C Ideal Quantum Gases

16 Ideal Monatomic Quantum Gas

16.a Grandcanonical Potential

The simplest way to treat the monatomic quantum gas is by means of the grandcanonical ensemble. The ideal gas is distinguished by the fact, that there is no interaction between the particles. Wie indicate the one-particle states by $|\mathbf{k}, m\rangle$. These states be eigenstates of the Hamiltonian H and of the momentum Operator $\mathbf{P}$,

$$H|\mathbf{k}, m\rangle = \epsilon_{\mathbf{k},m}|\mathbf{k}, m\rangle, \quad \mathbf{P}|\mathbf{k}, m\rangle = \hbar\mathbf{k}|\mathbf{k}, m\rangle. \tag{16.1}$$

Other quantum-numbers as e.g. the z-component of the spin are indicated by m

$$S_z|\mathbf{k}, m\rangle = m|\mathbf{k}, m\rangle, \quad \epsilon_{\mathbf{k},m} = \frac{\hbar^2}{2m}k^2 - \mu_{\mathrm{B}} g m H_z. \tag{16.2}$$

(More precisely one should indicate the splitting into Landau-levels.)
The many-particle state consists of symmetrized (bosons) and antisymmetrized (fermions) wave-functions, which are determined by the occupation numbers $n_{\mathbf{k},m}$ for each one-particle state. Allowed are

$$\begin{array}{ll} n_{\mathbf{k},m} = 0, 1, 2, ... & \text{for bosons} \\ n_{\mathbf{k},m} = 0, 1 & \text{for fermions} \end{array} \tag{16.3}$$

The occupation-numbers $n_{\mathbf{k},m}$, which indicate how many particles are in the corresponding state, can be considered eigenvalues of occupation-number operators $\hat{n}_{\mathbf{k},m}$. Then the particle number operator $\hat{N}$ and the Hamiltonian H read

$$\hat{N} = \sum_{\mathbf{k},m} \hat{n}_{\mathbf{k},m}, \quad H = \sum_{\mathbf{k},m} \epsilon_{\mathbf{k},m}\hat{n}_{\mathbf{k},m}. \tag{16.4}$$

In order to calculate the grandcanonical partition function we have to sum independently over the occupation numbers of the various $\mathbf{k}, m$. This yields a product over all $\mathbf{k}, m$,

$$Y = \mathrm{tr}(\mathrm{e}^{-\beta(H-\mu\hat{N})}) = \sum_{\ldots n_{\mathbf{k},m}\ldots} \mathrm{e}^{-\beta(E(\{n\})-\mu N(\{n\})} = \prod_{\mathbf{k},m}\left(\sum_{n_{\mathbf{k},m}} \mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)n_{\mathbf{k},m}}\right) = \prod_{\mathbf{k},m} y_{\mathbf{k},m} \tag{16.5}$$

with

$$y_{\mathbf{k},m} = \begin{cases} \dfrac{1}{1-\mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)}} & \text{bosons} \\ 1+\mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)} & \text{fermions} \end{cases} \tag{16.6}$$

This yields the grandcanonical potential

$$J(\beta, \mu, V) = -k_{\mathrm{B}}T\ln Y = -k_{\mathrm{B}}T\sum_{\mathbf{k},m}\ln y_{\mathbf{k},m} = \pm k_{\mathrm{B}}T\sum_{\mathbf{k},m}\ln(1 \mp \mathrm{e}^{-\beta(\epsilon_{\mathbf{k},m}-\mu)}), \tag{16.7}$$

where the upper sign applies to bosons, the lower to fermions.

16.b Particle Number

The averaged particle number of the system is obtained from

$$N = -\frac{\partial J}{\partial \mu} = k_{\rm B}T\sum_{\mathbf{k},m}\frac{\partial \ln y_{\mathbf{k},m}}{\partial \mu} = \sum_{\mathbf{k},m}\frac{\mathrm{e}^{-\beta(\epsilon-\mu)}}{1\mp \mathrm{e}^{-\beta(\epsilon-\mu)}} = \sum_{\mathbf{k},m}\frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}\mp 1}. \tag{16.8}$$

The terms of the sum are the averaged occupation numbers

$$\bar{n}_{\rm B} = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}-1} \qquad \text{Bose-function} \tag{16.9}$$

$$\bar{n}_{\rm F} = \frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}+1} \qquad \text{Fermi-function} \tag{16.10}$$

The probability that a one-particle state is n times occupied is given by ($q = \mathrm{e}^{-\beta(\epsilon-\mu)}$)

$$\text{bosons} \qquad w_{\hat{n}} = \frac{q^n}{\sum_{n'=0}^{\infty} q^{n'}} = q^n(1-q), \tag{16.11}$$

$$\text{fermions} \qquad w_{\hat{n}} = \frac{q^n}{1+q} \tag{16.12}$$

This allows to determine the averaged occupation number

$$\text{bosons} \qquad \bar{n}_{\rm B} = \langle \hat{n}\rangle = (1-q)(q+2q^2+3q^3+...) = q+q^2+q^3+... = \frac{q}{1-q}, \tag{16.13}$$

$$\text{fermions} \qquad \bar{n}_{\rm F} = \langle \hat{n}\rangle = \frac{q}{1+q}. \tag{16.14}$$

This yields

$$q = \frac{\bar{n}}{1\pm\bar{n}}. \tag{16.15}$$

The total (averaged) particle number is given by

$$N = \sum_{\mathbf{k},m}\langle \hat{n}_{\mathbf{k},m}\rangle = \sum_{\mathbf{k},m}\bar{n}_{\mathbf{k},m}. \tag{16.16}$$

16.c Entropy

The entropy is obtained from

$$S = -\frac{\partial J}{\partial T} = \mp k_{\rm B}\sum \ln(1\mp q) + \frac{1}{T}\sum\frac{(\epsilon-\mu)q}{1\mp q}, \tag{16.17}$$

where

$$1\mp q = \frac{1}{1\pm\bar{n}}, \qquad \frac{\epsilon-\mu}{T} = -k_{\rm B}\ln q = -k_{\rm B}\ln\frac{\bar{n}}{1\pm\bar{n}}. \tag{16.18}$$

