

Problems in Statistical Physics and Thermodynamics

1. Calculation of equation of state

Helmholtz free energy of a gas is given by

$$F(V, T) = -\frac{1}{3}C \cdot V \cdot T^4,$$

where C is a constant. Calculate equation of state of a given gas.

Solution: We shall start from the definition of Helmholtz free energy

$$F(V, T) = E - TS,$$

from which

$$dF = -pdV - SdT.$$

Because this is an exact differential,

$$\left(\frac{\partial F}{\partial V}\right)_T = -p$$

should hold, and, consequently

$$\frac{1}{3}C \cdot T^4 = p,$$

which is the equation of state we were looking for.

2. Gamma function

Gamma function is defined by

$$\Gamma(n) := \int_0^{\infty} dt \exp(-t)t^{n-1}.$$

(a) Prove that

$$\Gamma(n+1) = n\Gamma(n),$$

(b) evaluate $\Gamma(n)$, $n \in \mathbb{N}$,

(c) evaluate

$$\Gamma\left(n + \frac{1}{2}\right), n \in \mathbb{N}.$$

Solution: We will start with 2a, because we will use the formula later. From the definition, we shall express $\Gamma(n+1)$ and manipulate the expression using integration by parts

$$\Gamma(n+1) = \int_0^{\infty} dt \exp(-t)t^n = \underbrace{-t^n \exp(-t)}_0^{\infty} + n \int_0^{\infty} dt t^{n-1} \exp(-t) = n\Gamma(n).$$

To calculate 2b, we shall start with $\Gamma(1)$:

$$\Gamma(1) = \int_0^{\infty} dt \exp(-t) = -\exp(-t)|_0^{\infty} = 1.$$

Using expression from 2a, we calculate values of gamma function for other natural numbers

$$\Gamma(2) = \Gamma(1+1) = 1 \cdot \Gamma(1) = 1,$$

$$\Gamma(3) = 2 \cdot \Gamma(2) = 1 \cdot 2,$$

$$\Gamma(4) = 3 \cdot \Gamma(3) = 1 \cdot 2 \cdot 3 = 6,$$

$$\Gamma(5) = 4 \cdot \Gamma(4) = 1 \cdot 2 \cdot 3 \cdot 4 = 24;$$

we can obtain formula for general n :

$$\Gamma(n+1) = n \cdot (n-1) \cdot \dots \cdot 3 \cdot 2 \cdot 1 = n!.$$

We will work out the formula 2c in a same way: we will start with $\Gamma(1/2)$:

$$\Gamma\left(\frac{1}{2}\right) = \int_0^{\infty} dt \exp(-t)t^{-\frac{1}{2}} = 2 \int_0^{\infty} ds \exp(-s^2) = \sqrt{\pi},$$

where we have introduced a substitution $t = s^2$ in the last integral. We continue with evaluation of values of gamma function for other n :

$$\Gamma\left(\frac{3}{2}\right) = \Gamma\left(\frac{1}{2} + 1\right) = \frac{1}{2}\Gamma\left(\frac{1}{2}\right) = \frac{1}{2}\sqrt{\pi},$$

$$\Gamma\left(\frac{5}{2}\right) = \frac{3}{2}\Gamma\left(\frac{3}{2}\right) = \frac{1}{2} \cdot \frac{3}{2}\sqrt{\pi} = \frac{3}{4}\sqrt{\pi},$$

$$\Gamma\left(\frac{7}{2}\right) = \frac{5}{2}\Gamma\left(\frac{5}{2}\right) = \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2}\sqrt{\pi} = \frac{15}{8}\sqrt{\pi},$$

$$\Gamma\left(\frac{9}{2}\right) = \frac{7}{2}\Gamma\left(\frac{7}{2}\right) = \frac{1}{2} \cdot \frac{3}{2} \cdot \frac{5}{2} \cdot \frac{7}{2}\sqrt{\pi} = \frac{105}{16}\sqrt{\pi};$$

for a general n

$$\Gamma\left(n + \frac{1}{2}\right) = \frac{2n-1}{2} \cdot \frac{2n-3}{2} \cdot \dots \cdot \frac{7}{2} \cdot \frac{5}{2} \cdot \frac{3}{2} \cdot \frac{1}{2}\sqrt{\pi} = \frac{(2n-1)!!}{2^n}\sqrt{\pi}.$$

3. Stirling's formula

Using the gamma function, approximate $\ln(n!)$ for large n .

