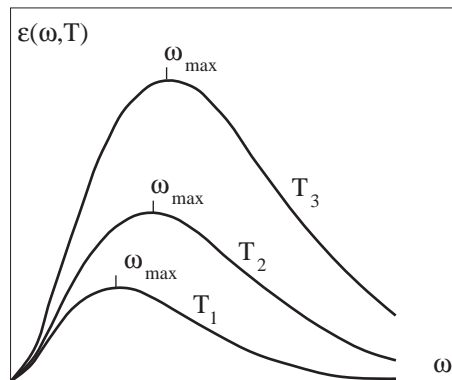


Figure 8–3: Spectral energy density of the radiation field according to Planck’s radiation law.

In Fig. 8–3 the form of the intensity distribution of the radiation according to Planck’s law is depicted. In the limit of large frequency or low temperature this law tends to *Wien’s law*

$$\mathcal{E}(\omega, T) \propto \nu^3 \exp(-h\nu/T),$$

where $\nu = \omega/2\pi$ and h is a fitting parameter. In the limit of small frequency the *Rayleigh–Jeans law* is recovered

$$\mathcal{E}(\omega, T) \propto \omega^2 T,$$

which corresponds to the classical equipartition theorem. In Planck’s radiation law the frequency of the maximum energy density $\omega_{\max} \propto T$ thus explaining *Wien’s law* for the peak of the spectrum.

Integration over the frequency in Planck's radiation law yields

$$\mathcal{E}(T) = \int_0^\infty d\omega \frac{\hbar\omega^3}{\pi^2 c^3 (e^{\beta\hbar\omega} - 1)} = \frac{T^4}{\pi^2 c^3 \hbar^3} \int_0^\infty dx \frac{x^3}{e^x - 1}.$$

The remaining integral is of the familiar type, thus

$$\int_0^\infty dx \frac{x^3}{e^x - 1} = \Gamma(4)\zeta(4) = \frac{\pi^4}{15}$$

leading to the energy density

$$\boxed{\mathcal{E}(T) = \frac{4}{c}\sigma T^4}, \quad (8.37)$$

where σ is the *Stefan–Boltzmann constant*

$$\sigma = \frac{\pi^2}{60\hbar^3 c^2}. \quad (8.38)$$

In the ordinary units $\sigma = \pi^2 k_B^4 / (60\hbar^3 c^2) \approx 5.671 \times 10^{-8} \text{ W}/(\text{m}^2 \text{ K}^4)$.

■ **Thermodynamics.** Thermodynamics of the photon gas may be deduced from the expression for the energy density (8.37), since the internal energy $U = \mathcal{E}V$, i.e.

$$U = \frac{4\sigma}{c}VT^4. \quad (8.39)$$

Therefore, the heat capacity is

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{16}{c}\sigma T^3 = T \left(\frac{\partial S}{\partial T} \right)_V. \quad (8.40)$$

Integrating the last equation with the account of the condition $S \rightarrow 0, T \rightarrow 0$ we arrive at the expression for the entropy

$$S = \frac{16\sigma}{3c}VT^3. \quad (8.41)$$

Therefore, the free energy $F = U - TS$ is

$$\boxed{F = -\frac{4\sigma}{3c}VT^4}. \quad (8.42)$$

Calculation of the pressure $p = -\partial F/\partial V$ yields the equation of state as

$$p = \frac{4\sigma}{3c}T^4 = \frac{1}{3}\mathcal{E}(T). \quad (8.43)$$

It is worth noting that the pressure is independent of the volume leading to infinite isothermal compressibility as in the Bose condensate.

It should be borne in mind that as a many-particle system photons constitute an extremely ideal gas, because even scattering events between photons are very rare. Therefore, a pure photon gas is a *non-ergodic* system that cannot thermalize due to intrinsic dynamics. If the photon gas is in equilibrium, which strictly speaking hardly ever is the case, then this is solely due to interaction with a suitable environment, a *black body*. The black body is an equilibrium system acting as a heat bath by emitting and absorbing photons without reflection, isotropically in spatial directions and within a continuous spectrum.

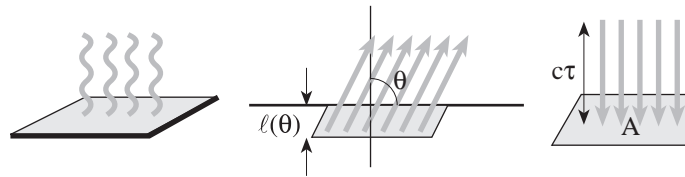


Figure 8–4: Black-body radiation and absorption.