Thus one obtains

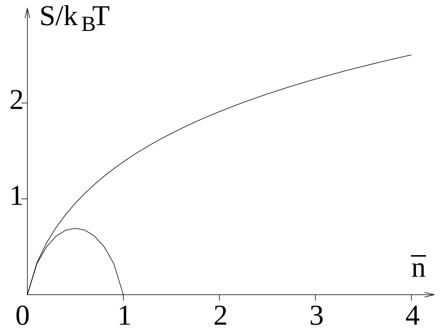
$$S = \pm k_{\rm B}\sum\ln(1\pm\bar{n}) - k_{\rm B}\sum\bar{n}\ln\frac{\bar{n}}{1\pm\bar{n}} \tag{16.19}$$

and therefore

$$S_{\rm Bose} = k_{\rm B}\sum_{\mathbf{k},m}\left((1+\bar{n}_{\mathbf{k},m})\ln(1+\bar{n}_{\mathbf{k},m}) - \bar{n}_{\mathbf{k},m}\ln\bar{n}_{\mathbf{k},m}\right), \tag{16.20}$$

$$S_{\rm Fermi} = k_{\rm B}\sum_{\mathbf{k},m}\left(-(1-\bar{n}_{\mathbf{k},m})\ln(1-\bar{n}_{\mathbf{k},m}) - \bar{n}_{\mathbf{k},m}\ln\bar{n}_{\mathbf{k},m}\right). \tag{16.21}$$

Entropy as function of the average particle number $\bar{n}$ for fermions and bosons



16.d Energy

We obtain for the energy

$$\begin{aligned} E &= TS + \mu N - PV = TS + \mu N + J \\ &= \mp k_{\rm B} T \sum \ln(1 \mp q) + \sum \frac{(\epsilon - \mu) q}{1 \mp q} + \sum \frac{\mu q}{1 \mp q} \pm k_{\rm B} T \sum \ln(1 \mp q) \\ &= \sum \epsilon \frac{q}{1 \mp q} = \sum_{\mathbf{k},m} \epsilon_{\mathbf{k},m} \bar{n}_{\mathbf{k},m}, \end{aligned} \tag{16.22}$$

where we expected the final result anyhow. Each particle with quantum nunbers $\mathbf{k}, m$ contributes $\epsilon_{\mathbf{k},m}$ to the energy.

17 Dilute Ideal Gas: Classical Limit

We have obtained the averaged occupation number of the one-particle states

$$\bar{n}_{\mathbf{k},m} = \frac{1}{\mathrm{e}^{\beta(\epsilon_{\mathbf{k},m}-\mu)} \mp 1}. \tag{17.1}$$

The classical limit is obtained, if the average occupation is small in comparison to 1. Then one has $\mathrm{e}^{\beta(\epsilon-\mu)} \gg 1$ for all $\mathbf{k}, m$. Then the logarithm in (16.7) can be expanded and one obtains for the grandcanonical potential

$$J = \pm k_\mathrm{B}T \sum_{\mathbf{k},m} \ln(1 \mp \mathrm{e}^{-\beta(\epsilon-\mu)}) = -k_\mathrm{B}T \sum_{\mathbf{k},m} \mathrm{e}^{-\beta(\epsilon-\mu)} \mp \frac{k_\mathrm{B}T}{2} \sum_{\mathbf{k},m} \mathrm{e}^{-2\beta(\epsilon-\mu)} - ... \tag{17.2}$$

We assume $\epsilon_k = \hbar^2 k^2/(2m)$. We use $\sum_{\mathbf{k}} \to V/(2\pi)^3 \times \int \mathrm{d}^3k$ as derived in section 6

$$\begin{aligned} J &= -k_\mathrm{B}T(2S+1)\mathrm{e}^{\beta\mu}\frac{V}{(2\pi)^3}\int \mathrm{d}^3k \mathrm{e}^{-\beta\hbar^2k^2/(2m)} \\ &\mp \frac{k_\mathrm{B}T}{2}(2S+1)\mathrm{e}^{2\beta\mu}\frac{V}{(2\pi)^3}\int \mathrm{d}^3k \mathrm{e}^{-\beta\hbar^2k^2/m} - ... \\ &= -(k_\mathrm{B}T)^{5/2}V\mathrm{e}^{\beta\mu}(2S+1)\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\left(1 \pm \frac{\mathrm{e}^{\beta\mu}}{\sqrt{32}} + ...\right) \end{aligned} \tag{17.3}$$

The particle-number is given by

$$N = -\frac{\partial J}{\partial \mu} = (k_\mathrm{B}T)^{3/2}V\mathrm{e}^{\beta\mu}(2S+1)\left(\frac{m}{2\pi\hbar^2}\right)^{3/2}\left(1 \pm \frac{\mathrm{e}^{\beta\mu}}{\sqrt{8}} + ...\right). \tag{17.4}$$

In lowest order one obtains

$$\mathrm{e}^{\beta\mu} = \frac{N\lambda^3}{V(2S+1)} \tag{17.5}$$

with the thermal de Broglie wavelength $\lambda = \left(2\pi\hbar^2/(mk_\mathrm{B}T)\right)^{1/2}$ from eq. (7.7). This yields

$$PV = -J = Nk_\mathrm{B}T\left(1 \mp \frac{\mathrm{e}^{\beta\mu}}{\sqrt{32}} + ...\right) = Nk_\mathrm{B}T\left(1 \mp \frac{N\lambda^3}{V(2S+1)\sqrt{32}} + ...\right) \tag{17.6}$$

The second term in brackets gives the derivation from the classical behavior due to the quantum statistics. It is proportional to $\lambda^3 \propto \hbar^3$. The energy is obtained from the virial theorem (11.22) as

$$E = \frac{3}{2}PV. \tag{17.7}$$

18 Blackbody Radiation

Photons are bosons with spin 1; but there are no longitudinal photons, thus to any wave-vector $\mathbf{k}$ there are only two polarizations ($\mathbf{E}, \mathbf{B} \perp \mathbf{k}$). Thus we have to replace the multiplicity $2S+1$ by 2. For the energy of the photons we have

$$\epsilon_{\mathbf{k}} = \hbar\omega_{\mathbf{k}} = \hbar ck = cp. \tag{18.1}$$

There is no particle-number conservation for photons, they may be absorbed and emmitted. Thus we put $\mu = 0$. Then we obtain

$$\begin{aligned} PV &= k_{\mathrm{B}}T \ln Y = -2k_{\mathrm{B}}T \sum_{\mathbf{k}} \ln(1 - \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}}) \\ &= -\frac{2k_{\mathrm{B}}TV}{(2\pi)^3} \int \mathrm{d}^3k \ln(1 - \mathrm{e}^{-\beta\epsilon_{\mathbf{k}}}). \end{aligned} \tag{18.2}$$