Solution:

We will use formula $\Gamma(n+1) = n!$ from the previous problem. We will rearrange the Gamma function

$$\Gamma(n+1) = \int_0^{\infty} dt \exp(-t)t^n = \int_0^{\infty} dt \exp(-t) \cdot \exp[n \ln(t)] = \int_0^{\infty} dt \exp[n \ln(t) - t].$$

After a substitution $t = n + x$

$$\begin{aligned} \int_0^{\infty} dt \exp[n \ln(t) - t] &= \int_{-n}^{\infty} dx \exp[n \ln(n+x) - n - x] \\ &\approx \int_{-n}^{\infty} dx \exp\left[n \ln(n) - n - \frac{x^2}{2n}\right] = \exp[n \ln(n) - n] \int_{-n}^{\infty} dx \exp\left(-\frac{x^2}{2n}\right). \end{aligned}$$

Because the Gaussian function significantly differs from zero just in an interval with width much smaller than n , we can approximate the lower bound of integral by $-\infty$. Then we can easily integrate the Gaussian function

$$\exp[n \ln(n) - n] \int_{-n}^{\infty} dx \exp\left(-\frac{x^2}{2n}\right) = \int_{-\infty}^{+\infty} dx \exp\left(-\frac{x^2}{2n}\right) = \sqrt{2\pi n} \exp[n \ln(n) - n].$$

4. Multidimensional calculations

Determine volume and surface area of n -dimensional sphere.

Solution:

There are two ways how to solve this. One can either calculate the Jacobian matrix of the transformation

to n -dimensional spherical coordinates or to try some other way. In 3D case, the sphere is described as a set of points that fulfill

$$B^3(R) : x_1^2 + x_2^2 + x_3^2 \leq R^2, \quad (1)$$

with a boundary described by

$$S^2(R) : x_1^2 + x_2^2 + x_3^2 = R^2. \quad (2)$$

The general form in a higher dimension d :

$$B^d(R) : x_1^2 + x_2^2 + \dots + x_d^2 \leq R^2, \quad (3)$$

and the boundary

$$S^{d-1}(R) : x_1^2 + x_2^2 + \dots + x_d^2 = R^2. \quad (4)$$

We define a volume in a general form; in 1D the volume corresponds to the length of a line, in 2D it correspond to area of circle, etc.,

$$\text{Vol}(S^1(R)) = 2\pi R, \quad (5)$$

$$\text{Vol}(S^2(R)) = 4\pi R^2. \quad (6)$$

Since the unit of volume corresponds to unit of length raised to a power of d , we can write the volume in terms of unit sphere volume,

$$\text{Vol}(S^{d-1}(R)) = R^{d-1} \text{Vol}(S^{d-1}). \quad (7)$$

In a special case of $d = 2$ and $d = 3$ we have:

$$\text{Vol}(S^1) = 2\pi, \quad (8)$$

$$\text{Vol}(S^2) = 4\pi. \quad (9)$$

So, we have to find the volume of unit sphere. Let us assume space \mathbb{R}^d with coordinates x_1, x_2, \dots, x_d let r be the radial coordinate,

$$r^2 = x_1^2 + x_2^2 + \dots + x_n^2. \quad (10)$$

Let us calculate an integral

$$I_d = \int_{\mathbb{R}^d} dx_1 dx_2 \dots dx_d \exp(-r^2). \quad (11)$$

First method: we divide an integral into d parts each of which is integrated separately, namely

$$I_d = \prod_{i=1}^d \int_{-\infty}^{+\infty} dx_i e^{-x_i^2} = (\sqrt{\pi})^d = \pi^{\frac{d}{2}}. \quad (12)$$