■ **Emission and absorption of a black body.** A black body may be modelled as a hole in the wall of a hollow container with isotropic black-body radiation in it. Then the radiation power in a fixed direction may be calculated with the aid of the geometric construction depicted in Fig. 8–4b. During the time τ the radiation in the direction of the angle θ from the outward normal of the surface comes from the region, whose depth is $\ell(\theta) = c\tau \cos \theta$ and the volume $A\ell(\theta)$. The total energy of the photons propagating from this region in the solid angle element $d\Omega$ in the direction θ is therefore

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

since of all the photons in a volume element the part $d\Omega/(4\pi)$ is propagating in the required direction.

The *radiance* L is the radiation power in a given direction in a unit solid angle per visible surface area of the radiating body. Since in the direction θ the visible emitting area is $A_{\perp} = A \cos \theta$, the radiance of the black body is (to obtain power, divide energy by τ)

$$L = \frac{c\mathcal{E}(T)}{4\pi}.$$

Since L is independent of direction (i.e., the black-body radiation is *diffuse*), the radiating surface appears equally bright from any oblique direction as from the direction of the normal.

Radiant exitance M is the radiant power to the half-space above the surface per surface area. Thus, it may be written as the integral of the

radiance multiplied by the ratio $\cos \theta = A_{\perp}/A$ over the corresponding solid angle:

$$M_b = \int_0^{\pi/2} d\theta \sin \theta \int_0^{2\pi} d\varphi L \cos \theta = 2\pi \frac{c \mathcal{E}(T)}{4\pi} \int_0^{\pi/2} d\theta \sin \theta \cos \theta = \frac{1}{4} \mathcal{E}(T) c. \quad (8.44)$$

Thus, black-body radiation obeys *Lambert's law*

$$M = \pi L_s.$$

Due to relation (8.37), the *Stefan–Boltzmann law* for the radiant excittance

$$M_b = \sigma T^4 \quad (8.45)$$

follows from equation (8.44).

A black body absorbs all the incident radiation, emits diffuse radiation and its spectral excittance (or spectral radiance) is a universal function depending on the temperature and the angular frequency of the radiation only.

Irradiance E is the radiant power incident to the surface per surface area. It may be absorbed (denote the corresponding portion by E_a), reflected (E_r) or transmitted (E_t). Thus, radiant properties of the surface are characterized by the (*spectral*) *absorption ratio* ($E_a(\omega) = \alpha(\omega)E(\omega)$) $E_a = \alpha E$, *reflection ratio* $E_r = \rho E$ and *transmission ratio* $E_t = \tau E$. Energy conservation implies that $\alpha + \rho + \tau = 1$. For a black body $\alpha = 1$, $\rho = \tau = 0$.

Emission of a generic radiating body is characterized by its *emissivity* (or *spectral emissivity*) ϵ :

$$M(\omega, T) = \epsilon(\omega, T) M_b(\omega, T),$$

where $M(\omega, T)$ is the excittance of the body at hand. The spectral emissivity of a *grey body* is independent of the frequency.

If the body is at equilibrium with the radiation field, then *Kirchhoff's radiation law*

$$\epsilon(\omega, T) = \alpha(\omega, T)$$

holds.

8.3 Lattice vibrations

The relative motion of nuclei in molecules and solids is so slow in comparison with the motion of electrons that these degrees of freedom may be separated in the *Born–Oppenheimer* or *adiabatic* approximation. The system of nuclei is then described the Hamilton operator on which the influence of electrons appears as a potential energy depending on the nuclear configuration

$$H = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2M_j} + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N), \quad (8.46)$$

where M_j are the masses of the nuclei (atoms). Denote the equilibrium positions by \mathbf{R}_j and displacements thereof $\mathbf{u}_j = \mathbf{r}_j - \mathbf{R}_j$. Expanding with respect to the latter we obtain

$$V = V_0 + \sum_{jx} V_j^x u_{jx} + \frac{1}{2!} \sum_{jk,xy} V_{jk}^{xy} u_{jx} u_{ky} + \cdots,$$

because the linear in displacements terms vanish due to the equilibrium condition.