With $x = \beta\hbar ck$ one obtains

$$P = -\frac{2}{(2\pi)^3}(k_{\mathrm{B}}T)^4 \frac{1}{\hbar^3 c^3} \int \mathrm{d}^3x \ln(1 - \mathrm{e}^{-x}). \tag{18.3}$$

The integral can be evaluated (see appendix)

$$-\int \mathrm{d}^3x \ln(1 - \mathrm{e}^{-x}) = -4\pi \int_0^\infty \mathrm{d}x x^2 \ln(1 - \mathrm{e}^{-x}) = \frac{4\pi^5}{45} \tag{18.4}$$

By means of the Stefan-Boltzmann constant

$$\sigma = \frac{\pi^2 k_{\mathrm{B}}^4}{60\hbar^3 c^2} = 5.67 \cdot 10^{-5}\,\mathrm{ergs}^{-1}\,cm^{-2}\,\mathrm{K}^{-4} \tag{18.5}$$

one obtains the pressure

$$P = \frac{4\sigma}{3c}T^4 \tag{18.6}$$

and the energy reads

$$E = -T^2 \frac{\partial(J/T)}{\partial T} = T^2 \frac{\partial(PV/T)}{\partial T} = \frac{4\sigma}{c}VT^4. \tag{18.7}$$

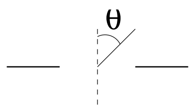
The energy-flux density per solid angle is given by the energy density times velocity of light divided by the total solid angle

$$\frac{\frac{E}{V}}{4\pi}c = \frac{\sigma T^4}{\pi}. \tag{18.8}$$

The energy flux (energy per time) in one direction through an area F is obtained by

$$\int \text{Energy flux density} \times F \cos\theta \mathrm{d}\Omega = \frac{\sigma T^4}{\pi} F \int_0^1 \cos\theta \mathrm{d}\cos\theta \int_0^{2\pi} \mathrm{d}\phi = \sigma T^4 F. \tag{18.9}$$

On energy flux through an area



Actually the Stefan-Boltzmann constant had been introduced for this energy flux. This law is called Stefan-Boltzmann law.
Finally we consider the spectral distribution of the energy density per frequency ω,

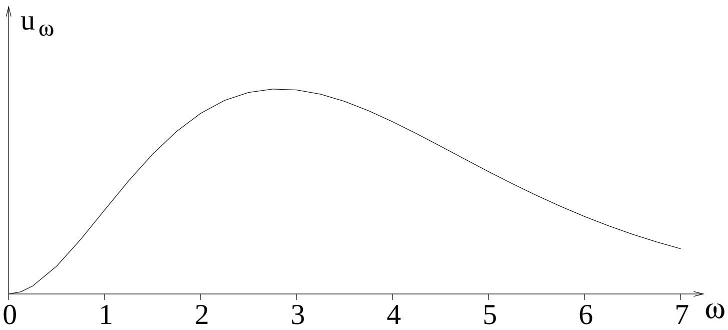
$$\mathrm{d}E = 2\hbar\omega n_{\mathbf{k}} \frac{V}{(2\pi)^3}\mathrm{d}^3k = \frac{V}{4\pi^3}\frac{\hbar\omega \mathrm{d}^3k}{\mathrm{e}^{\beta\hbar\omega} - 1} = \frac{V}{\pi^2}\frac{\hbar\omega k^2 \mathrm{d}k}{\mathrm{e}^{\beta\hbar\omega} - 1} = \frac{V}{\pi^2 c^3}\frac{\hbar\omega^3 \mathrm{d}\omega}{\mathrm{e}^{\beta\hbar\omega} - 1} = Vu_\omega \mathrm{d}\omega, \tag{18.10}$$

where

$$u_\omega = \frac{\hbar\omega^3}{\pi^2 c^3(\mathrm{e}^{\beta\hbar\omega} - 1)} \tag{18.11}$$

is the spectral distribution of the energy density. (Planck 1900)

Spectral energy density of black body radiation.
ω in $k_\mathrm{B}T/\hbar$



The maximum of u_ω is at $\hbar\omega_\mathrm{max} = 2.82 k_\mathrm{B}T$ (Wien's displacement law). If the spectral energy density is related to the wavelength then one obtains a different expression. For small frequencies one obtains the Rayleigh-Jeans-law

$$u_\omega \approx \frac{\hbar\omega^3}{\pi^2 c^3 \beta\hbar\omega} = \frac{k_\mathrm{B}T\omega^2}{\pi^2 c^3}, \tag{18.12}$$

which can be obtained classically. For large frequencies one obtains

$$u_\omega = c_1 \omega^3 \mathrm{e}^{-c_2\omega/T}, \tag{18.13}$$

which had been found by Wien in 1896 without explaination of the constants.

19 Phonons in a Solid

We assume that the phonons can be considered in harmonic approximation, that is, the potential is only expanded up to second order in the displacements. (Anharmonicities normally become important at higher temperatures.) One transforms to normal coordinates and obtains in this way decoupled harmonic oscillators. The excitations are the same as in a system of bosons: Phonons are quasi-particles. The Hamiltonian may be written

$$H = E_0 + \sum \hbar\omega_{\mathbf{k},m}(\hat{n}_{\mathbf{k},m} + \frac{1}{2}). \tag{19.1}$$

If there are r atoms per elementary cell of a crystal, then one has $3r$ vibrational modes for each wave-vector $\mathbf{k}$, $m = 1, ...3r$. $3(r-1)$ branches are optical branches, the three other ones are acoustic branches, one longitudinal and two transversal ones.
One obtains for the energy of the system

$$E = E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\langle\hat{n}_{\mathbf{k},m} + \frac{1}{2}\rangle = E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\left(\frac{1}{\mathrm{e}^{\beta\hbar\omega_{\mathbf{k},m}} - 1} + \frac{1}{2}\right). \tag{19.2}$$

19.a High Temperatures

For high temperatures, $k_\mathrm{B}T \gg \hbar\omega_\mathrm{max}$ one expands

$$\frac{1}{\mathrm{e}^x - 1} + \frac{1}{2} = \frac{1}{x} + \frac{x}{12} + O(x^3), \quad x \ll 1. \tag{19.3}$$

Thus

$$\begin{aligned} E &= E_0 + \sum_{\mathbf{k},m} \hbar\omega_{\mathbf{k},m}\left(\frac{k_\mathrm{B}T}{\hbar\omega_{\mathbf{k},m}} + \frac{\hbar\omega_{\mathbf{k},m}}{12k_\mathrm{B}T} + ...\right) \\ &= E_0 + 3Nrk_\mathrm{B}T + \frac{1}{12k_\mathrm{B}T}\sum_{\mathbf{k},m}(\hbar\omega_{\mathbf{k},m})^2 + O(T^{-3}). \end{aligned} \tag{19.4}$$

N is the number of elementary cells, Nr the number of atoms.
For the specific heat one obtains

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = 3Nrk_\mathrm{B} - \frac{1}{12k_\mathrm{B}T^2}\sum_{\mathbf{k},m}(\hbar\omega_{\mathbf{k},m})^2 + ... \tag{19.5}$$

The first term yields the Dulong-Petit law. The second one shows, that the specific heat becomes smaller at lower temperatures.