Second method: let us divide \mathbb{R}^d into thin spherical shells. The volume given by r is $S^{d-1}(r)$ sphere and the volume of shell between r and $r + dr$ is given by $S^{d-1}(r)$ multiplied by dr . As a result,

$$I_d = \int_0^{\infty} dr \text{Vol}(S^{d-1}(r)) \exp(-r^2) = \text{Vol}(S^{d-1}) \int_0^{\infty} dr r^{d-1} \exp(-r^2) \quad (13)$$

$$= \frac{1}{2} \text{Vol}(S^{d-1}) \int_0^{\infty} dt \exp(-t) t^{\frac{d}{2}-1}, \quad (14)$$

where we used (7) and performed a substitution $t = r^2$. The last integral can be written in terms of gamma function,

$$I_d = \frac{1}{2} \text{Vol}(S^{d-1}) \Gamma\left(\frac{d}{2}\right). \quad (15)$$

This integral should be also equal to $I_d = \pi^{\frac{d}{2}}$, as we have already calculated. As a result, the unit sphere volume is equal to

$$\text{Vol}(S^{d-1}) = \frac{2\pi^{\frac{d}{2}}}{\Gamma(\frac{d}{2})}. \quad (16)$$

We can easily determine $\text{Vol}(B^d)$:

$$\text{Vol}(B^d) = \int_0^1 dr \text{Vol}(S^{d-1}(r)) = \text{Vol}(S^{d-1}) \int_0^1 dr r^{d-1} = \text{Vol}(S^{d-1}) \left. \frac{r^d}{d} \right|_0^1 = \frac{\text{Vol}(S^{d-1})}{d}, \quad (17)$$

therefore

$$\text{Vol}(B^d) = \frac{2\pi^{\frac{d}{2}}}{d\Gamma(\frac{d}{2})} = \frac{\pi^{\frac{d}{2}}}{\frac{d}{2}\Gamma(\frac{d}{2})} = \frac{\pi^{\frac{d}{2}}}{\Gamma(1 + \frac{d}{2})}. \quad (18)$$

5. Occupation numbers of hydrogen energy levels

Let us assume that the hydrogen atom exists in a level with principal quantum number $n = 3$. Assuming that the level occupation numbers are given by microcanonical distribution, calculate a probability that the atom exists in states with the same orbital quantum number l .

Solution: We shall first determine the number of states for each state described by a given l . For $n = 3$ the possible values of orbital quantum number are $l = \{0, 1, 2\}$. Each state with a given l is split according to a given magnetic quantum number $m = \{-l, -l+1, \dots, l-1, l\}$. Furthermore, each of these states is split according to spin quantum number $s = \pm 1/2$. Now the number of possible states with given l is :

- $l = 0$: $m = \{0\}$, $s = \{\pm 1/2\}$, this gives two states,
- $l = 1$: $m = \{-1, 0, +1\}$, $s = \{\pm 1/2\}$, this gives six states,
- $l = 2$: $m = \{-2, -1, 0, +1, +2\}$, $s = \{\pm 1/2\}$, what gives ten states.

The probability is given by a formula

$$w_i = \frac{\# \text{ states with } l = i}{\# \text{ all possible states}},$$

from which we can easily find

$$w_0 = \frac{1}{9}, w_1 = \frac{1}{3}, w_2 = \frac{5}{9}.$$

6. Expression for entropy

Entropy of an isolated system is given by

$$S = k_B \ln \Omega, \quad (19)$$

where Ω is the number of microstates. For a closed system

$$S = -k_B \sum_n w_n \ln w_n. \quad (20)$$

Show that these formulae give the same result for an isolated system.

Assume that the system can be divided into a physical object A and thermostat A' , which form an isolated system. Calculate the entropy of a) the whole isolated system $A + A'$ and b) sum of entropies of A and A' and show that they yield the same result.