In the *harmonic approximation* the Hamilton function is

$$H = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2M_j} + \frac{1}{2!} \sum_{jk} \sum_{xy} V_{jk}^{xy} u_{jx} u_{ky}. \quad (8.47)$$

A Hamilton function of this form may always be diagonalized with the aid of a canonical transformation which leads to the representation in the normal coordinates as a system of independent harmonic oscillators:

$$H = \frac{1}{2} \sum_{\ell} (P_{\ell}^2 + \omega_{\ell}^2 Q_{\ell}^2), \quad (8.48)$$

where the angular frequencies ω_{ℓ} are obtained from the characteristic equation

$$\det \left[V_{jk}^{xy} - \omega^2 M_j \delta_{jk} \delta_{xy} \right] = 0.$$

In the quantized theory the canonical variables P_{ℓ}, Q_{ℓ} are replaced by operators obeying the usual commutation rules (8.28) so that the Hamilton operator is obtained by the substitution $P_{\ell}, Q_{\ell} \rightarrow \hat{P}_{\ell}, \hat{Q}_{\ell}$ in (8.48). Thus, the energy eigenvalues may be written as

$$E = \sum_{\ell} \hbar \omega_{\ell} \left(n_{\ell} + \frac{1}{2} \right) \quad (8.49)$$

giving rise, as in the case of electromagnetic radiation, to the interpretation of the excited states of the lattice vibrations as a system of particle-like entities, *phonons*.

■ **Exact solution.** The set of harmonic oscillators (8.48) with the energy eigenvalues (8.49) gives rise – in analogy with the quantized electromagnetic field – to statistical description in terms of grand canonical ensemble with vanishing chemical potential. Thus, $F = \Omega$ and we arrive at the formally exact relation

$$F = T \sum_{\ell} \ln (1 - e^{-\beta \hbar \omega_{\ell}}). \quad (8.50)$$

This expression gives rise to a simple analytic form in the limits $\beta \hbar \omega_{\ell} \gg 1$ and $\beta \hbar \omega_{\ell} \ll 1$.

In a box with periodic boundary conditions the wave functions may be labeled by the components of the wave vector \mathbf{k} and the polarization index λ . Then (8.49) is replaced by

$$E = \sum_{\mathbf{k}, \lambda} \hbar \omega_{\lambda}(\mathbf{k}) \left(n_{\lambda}(\mathbf{k}) + \frac{1}{2} \right). \quad (8.51)$$

In a lattice no continuum limit is taken, so the number of components of \mathbf{k} remains finite and equal to the number N of *elementary cells* in the specimen. Roughly speaking, the elementary cell is the smallest volume element of the solid whose periodic continuation to fill the space reproduces the lattice at hand. The elementary cell does not always convey all the symmetry properties of the lattice, therefore it is often replaced by the Wigner-Seitz cell, which obeys the lattice symmetries. The corresponding entity in the wave-vector space is the first *Brillouin zone*.

The number of components of the wave vector is usually restricted to the value N by requiring that all \mathbf{k} belong to the first Brillouin zone in the wave-vector space. It should be borne in mind, although it is not used here, that the components of \mathbf{k} are not necessarily orthogonal. The elementary cell may contain several atoms. Let the number of atoms in the elementary cell be ν , then there are, in general, 3ν polarization states of the lattice vibrations. Due to translational invariance, there are always three polarization states with the dispersion law $\omega \propto k$. These are *sound waves* or *acoustic modes* of lattice vibrations. If the lattice is not simple, i.e. $\nu > 1$, then *optical modes* of lattice vibrations appear whose frequency has finite limit, when $k \rightarrow 0$. Fig. 8-5 shows typical dispersion laws for a lattice with two atoms in the elementary cell.

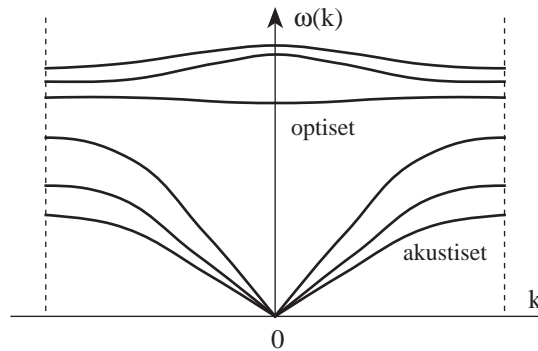


Figure 8-5: Dispersion curves of phonons.