19.b Low Temperatures

At low temperatures $k_\mathrm{B}T \ll \hbar\omega_\mathrm{max}$ it is sufficient to consider the acoustic branches, since the optical branches (compare 19.d) are frozen. For the acoustic branches we put $\omega_{\mathbf{k},m} \approx c_\mathrm{l}k, c_\mathrm{t}k$ for the longitudinal and transversal acoustic vibrations. We approximate the longitudinal und transversal sound-velocities c_l and c_t as independent of the direction. Then we obtain

$$E = E_0' + \frac{V}{(2\pi)^3}\sum_{m=1}^{3}\int \mathrm{d}^3k \frac{\hbar c_m k}{\mathrm{e}^{\beta\hbar c_m k} - 1}, \tag{19.6}$$

with the groundstate energy $E_0' = E_0 + \frac{1}{2}\sum_{\mathbf{k},m}\hbar\omega_{\mathbf{k},m}$. If we now substitute as for photons in an enclosure $x = \beta\hbar c_m k$, then one obtains

$$E = E_0' + \frac{V}{(2\pi)^3}\sum_m \frac{(k_\mathrm{B}T)^4}{(\hbar c_m)^3}\int \mathrm{d}^3x \frac{x}{\mathrm{e}^x - 1}. \tag{19.7}$$

Since the integral decays rapidly we integrate up to ∞,

$$\int d^3x \frac{x}{e^x - 1} = 4\pi \int_0^\infty dx \frac{x^3 e^{-x}}{1 - e^{-x}} = 24\pi\zeta(4) = \frac{4\pi^5}{15} \tag{19.8}$$

This yields the energy

$$E = E_0' + \frac{\pi^2 (k_B T)^4 V}{30\hbar^3} (\frac{1}{c_l^3} + \frac{2}{c_t^3}) \tag{19.9}$$

and a specific heat proportional to T^3.

19.c Debye-Approximation for intermediate temperatures (acoustic vibrations)

One introduces the density of states $z(\omega)$, so that the number of normal modes in the interval $\omega ... \omega + d\omega$ is $z(\omega)d\omega$. Then the number of normal modes with $\omega \leq \omega_0$ is given by

$$\int_0^{\omega_0} d\omega z(\omega) = \frac{V}{(2\pi)^3} \frac{4\pi}{3} \left[\left(\frac{\omega_0}{c_l} \right)^3 + 2 \left(\frac{\omega_0}{c_t} \right)^3 \right] = \frac{C}{3} \omega_0^3, \tag{19.10}$$

since the volumina of the spheres with radii ω_0 / c in k-space enter. With the constant

$$C = \frac{V}{2\pi^2} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right) \tag{19.11}$$

one obtains

$$z(\omega) = C\omega^2. \tag{19.12}$$

We assume now that this behavior is cut off at a frequency ω_D, which is called Debye-frequency,

$$z(\omega) = \begin{cases} C\omega^2 & \omega \leq \omega_D, \\ 0 & \omega > \omega_D. \end{cases} \tag{19.13}$$

Then

$$\int_0^{\omega_D} z(\omega) d\omega = 3N = \frac{C}{3} \omega_D^3 \tag{19.14}$$

must hold, thus

$$\frac{1}{\omega_D^3} = \frac{C}{9N} = \frac{V}{18\pi^2 N} \left(\frac{1}{c_l^3} + \frac{2}{c_t^3} \right), \tag{19.15}$$

since there are in total $3N$ acoustical vibration modes. Then the energy reads

$$E = E_0' + \int_0^{\omega_D} z(\omega) \frac{\hbar\omega d\omega}{e^{\beta\hbar\omega} - 1} = E_0' + \frac{9N}{\omega_D^3} \int_0^{\omega_D} \frac{\hbar\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}. \tag{19.16}$$

With $x = \beta\hbar\omega$ one obtains

$$E = E_0' + \frac{9N(k_B T)^4}{\hbar^3 \omega_D^3} \int_0^{\beta\hbar\omega_D} \frac{x^3 dx}{e^x - 1} = E_0' + 3N k_B T D(\frac{T}{\Theta_D}) \tag{19.17}$$

with the Debye-temperature Θ_D, which is determined by $k_B \Theta_D = \hbar\omega_D$, and the Debye-function

$$D(y) = 3y^3 \int_0^{1/y} \frac{x^3 dx}{e^x - 1}. \tag{19.18}$$

For small y one finds $D(y) = \pi^4 y^3 / 5$ and for large y one obtains $D(y) = 1$ in agreement with our estimates for low and high temperatures.

19.d Optical Vibrations

If one assumes that the frequencies $\omega_{\rm opt}$ of the optical phonons are approximately independent of $\mathbf{k}$, then one obtains the contribution

$$\Delta E_{\rm opt} = N \sum_{m({\rm opt})} \hbar\omega_m \frac{1}{{\rm e}^{\beta\hbar\omega_m} - 1} \tag{19.19}$$

to the energy and

$$C_{V,{\rm opt}} = N k_{\rm B} \sum_{m({\rm opt})} \left(\frac{\hbar\omega_m}{k_{\rm B}T}\right)^2 \frac{{\rm e}^{\beta\hbar\omega_m}}{({\rm e}^{\beta\hbar\omega_m} - 1)^2}. \tag{19.20}$$

to the specific heat. The exponential function becomes very large for temperatures $k_{\rm B}T \ll \hbar\omega_m$, so that the contribution to the specific heat vanishes like $Nk_{\rm B}(\hbar\omega_m/(k_{\rm B}T))^2{\rm e}^{-\hbar\omega_m/(k_{\rm B}T)}$. But as soon as $k_{\rm B}T \approx \hbar\omega_m$, then also the optical phonons contribute essentially. For high temperatures $k_{\rm B}T \gg \hbar\omega_m$ one obtains the contribution $k_{\rm B}N$ to the specific heat.
In total all contributions have to be added,

$$E = E_0' + 3Nk_{\rm B}TD(\frac{T}{\Theta_D}) + N \sum_{m({\rm opt})} \hbar\omega_m \frac{1}{{\rm e}^{\beta\hbar\omega_m} - 1}. \tag{19.21}$$