Solution: For an isolated system, according to the postulate of a priori equal probabilities $w_n = 1/\Omega$. Consequently

$$S = -k_B \sum_n w_n \ln w_n = -k_B \sum_{n=1}^{\Omega} \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) = k_B \ln \Omega \sum_{n=1}^{\Omega} \frac{1}{\Omega} = k_B \ln \Omega.$$

Let assume the system composed of two subsystems A and A' . Energy of the isolated system is given by the sum of energies of these subsystems, $E_0 = E + E' = \text{const}$. Let us now calculate the entropy in both cases. In the case a), $\Omega(E_0 - E_n)$ state of A' system correspond to each n state of A system. Taking the logarithm of the number of states and expanding to the first order in E_n

$$k_B \ln[\Omega(E_0 - E_n)] \approx k_B \ln \Omega(E_0) - \frac{\partial}{\partial E} k_B \ln \Omega(E) E_n = k_B \ln \Omega(E_0) - \frac{\partial S}{\partial E} E_n = k_B \ln \Omega(E_0) - \frac{E_n}{T}, \quad (21)$$

after exponentiation we arrive at

$$\Omega(E_0 - E_n) \approx \Omega(E_0) \exp\left(-\frac{E_n}{k_B T}\right). \quad (22)$$

The total entropy of the isolated system is then

$$S_0 = k_B \ln \left[\sum_n \Omega(E_0) \exp\left(-\frac{E_n}{k_B T}\right) \right] = k_B \ln \Omega(E_0) + k_B \ln \sum_n \exp\left(-\frac{E_n}{k_B T}\right) = k_B \ln \Omega(E_0) + k_B \ln Z. \quad (23)$$

In the case b) we have to sum up the entropies of both subsystems

$$\begin{aligned} S_0 = S + S' &= -k_B \sum_n w_n \ln w_n + k_B \ln \Omega(E_0 - E) = \\ &= -k_B \sum_n \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T}\right) \left(-\ln Z - \frac{E_n}{k_B T}\right) + k_B \ln \Omega(E_0) - \frac{\partial k_B \ln \Omega(E_0)}{\partial E_0} E = \\ &= k_B \ln Z + \frac{1}{T} \sum_n \frac{1}{Z} \exp\left(-\frac{E_n}{k_B T}\right) E_n + k_B \ln \Omega(E_0) - \frac{E}{T} = k_B \ln Z + \frac{E}{T} + k_B \ln \Omega(E_0) - \frac{E}{T} = \\ &= k_B \ln \Omega(E_0) + k_B \ln Z. \end{aligned} \quad (24)$$

This gives the same formula at the end.

7. Heat capacity

Show that c_V is given by the fluctuation of energy,

$$c_V = \frac{1}{k_B T^2} \langle \Delta E^2 \rangle.$$

Solution: Mean energy is given by

$$E = \sum_n w_n E_n,$$

E_n is constant for $V = \text{const.}$, therefore we can rewrite the heat capacity as

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \sum_n E_n \left(\frac{\partial w_n}{\partial T} \right)_V.$$

The probability corresponding to each state is

$$w_n = \exp\left(\frac{F - E_n}{k_B T}\right),$$

from which we obtain using differentiation

$$\left(\frac{\partial w_n}{\partial T} \right)_V = \frac{\partial}{\partial T} \left(\frac{F - E_n}{k_B T} \right)_V \exp\left(\frac{F - E_n}{k_B T}\right) = \frac{T \left(\frac{\partial F}{\partial T} \right)_V - F + E_n}{k_B T^2} \exp\left(\frac{F - E_n}{k_B T}\right).$$

Now we can apply thermodynamics relation for Helmholtz free energy

$$F = E - TS, \quad dF = -pdV - SdT,$$

giving us

$$\left(\frac{\partial F}{\partial T}\right)_V = -S,$$

and

$$E = F + TS;$$

inserting this to the formula for derivative of w_n with respect to temperature

$$\left(\frac{\partial w_n}{\partial T}\right)_V = \frac{E_n - E}{k_B T^2} \exp\left(\frac{F - E_n}{k_B T}\right) = \frac{E_n - E}{k_B T^2} w_n.$$