At low temperatures ($\beta \hbar \omega_{\ell} \gg 1$) the exponential cuts off the large-energy vibrations. The vibration modes with the lowest energy are sound waves. In an isotropic substance – which is assumed for simplicity – the sound waves have three independent vibration modes: one longitudinal and

two transversal modes, for which the dispersion relations may be written as

$$\omega_t = c_t k, \quad \omega_l = c_l k, \quad (8.52)$$

which allow for transformation from the wave-vector sum to wave-vector integral in a fashion similar to that used for the photon gas. Since the speed of sound for the transversal components is the same, the energies have a twofold degeneracy with respect to polarization and we obtain, at $T \rightarrow 0$:

$$\begin{aligned} F &= \frac{TV}{2\pi^2} \int_0^\infty dk k^2 [2 \ln(1 - e^{-\beta\hbar\omega_t}) + \ln(1 - e^{-\beta\hbar\omega_l})] \\ &= \frac{TV}{2\pi^2} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right) \int_0^\infty d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega}) \\ &= \frac{3TV}{2\pi^2 \bar{c}^3} \int_0^\infty d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega}), \quad (8.53) \end{aligned}$$

where \bar{c} is the geometric-like mean speed of sound. We see that the free energy is formally the same as for the photon gas, therefore the substitution $c \rightarrow \bar{c}$ and $g = 3$ immediately yields the basic thermodynamic quantities of the phonon gas:

$$F - F_0 = -\frac{\pi^2 VT^4}{30(\hbar\bar{c})^3}, \quad S = \frac{2\pi^2 VT^3}{15(\hbar\bar{c})^3}, \quad C_V = \frac{2\pi^2 VT^3}{5(\hbar\bar{c})^3}. \quad (8.54)$$

Here, F_0 is the free energy of zero-mode vibrations, which is independent of the temperature. The physically most important conclusion is the temperature dependence $C_V \propto T^3$ of lattice vibrations, so that the vibrational contribution at low temperatures vanishes faster than the electronic contribution.

At high temperatures ($\beta\hbar\omega_\ell \ll 1$) we approximate $1 - e^{-\beta\hbar\omega_\ell} \approx \beta\hbar\omega_\ell$ and write

$$F = F_0 + \sum_\ell \ln \beta\hbar\omega_\ell = F_0 + \ln \left(\frac{\hbar\bar{\omega}}{T} \right)^{3N\nu}, \quad (8.55)$$

where $\bar{\omega}$ is the geometric mean frequency and $3N\nu$ is the number of vibration modes (N is the number of elementary cells in the lattice and ν the number of atoms in the elementary cell). Relation (8.55) gives rise to the heat capacity

$$C_V = 3N\nu, \quad \hbar\omega_\ell \ll T$$

in accordance with the Dulong-Petit law conforming to the classical equipartition theorem (the average energy of each vibration mode is T).

■ **Debye model.** A fairly realistic analytic approximation to the lattice heat capacity of solids is provided by the *Debye model*, whose basic assumptions are:

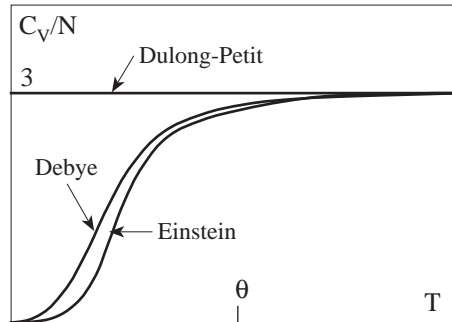


Figure 8-6: Lattice heat capacity of a solid.

- Take into account only acoustic modes: one longitudinal and two transversal modes.
- Assume linear dispersion relations:

$$\begin{cases} \omega_l(k) = c_l k \\ \omega_t(k) = c_t k \end{cases} \quad (8.56)$$

- Cut off the spectra at the *Debye frequency* $\omega_D = \theta_D/\hbar$ (where θ_D is the *Debye temperature*) chosen such that the number of vibrational modes is $3N\nu$.