20 Bose Einstein Condensation

Now we consider an ideal Bose-gas at low temperatures. If for simplicities' sake we assume spin 0 for the bosons then its particle number is given by

$$N = \sum_{\mathbf{k}} \frac{1}{\mathrm{e}^{\beta(\epsilon_k - \mu)} - 1}. \tag{20.1}$$

In order that this expression make sense, μ has to be less then ϵ_k for all k. Thus for a dispersion

$$\epsilon_k = \frac{\hbar^2 k^2}{2m} \tag{20.2}$$

μ has to be negative. What happens in the limit $\mu = 0$? First we perform the limit $\sum_k \to V(2\pi)^{-3} \int \mathrm{d}^3k$. Then we obtain for $\mu = 0$

$$N = \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{1}{\mathrm{e}^{\beta\hbar^2 k^2/(2m)} - 1} \tag{20.3}$$

The substitution $x = \beta\hbar^2 k^2/(2m)$ yields

$$N = \frac{V}{(2\pi)^3} \left(\frac{2mk_\mathrm{B}T}{\hbar^2}\right)^{3/2} \frac{4\pi}{2} \int_0^\infty \mathrm{d}x \frac{x^{1/2}}{\mathrm{e}^x - 1} = \zeta(3/2) V \left(\frac{2\pi m k_\mathrm{B} T}{h^2}\right)^{3/2} = \zeta(3/2) V/\lambda(T)^3 \tag{20.4}$$

with $\zeta(3/2) = 2.612$.
What happens if the particle density becomes larger than $\zeta(3/2)/\lambda^3$? Then μ is so close to 0, that the state $k = 0$ accepts all particles, which do not fit into the particle number calculated above. Then one has a macroscopic occupation for $k = 0$

$$N_0 = N - \zeta(3/2) V/\lambda(T)^3. \tag{20.5}$$

Below a critical temperature T_c, which is determined by

$$N = \zeta(3/2) V/\lambda(T_\mathrm{c})^3 \tag{20.6}$$

one obtains

$$N_0 = N \left(1 - \left(\frac{T}{T_c}\right)^{3/2}\right). \tag{20.7}$$

Thus equation (20.4) yields for $T < T_c$ only the number of excited bosons but not their complete number.
Then one obtains for the energy of the system

$$E = \frac{V}{(2\pi)^3} \int \mathrm{d}^3k \frac{\hbar^2 k^2}{2m(\mathrm{e}^{\beta\hbar^2 k^2/(2m)} - 1)}. \tag{20.8}$$

The substitution $x = \beta\hbar^2 k^2/(2m)$ yields

$$\begin{aligned} E &= \frac{V}{(2\pi)^3} \frac{\hbar^2}{2m} \left(\frac{2m}{\beta\hbar^2}\right)^{5/2} 2\pi \int_0^\infty \mathrm{d}x \frac{x^{3/2}}{\mathrm{e}^x - 1} \\ &= \frac{3}{2} V \zeta(5/2) k_\mathrm{B} T/\lambda^3(T) = 0.770 N k_\mathrm{B} T^{5/2} T_\mathrm{c}^{-3/2}, \end{aligned} \tag{20.9}$$

where the Faktor 0.770 is obtained from $3\zeta(5/2)/(2\zeta(3/2))$. The specific heat at constant volume increases like

$$C_V = 1.926 N k_\mathrm{B} \left(\frac{T}{T_\mathrm{c}}\right)^{3/2} \tag{20.10}$$

The pressure is obtained from the virial theorem

$$P = 2E/(3V) = \zeta(5/2) k_\mathrm{B} T/\lambda^3(T) \tag{20.11}$$

It increases proportional to $T^{5/2}$ independent of the particle density. The reason for this independence is that the particles with momenta 0 do not contribute to the pressure and the particle density of the other particles does not depend on temperature.
For $T > T_\mathrm{c}$ μ becomes negative. Then there is no longer a macroscopic occupation of the state with $k = 0$. A little bit above T_c μ may be calculated from

$$N = \frac{V}{(2\pi)^3}\int \mathrm{d}^3k \frac{1}{\mathrm{e}^{x-\beta\mu}-1} - \left(\frac{V}{(2\pi)^3}\int \mathrm{d}^3k \frac{1}{\mathrm{e}^{x}-1} - \zeta(3/2)\frac{V}{\lambda(T)^3}\right) \tag{20.12}$$

where the expression in parenthesis vanishes. We determine the difference of the particle number at T and that, we would have at $T = T_\mathrm{c}$. Then one obtains

$$N = \zeta(3/2)\frac{V}{\lambda(T)^3} + \frac{V}{(2\pi)^3}\int \mathrm{d}^3k \frac{\mathrm{e}^x(1-\mathrm{e}^{-\beta\mu})}{(\mathrm{e}^x-1)(\mathrm{e}^{x-\beta\mu}-1)}. \tag{20.13}$$

The main contribution of this integral comes from small x. Thus we replace $\mathrm{e}^x = 1$ in the numerator and $\mathrm{e}^x - 1 = x$ and $\mathrm{e}^{x-\beta\mu} - 1 = x - \beta\mu$ in the denominator. Since $\beta\mu$ is small we replace $1 - \mathrm{e}^{-\beta\mu} = \beta\mu$ and obtain

$$N = \zeta(3/2)\frac{V}{\lambda(T)^3} + \frac{V\beta\mu}{(2\pi)^3}\int \frac{\mathrm{d}^3k}{x(x-\beta\mu)} = \frac{V}{\lambda(T)^3}\left(\zeta(3/2) - 2\sqrt{-\pi\beta\mu}\right) \tag{20.14}$$