The heat capacity takes the form of

$$c_V = \sum_n E_n w_n \frac{E_n - E}{k_B T^2} = \frac{1}{k_B T^2} \left(\sum_n E_n^2 w_n - E \sum_n E_n w_n \right) = \frac{1}{k_B T^2} (\langle E^2 \rangle - E^2),$$

from which we derive the final relationship

$$c_V = \frac{1}{k_B T^2} \langle \Delta E^2 \rangle.$$

8. Fraction of nitrogen molecules in individual states

Nitrogen atom nucleus ${}^7\text{N}_{14}$ has a nuclear spin $I = 1$. Let us assume that that diatomic molecule N_2 excite just rotational states at normal temperatures, but not the vibrational ones. Let us neglect the dynamics of electrons. Determine fraction of „ortho“ and „para“ molecules in a gas composed of nitrogen molecules. („Ortha“ – symmetric spin state, „Para“ – antisymmetric spin state). How the fraction of molecules in individual states behaves when the temperature of gas approaches zero?

Solution: ${}^7\text{N}_{14}$ nucleus has a bosonic spin of $I = 1$; the total wave function of system of two nuclei should be symmetric. The rotational quantum number J should be odd number for ortho-state to ensure symmetry of the total wave function. In a para state, J should be even number. Rotational energy of nitrogen molecule is

$$E_J = \frac{\hbar^2}{2H} J(J+1), J \in \mathbb{N}_0,$$

where H is angular momentum. The ratio of population of individual states is

$$\frac{\text{\#population of para-nitrogen}}{\text{\#population of ortho-nitrogen}} = \frac{\sum_{\text{odd } J} (2J+1) \exp\left[-\frac{\hbar^2}{2Hk_B T} J(J+1)\right]}{\sum_{\text{even } J} (2J+1) \exp\left[-\frac{\hbar^2}{2Hk_B T} J(J+1)\right]} \cdot \frac{I+1}{I},$$

where I is nitrogen nuclear spin. For

$$\frac{\hbar^2}{Hk_B T} \ll 1$$

we can replace sums by integrals obtaining

$$\begin{aligned} \sum_{\text{sudé } J} (2J+1) \exp\left[-\frac{\hbar^2}{2Hk_B T} J(J+1)\right] &= \\ \sum_{m=0}^{\infty} (4m+1) \exp\left[-\frac{\hbar^2}{2Hk_B T} 2m(2m+1)\right] &\approx \int_0^{\infty} dm (4m+1) \exp\left[-\frac{\hbar^2}{2Hk_B T} 2m(2m+1)\right] = \\ &= \int_0^{\infty} dx \exp\left[-\frac{\hbar^2}{Hk_B T} x\right] = \frac{Hk_B T}{\hbar^2}. \quad (25) \end{aligned}$$

The second integral can be evaluated in the same way:

$$\begin{aligned}
& \sum_{\text{odd } J} (2J+1) \exp \left[-\frac{\hbar^2}{2Hk_B T} J(J+1) \right] = \\
& \sum_{m=0}^{\infty} (4m+3) \exp \left[-\frac{\hbar^2}{2Hk_B T} (2m+1)(2m+2) \right] = \int_0^{\infty} dm (4m+3) \exp \left[-\frac{\hbar^2}{2Hk_B T} (2m+1)(2m+2) \right] = \\
& = \exp \left(\frac{-\hbar^2}{Hk_B T} \right) \int_0^{\infty} dm (4m+3) \exp \left[-\frac{\hbar^2}{Hk_B T} (2m^2 + 3m) \right] = \\
& = \exp \left(\frac{-\hbar^2}{Hk_B T} \right) \int_0^{\infty} dy \exp \left[-\frac{\hbar^2}{Hk_B T} y \right] = \frac{Hk_B T}{\hbar^2} \exp \left(\frac{-\hbar^2}{Hk_B T} \right). \quad (26)
\end{aligned}$$

This after the substitution gives

$$\frac{\text{\#para-nitrogen population}}{\text{\#ortho-nitrogen population}} = \frac{I+1}{I} \exp \left(\frac{\hbar^2}{Hk_B T} \right) \approx \frac{I+1}{I};$$

because $I = 1$ the ratio is

$$\frac{\text{\#para-nitrogen population}}{\text{\#ortho-nitrogen population}} = \frac{2}{1}. \quad (27)$$