Density of states in each mode is

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

so that the total density of states is

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

The total number of modes is $3N\nu = \int_{\omega=0}^{\omega_D} dN$, yielding

$$\omega_D^3 = \frac{N\nu}{V} 18\pi^2 \left(\frac{2}{c_t^3} + \frac{1}{c_l^3}\right)^{-1}. \quad (8.57)$$

The density of states is thus

$$dN(\omega) = \frac{9N\nu}{\omega_D^3} \omega^2 d\omega. \quad (\omega < \omega_D) \quad (8.58)$$

Substance	θ_D (K)	Substance	θ_D (K)	Substance	θ_D (K)
Li	400	B	1250	Cu	315
Na	150	Al	394	Ag	215
K	100	Ga	240	Au	170
Be	1000	C*	1860	Zn	234
Mg	318	Si	625	Cr	460
Ca	230	Ge	360	Fe	420

* diamond

Debye temperatures of some substances

In the Debye model the free energy is

$$F = F_0 + \frac{9N\nu}{\omega_D^3} \int_0^{\omega_D} d\omega \omega^2 \ln(1 - e^{-\beta\hbar\omega}) . \quad (8.59)$$

Stretching integration variable we obtain

$$F = F_0 + 9N\nu T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} dz z^2 \ln(1 - e^{-z}) . \quad (8.60)$$

From this expression the internal energy follows in the form

$$E = F + TS = E_0 + 3N\nu T \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{z^3 dz}{e^z - 1} = E_0 + 3N\nu TD \left(\frac{T}{\theta_D}\right) , \quad (8.61)$$

where the last equality defines the *Debye function* $D(x)$. In the Debye model

$$C_V \xrightarrow{T \rightarrow 0} N \frac{12\pi^4}{5} \left(\frac{T}{\theta_D}\right)^3 . \quad (8.62)$$

which is an exact result, because the model is tailored to exact for low-energy phonons. In Fig. 8–6 the specific heat of the Debye model is compared with results of other models. The best fit is given by the Debye model. For solids with complex elementary cells the agreement with the experiment is worse.

8.4 Problems

Problem 8.1. Derive the following expressions for the fugacity, chemical potential and internal energy of the ideal Bose gas:

$$\begin{aligned} z &= \eta - \frac{\eta^2}{2^{3/2}} + \left(\frac{1}{4} - \frac{1}{3^{3/2}} \right) \eta^3 + \mathcal{O}(\eta^4) \\ \mu &= T \left[\ln \eta - \frac{\eta}{2^{3/2}} + 3 \left(\frac{1}{2^4} - \frac{1}{3^{5/2}} \right) \eta^2 \right] + \mathcal{O}(\eta^3) \\ E &= \frac{3}{2} NT \left[1 - \frac{\eta}{2^{5/2}} - 2 \left(\frac{1}{3^{5/2}} - \frac{1}{2^4} \right) \eta^2 \right] + \mathcal{O}(\eta^3) \end{aligned}$$

where $\eta = N\lambda_T^3/gV$.

Problem 8.2. Consider an ideal BE gas in the harmonic potential

$$V(x, y, z) = \frac{1}{2}k_1x^2 + \frac{1}{2}k_2y^2 + \frac{1}{2}k_3z^2.$$

This is the effective potential energy of alkali atoms in the experimental observations of the BE condensation in alkali vapours. The BE condensation takes place in the limit $k_i \rightarrow 0$, $N \rightarrow \infty$, which replaces the usual thermodynamic limit. In this limit, the density of states of non-relativistic boson gas may be written as

$$\frac{dN}{d\varepsilon} = \frac{\varepsilon^2}{2\hbar^3\omega_1\omega_2\omega_3},$$

where ω_i are the angular frequencies of the harmonic oscillations in the potential V .

Calculate the internal energy U , heat capacity C_N and entropy S of this gas below the condensation temperature, and find also the equation of state.

Problem 8.3. Is the BE condensation possible in a two-dimensional perfect boson gas? Consider the gas both in a box and harmonic potential well.

Problem 8.4. Calculate the radiant energy of the Sun emitted in the microwave band of width 1,0 MHz centered at the wavelength 3,0 cm. Consider the Sun a black body at the temperature 5800 K.

Problem 8.5. Show that in an adiabatic expansion of isolated photon gas the wavelengths of the photons grow proportionally to the diameter of the space they occupy. What was the radius of the Universe in the end of the radiation era (i.e. when the ions formed atoms and radiation and matter decoupled), if it is now about $15 \cdot 10^9$ light years?

Problem 8.6. Show that, according to the Debye theory, the heat capacity of lattice vibrations at $T \ll \theta_D$ (=Debye temperature) is

$$C_V = \frac{12\pi^4}{5} N \left(\frac{T}{\theta_D} \right)^3,$$

and at $T \gg \theta_D$

$$C_V = 3N \left[1 - \frac{1}{20} \left(\frac{\theta_D}{T} \right)^2 + \dots \right].$$