For constant N and V one obtains for T close to T_c, that $\sqrt{-\mu}$ is proportional to $T - T_\mathrm{c}$, that is $\mu \propto -(T - T_\mathrm{c})^2$. Finally we consider the energy. From

$$\frac{\partial(\beta J)}{\partial\beta} = E - \mu N, \quad \frac{\partial(\beta J)}{\partial\mu} = -\beta N \tag{20.15}$$

one obtains for the mixed derivative

$$\frac{\partial^2(\beta J)}{\partial\beta\partial\mu} = \frac{\partial E}{\partial\mu} - N - \mu\frac{\partial N}{\partial\mu} = -N - \beta\frac{\partial N}{\partial\beta} \tag{20.16}$$

and therefore

$$\frac{\partial E}{\partial\mu} = \mu\frac{\partial N}{\partial\mu} - \beta\frac{\partial N}{\partial\beta}, \tag{20.17}$$

which yields with the approximation above

$$\frac{\partial E}{\partial\mu} = \frac{3}{2}N \tag{20.18}$$

and therefore

$$E = E(T, \mu = 0) + \frac{3}{2}N\mu \tag{20.19}$$

Since $\mu \propto -(T - T_\mathrm{c})^2$, one obtains a deviation of the energy from the behavior (20.9) proportional to $(T - T_\mathrm{c})^2$ and therefore of the specific heat proportional to $T - T_\mathrm{c}$. The specific heat shows a kink at T_c. We note, that a Bose-Einstein condensation is observed in fluid He^4 at approximately 2 K and during the last years also at extremely low temperatures (10^{-7} K) in gases of alkali-atoms. The behavior is, however, considerably modified due to the interaction between the atoms.

21 Diatomic Gases

In a polyatomic gas one has to consider not only translational degrees of freedom but also internal excitations. In molecules these can be rotations and vibrations, that is movements of the atoms against each other. Finally (also in the monatomic case) electronic excitations are possible. They yield additional contributions to energy and entropy in dilute gases.

21.a Rotations

We consider rotations of diatomic molecules. As a model we consider them to constitute of two masses m_1 and m_2 at distanve r_0. Then their moment of inertia is

$$I = \frac{m_1 m_2}{m_1 + m_2} r_0^2. \tag{21.1}$$

The angular momentum is $\hbar l$, and the corresponding energy

$$\epsilon_l = \frac{\hbar^2 l(l+1)}{2I} = k_\mathrm{B}\Theta_\mathrm{rot}\frac{l(l+1)}{2}, \tag{21.2}$$

where Θ_rot is the characteristic temperature for the rotations. For given l one has a $2l+1$-fold degeneracy. Then the partition function of a molecule is

$$z_\mathrm{rot} = \sum_{l=0}^{\infty}(2l+1)\mathrm{e}^{-l(l+1)\Theta_\mathrm{rot}/(2T)}. \tag{21.3}$$

For N molecules one has to take the N-th power, since each molecule can assume its rotational states independently of the other molecules, $Z_\mathrm{rot} = z_\mathrm{rot}^N$.
If the atoms are distinguishible, then all $l = 0, 1, 2, ...$ are possible. If the atoms are equal, then the appropriate statistics (Bose-Fermi) has to be taken into account.
For Fermions (for example H_2) the spin-function of the spin-singlett ($S = 0$) is antisymmetric and thus the wave-function in real space is symmetric (para-state). Then $l = 0, 2, 4, ...$ applies. In the spin-triplett state ($S = 1$) the wave-function in real space is antisymmetric (ortho-state) and $l = 1, 3, 5, ...$
For bosons with atomic spin $S_1 = S_2 = 0$ the wave-function is symmetric (para-state) with even l. For bosons with atomic spin $S_1 = S_2 = 1$ (e.g. D_2) one obtains para-states for the spin-singulett ($S = 0$) and the spin-quintuplett ($S = 2$) and ortho-states for the spin-triplett ($S = 1$).
Then one obtains at low temperatures, that is for $T \ll \Theta_\mathrm{rot}$:
For distinguishable atoms

$$\begin{aligned}
Z_\mathrm{rot} = z_\mathrm{rot}^N &= \left(1 + 3\mathrm{e}^{-\Theta_\mathrm{rot}/T} + ...\right)^N & (21.4)\\
E_\mathrm{rot} = -\frac{\partial \ln Z}{\partial \beta} &= 3Nk_\mathrm{B}\Theta_\mathrm{rot}\mathrm{e}^{-\Theta_\mathrm{rot}/T} + ... & (21.5)\\
C_{V,\mathrm{rot}} = \frac{\partial E}{\partial T} &= 3Nk_\mathrm{B}\left(\frac{\Theta_\mathrm{rot}}{T}\right)^2 \mathrm{e}^{-\Theta_\mathrm{rot}/T} + ... & (21.6)
\end{aligned}$$

For para-states one obtains

$$\begin{aligned}
Z_\mathrm{rot} &= \left(1 + 5\mathrm{e}^{-3\Theta_\mathrm{rot}/T} + ...\right)^N & (21.7)\\
E_\mathrm{rot} &= 15Nk_\mathrm{B}\Theta_\mathrm{rot}\mathrm{e}^{-3\Theta_\mathrm{rot}/T} + ... & (21.8)\\
C_{V,\mathrm{rot}} &= 45Nk_\mathrm{B}\left(\frac{\Theta_\mathrm{rot}}{T}\right)^2 \mathrm{e}^{-3\Theta_\mathrm{rot}/T} + ... & (21.9)
\end{aligned}$$

and for ortho-states

$$Z_\mathrm{rot} = \left(3\mathrm{e}^{-\Theta_\mathrm{rot}/T} + 7\mathrm{e}^{-6\Theta_\mathrm{rot}/T} + ...\right)^N \tag{21.10}$$

$$E_{\mathrm{rot}} = Nk_{\mathrm{B}}\Theta_{\mathrm{rot}}(1+\frac{35}{3}\mathrm{e}^{-5\Theta_{\mathrm{rot}}/T}+...) \tag{21.11}$$

$$C_{V,\mathrm{rot}} = \frac{175}{3}Nk_{\mathrm{B}}\left(\frac{\Theta_{\mathrm{rot}}}{T}\right)^2 \mathrm{e}^{-5\Theta_{\mathrm{rot}}/T}+... \tag{21.12}$$