To calculate the ratio for the case $T \rightarrow 0$, we will use

$$\frac{\hbar^2}{Hk_B T} \gg 1;$$

in this case the exponential function approaches zero, consequently, we will use just the first term of each sum,

$$\begin{aligned}
& \sum_{\text{even } J} (2J+1) \exp \left[-\frac{\hbar^2}{2Hk_B T} J(J+1) \right] = \sum_{m=0}^{\infty} (4m+1) \exp \left[-\frac{\hbar^2}{2Hk_B T} 2m(2m+1) \right] \approx 1, \\
& \sum_{\text{odd } J} (2J+1) \exp \left[-\frac{\hbar^2}{2Hk_B T} J(J+1) \right] = \sum_{m=0}^{\infty} (4m+3) \exp \left[-\frac{\hbar^2}{2Hk_B T} (2m+1)(2m+2) \right] \approx 3 \exp \left(-\frac{\hbar^2}{Hk_B T} \right).
\end{aligned}$$

The population ratio of individual molecules is then

$$\frac{\text{\#para-nitrogen population}}{\text{\#ortho-nitrogen population}} = \frac{I+1}{3I} \exp \left(\frac{\hbar^2}{Hk_B T} \right) \rightarrow \infty;$$

this implies that all nitrogen molecules appear in para-state for temperatures tending to zero.

9. Wien's displacement law

Derive Wien's displacement law from the Planck's law.

Solution: Planck's law reads

$$B(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp \left(\frac{h\nu}{k_B T} \right) - 1}. \quad (28)$$

Wien's displacement law is written in terms of wavelengths, consequently, we will transform (28) into wavelength space using

$$B(\nu, T) d\nu = \underbrace{B(\lambda(\nu), T)}_{B(\lambda, T)} \left| \frac{\partial \nu(\lambda)}{\partial \lambda} \right| d\lambda;$$

the transformation yields

$$B(\lambda, T) = \frac{8\pi ch}{\lambda^5} \frac{1}{\exp \left(\frac{hc}{k_B T \lambda} \right) - 1}. \quad (29)$$

Now we can determine the maximum of the function. Differentiating with respect to wavelength gives

$$-5 + \frac{hc}{k_B T \lambda} \frac{1}{1 - \exp\left(-\frac{hc}{k_B T \lambda}\right)} = 0.$$

We denote

$$x_{\max} = \frac{hc}{k_B T \lambda_{\max}},$$

where subscript „max“ denotes a point, where the function has its maximum. This is given by the solution of equation

$$\frac{x_{\max}}{1 - \exp(-x_{\max})} = 5.$$

From this the wavelength corresponding to the maximum is

$$\lambda_{\max} = \frac{b}{T}, \quad (30)$$

where

$$b = \frac{hc}{k_B x_{\max}}.$$

10. Stefan–Boltzmann law

Derive the Stefan–Boltzmann law for the amount of energy radiated by a black body per unit area and per unit of time.

Solution: The specific intensity is defined as

$$\delta E = I(\nu, \mathbf{n}) \cos \delta \cdot d\Omega \cdot dS \cdot dt \cdot d\nu. \quad (31)$$

Therefore, the specific intensity is given by the amount of radiative energy that passes through a surface area dS in solid angle $d\Omega$ in time dt in frequency range $d\nu$. Here δ is an angle between \mathbf{n} and $d\mathbf{S}$. During the time dt the surface intercepts radiation from a volume

$$dV = dS \cdot \cos \delta \cdot c \cdot dt.$$

The radiation has energy density $\varepsilon(\nu)$ and comes from all directions. Therefore from $d\Omega$ comes

$$c\varepsilon(\nu) \cos(\delta) \cdot \frac{d\Omega}{4\pi} d\nu \cdot dS \cdot dt,$$

which is equal to δE above. Moreover, in equilibrium $I(\nu, \mathbf{n}) = B(\nu)$ and therefore

$$B(\nu) = \frac{c}{4\pi} \varepsilon(\nu).$$

The total energy emitted by the unit surface element per unit of time and frequency is

$$F(\nu) = \frac{\delta E}{dS dt d\nu} = \iint_{\Omega^+} d\Omega \frac{c}{4\pi} \varepsilon(\nu) \cos \delta = \frac{c}{4\pi} \varepsilon(\nu) \underbrace{\int_0^{2\pi} d\phi \int_0^{\frac{\pi}{2}} d\delta \sin(\delta) \cos(\delta)}_{2\pi \cdot \frac{1}{2}} = \frac{c}{4} \varepsilon(\nu).$$