At high temperatures the sums can be replaced by integrals $\sum_l \to \int \mathrm{d}l$. Then one obtains

$$z_{\mathrm{rot}} = \int_0^\infty \mathrm{d}l(2l+1)\mathrm{e}^{-l(l+1)\Theta_{\mathrm{rot}}/(2T)} = 2\frac{T}{\Theta_{\mathrm{rot}}}\int_0^\infty \mathrm{d}x\mathrm{e}^{-x} = 2\frac{T}{\Theta_{\mathrm{rot}}}. \tag{21.13}$$

with $x = l(l+1)\Theta_{\mathrm{rot}}/(2T)$. This holds for distinguishable atoms. For undistinguishable ones the factor 2 has to be removed. Then one obtains for high temperatures (in all cases)

$$E_{\mathrm{rot}} = Nk_{\mathrm{B}}T, \quad C_{V,\mathrm{rot}} = Nk_{\mathrm{B}}. \tag{21.14}$$

For linear polyatomic molecules as e.g. CO_2 one obtains the same result with an appropriate momentum of inertia. Linear molecules are distinguished in so far as one of the principal momenta of inertia vanishes, which is the one around the axis which connects the atoms. For non-linear molecules, like H_2O all the main momenta of inertia are different from zero. In this case there are not $2l+1$, but $(2l+1)^2$ rotational states for given angular momentum $\hbar l$. These states are described by the square of the angular momentum and both a component of the angular momentum in the fixed coordinate system and in the system rotating with the molecule (the Poisson-brackets vanish between these components in classical mechanics). Both components run independently from $-l$ to $+l$. The corresponding wave-functions are the rotation matrix-functions (they describe the transformation of the spherical harmonics under rotation), which depend on the three Eulerian angles. If one of the moments of inertia vanishes then the rotational energy is finite only, if the component of the angular momentum along this axis vanishes. All other rotational energies along this axis become infinite. Generally the states with different z-component of angular momenta in the fixed system of coordinates are degenerate, but not with respect to the angular momentum components in the system rotating with the molecule, which yields multiplicities $2l+1$ (if it is not higher for some other reasons). If all principal moments of inertia are equal (spherical top), as for CH_4, then all states are degenerate and one obtains

$$z_{\mathrm{rot}} = \sum_l (2l+1)^2\mathrm{e}^{-l(l+1)\Theta_{\mathrm{rot}}/(2T)} \tag{21.15}$$

and for high temperatures, if we approximate one factor $2l+1$ by $2\sqrt{l(l+1)}$

$$z_{\mathrm{rot}} = 4\sqrt{2\pi}\left(\frac{T}{\Theta_{\mathrm{rot}}}\right)^{3/2}, \tag{21.16}$$

which yields

$$E_{\mathrm{rot}} = \frac{3}{2}Nk_{\mathrm{B}}T, \quad C_{V,\mathrm{rot}} = \frac{3}{2}Nk_{\mathrm{B}} \tag{21.17}$$

Thus at high temperatures we obtain for each rotational degree of freedom a contribution $k_{\mathrm{B}}/2$ to the specific heat.

21.b Vibrations

Apart from the rotations there are also vibrational degrees of freedom, where the atoms of the molecules oscillate against each other. A diatomic molecule can vibrate along its axis; thus it has one vibrational degree of freedom. A triatomic linear molecule has two vibrational degrees of freedom in the direction of its axis and two bending degrees of freedom perpendicular to the axis, thus in total four vibrational degrees of freedom. A non-linear triatomic molecule has three vibrational degrees of freedom. The lengths of the sides of the triangle can vary independently. Generally the number of translational degrees of freedom (three) plus the rotational degrees (two or three) plus the number of vibrationall degrees of freedom add up to three times the number of atoms in the molecule.
The vibrations have certain vibrational frequencies ω_{vib} (within harmonic approximation). For these the same holds as for the vibrations of the optical phonons.
Thus we obtain with $k_{\mathrm{B}}\Theta_{\mathrm{vib}} = \hbar\omega_{\mathrm{vib}}$ the contribution to the free energy for one vibrational frequency

$$F_{\mathrm{vib}} = -k_{\mathrm{B}}TN\ln\left(\sum_n \mathrm{e}^{-(n+\frac{1}{2})\Theta_{\mathrm{vib}}/T}\right) = -k_{\mathrm{B}}TN\ln\frac{\mathrm{e}^{-\Theta_{\mathrm{vib}}/(2T)}}{1-\mathrm{e}^{-\Theta_{\mathrm{vib}}/T}} \tag{21.18}$$

and the contribution to the specific heat

$$C_{\mathrm{vib}} = -T\frac{\partial^2 F_{\mathrm{vib}}}{\partial T^2} = k_{\mathrm{B}}N\left(\frac{\Theta_{\mathrm{vib}}}{T}\right)^2\frac{\mathrm{e}^{\Theta_{\mathrm{vib}}/T}}{(\mathrm{e}^{\Theta_{\mathrm{vib}}/T}-1)^2} \tag{21.19}$$

$$\approx k_{\mathrm{B}}N\left(\frac{\Theta_{\mathrm{vib}}}{T}\right)^2\mathrm{e}^{-\Theta_{\mathrm{vib}}/T} \text{ für } T \ll \Theta_{\mathrm{vib}}, \tag{21.20}$$

$$\approx k_{\mathrm{B}}N \text{ für } T \gg \Theta_{\mathrm{vib}}. \tag{21.21}$$

Characteristic temperatures for diatomic molecules (from the script Statistische Physik by Heinz Horner)

	Θ_{rot}	Θ_{vib}	Θ_{el} [K]
H_2	85	5958	129 000
D_2	43	4210	129 000
O_2	2.1	2228	11 300
I_2	0.05	305	17 000

Usually the electronic excitations are so high in energy, that the molecules dissociate before they would really contribute.

22 Metal Electrons

Electrons are fermions with spin 1/2. We consider the metal electrons approximately without interaction. However, the Hartree-Fock interaction may be incorporated into the one-particle energies. The averaged particle number be fixed. We introduce the chemical potential. Then with the Fermi-function

$$f(\epsilon-\mu)=\frac{1}{\mathrm{e}^{\beta(\epsilon-\mu)}+1} \tag{22.1}$$

we obtain the expressions for particle number, energy and entropy

$$\begin{aligned} N &= \langle\hat{N}\rangle=\sum_{\mathbf{k},m} f(\epsilon_{\mathbf{k},m}-\mu), && (22.2)\\ E &= \langle H\rangle=\sum_{\mathbf{k},m}\epsilon_{\mathbf{k},m} f(\epsilon_{\mathbf{k},m}-\mu), && (22.3)\\ S &= -k_{\mathrm{B}}\sum_{\mathbf{k},m}(f\ln f+(1-f)\ln(1-f)). && (22.4)\end{aligned}$$

Now we introduce the density of states $z(\epsilon)$; by $Vz(\epsilon)\mathrm{d}\epsilon$ we denote the number of one-particle states with energies between ϵ and $\epsilon+\mathrm{d}\epsilon$. For the ground-state that is at temperature $T=0$ all one-particle states are occupied up to an energy ϵ_{F}, which is called Fermi-energy. In the isotropic case the corresponding momentum $p_{\mathrm{F}}=\hbar k_{\mathrm{F}}$ is called Fermi momentum. For free electrons one finds

$$\begin{aligned} V\int_0^{\epsilon_{\mathrm{F}}} z(\epsilon')\mathrm{d}\epsilon' &= \frac{2V}{(2\pi)^3}\frac{4\pi}{3}k_{\mathrm{F}}^3 && (22.5)\\ &= V\left(\frac{2m\epsilon_{\mathrm{F}}}{\hbar^2}\right)^{3/2}/3\pi^2=N. && (22.6)\end{aligned}$$

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$$\int_0^{\epsilon} z(\epsilon')\mathrm{d}\epsilon'=\frac{N}{V}\left(\frac{\epsilon}{\epsilon_{\mathrm{F}}}\right)^{3/2}, \quad z(\epsilon)=\frac{N}{V\epsilon_{\mathrm{F}}}\frac{3}{2}\sqrt{\frac{\epsilon}{\epsilon_{\mathrm{F}}}}, \quad \epsilon>0. \tag{22.7}$$

In general $z(\epsilon)$ is given by the band-structure. Generally one has

$$\sum_{\mathbf{k},m} g(\epsilon_{\mathbf{k},m})=V\int g(\epsilon)z(\epsilon)\mathrm{d}\epsilon \tag{22.8}$$

and thus

$$\begin{aligned} \frac{N}{V} &= \int f(\epsilon-\mu)z(\epsilon)\mathrm{d}\epsilon, && (22.9)\\ \frac{E}{V} &= \int \epsilon f(\epsilon-\mu)z(\epsilon)\mathrm{d}\epsilon. && (22.10)\end{aligned}$$

The evaluation of the integrals is performed by the method of Sommerfeld for $\beta\mu\gg 1$ ($k_{\mathrm{B}}T\ll\epsilon_{\mathrm{F}}$). Let

$$G(\mu)=\int_0^\infty g(\epsilon)f(\epsilon-\mu)\mathrm{d}\epsilon=\int_0^\mu g(\epsilon)\mathrm{d}\epsilon+\int_0^\infty g(\epsilon)(f_T(\epsilon-\mu)-f_0(\epsilon-\mu))\mathrm{d}\epsilon. \tag{22.11}$$

The main contribution of the second integral comes from $\epsilon\approx\mu$, since $f_T(\epsilon-\mu)-f_0(\epsilon-\mu)$ is there essentially different from zero. One expands therefore $g(\epsilon)$ in a Taylor series around $\epsilon=\mu$ and obtains

$$G(\mu)=\int_0^\mu g(\epsilon)\mathrm{d}\epsilon+\int_{-\infty}^\infty (g(\mu)+(\epsilon-\mu)g'(\mu)+\ldots)\,(f_T(\epsilon-\mu)-f_0(\epsilon-\mu))\mathrm{d}\epsilon. \tag{22.12}$$

In the second integral we have replaced the lower bound by $-\infty$, which is allowed as long as $\mu\gg k_{\mathrm{B}}T$, since then $f_T(x)-f_0(x)$ is very small. Since $f_T(x)-f_0(x)$ is an odd function in x, only odd powers of $\epsilon-\mu$ contribute to the Taylor expansion of g

$$G(\mu) = \int_0^\mu g(\epsilon)\mathrm{d}\epsilon + 2g'(\mu)\int_0^\infty x f_T(x)\mathrm{d}x + ... \tag{22.13}$$

With $x = \epsilon - \mu = k_\mathrm{B}Ty$ one obtains

$$\int_0^\infty x f_T(x)\mathrm{d}x = (k_\mathrm{B}T)^2\int_0^\infty \frac{y\mathrm{d}y}{\mathrm{e}^y+1} = (k_\mathrm{B}T)^2\frac{\zeta(2)}{2} = \frac{\pi^2}{12}(k_\mathrm{B}T)^2 \tag{22.14}$$

and

$$G(\mu) = \int_0^\mu g(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 g'(\mu) + O(T^4). \tag{22.15}$$

For the particle density one obtains

$$\frac{N}{V} = \int_0^\mu z(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z'(\mu) + ... = \underbrace{\int_0^{\epsilon_\mathrm{F}} z(\epsilon)\mathrm{d}\epsilon}_{N/V} + (\mu-\epsilon_\mathrm{F})z(\epsilon_\mathrm{F}) + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z'(\epsilon_\mathrm{F}) + ... \tag{22.16}$$

Since the particle number is conserved, one obtains

$$\mu(T) = \epsilon_\mathrm{F} - \frac{\pi^2(k_\mathrm{B}T)^2 z'(\epsilon_\mathrm{F})}{6z(\epsilon_\mathrm{F})} + O(T^4) \tag{22.17}$$

One obtains for the energy

$$\begin{aligned}\frac{E}{V} &= \int_0^\mu \epsilon z(\epsilon)\mathrm{d}\epsilon + \frac{\pi^2}{6}(k_\mathrm{B}T)^2(\mu z(\mu))' + ... \\ &= \underbrace{\int_0^{\epsilon_F} \epsilon z(\epsilon)\mathrm{d}\epsilon}_{E_0/V} + \underbrace{(\mu-\epsilon_\mathrm{F})z(\epsilon_\mathrm{F})\epsilon_\mathrm{F} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2\epsilon_\mathrm{F} z'(\epsilon_\mathrm{F})}_{0} + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 z(\epsilon_\mathrm{F}) + ...\end{aligned} \tag{22.18}$$

Thus we are left with the energy

$$E = E_0 + \frac{\pi^2}{6}(k_\mathrm{B}T)^2 V z(\epsilon_\mathrm{F}) + O(T^4) \tag{22.19}$$

and a specific heat

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{\pi^2}{3}k_\mathrm{B}^2 T V z(\epsilon_F) \tag{22.20}$$

linear in T. This contribution is larger then the phononic contribution for metals up to approximately 10 K. The behavior for semiconductors and superconductors is different due to an energy gap in the excitation spectrum.