Inserting the energy density

$$F(\nu) = \frac{c}{4} \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1} = \frac{2\pi\nu^2}{c^2} \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1},$$

after integrating over all frequencies

$$F = \sigma T^4. \quad (32)$$

11. Rayleigh–Jeans law

Derive Rayleigh–Jeans law using the equipartition theorem.

Solution: Rayleigh–Jeans law describes the equilibrium electromagnetic radiation in a closed cavity. According to the equipartition theorem, this corresponds to the system of oscillators with energy

$$E_{\mathbf{v}} = 2 \cdot \frac{1}{2} k_{\text{B}} T = k_{\text{B}} T.$$

Energy of a system of oscillators is given by the sum of energies of individual oscillators. We can approximate the summation by integration. From the solution for a particle in a box we have

$$k_i = \frac{2\pi n_i}{L_i},$$

then the number of states in intervals Δn_i is given by

$$\Delta n_x \Delta n_y \Delta n_z = \underbrace{L_x \cdot L_y \cdot L_z}_V \frac{\Delta k_x \Delta k_y \Delta k_z}{(2\pi)^3}.$$

The total energy of all particles can be written as

$$E = \sum_{\mathbf{k}} E_{\mathbf{k}} \approx 2 \int_{\mathbb{R}^3} \frac{d^3 k}{(2\pi)^3} V E_{\mathbf{k}} = V \int_0^{2\pi} d\varphi \int_0^{\pi} d\theta \int_0^{\infty} dk' \frac{k'^2}{(2\pi)^3} 2k_{\text{B}} T = V \int_0^{\infty} dk 2k_{\text{B}} T \frac{k^2}{(2\pi)^3} 4\pi,$$

where we perform a substitution $k = 2\pi\nu/c$, yielding

$$E \approx V \int_0^{\infty} d\nu 2k_{\text{B}} T \cdot 4\pi \frac{\nu^2}{c^3}, \quad (33)$$

from which

$$\varepsilon_{\nu} \approx \frac{8\pi\nu^2}{c^3} k_{\text{B}} T. \quad (34)$$

12. Influence of Sun on Earth

Let us assume that both Sun and Earth radiate as black bodies in empty space. Temperature of Sun is $T_{\text{S}} = 6000\text{K}$. Let us assume that the temperature on Earth is the same everywhere. The radius of Earth is $R_{\text{E}} = 6 \cdot 10^8\text{cm}$ and the Earth-Sun distance is $d = 1.5 \cdot 10^{11}\text{m}$.

- Estimate temperature of Earth.
- Determine the radiative force of Sun on Earth.
- Compare the results with interplanetary chondrites of spherical shape. Chondrites can efficiently transfer heat and can be regarded as black bodies. Their radius is $d = 0.1\text{cm}$ and let us assume that they move at the same distance as our Earth, that is d .

Solution:

- The total radiative flux coming from our Sun is

$$F = 4\pi R_{\text{S}}^2 \sigma T_{\odot}^4;$$

the radiative flux per unit of surface at the distance d (Earth) is

$$\frac{F}{S} = \frac{4\pi R_{\text{S}}^2 \sigma T_{\odot}^4}{4\pi d^2},$$

therefore the Earth intercepts

$$F_{\oplus} = \frac{R_{\text{S}}^2 \sigma T_{\odot}^4}{d^2} \pi R_{\oplus}^2.$$

Because we assume that the Earth is in a state of thermodynamic equilibrium, it emits as a black body,

$$F_{\oplus} = 4\pi R_{\oplus}^4 \sigma T_{\oplus}^4,$$

therefore

$$\frac{R_s^2 \sigma T_{\odot}^4}{d^2} \pi R_{\oplus}^2 = 4\pi R_{\oplus}^4 \sigma T_{\oplus}^4,$$

$$T_{\oplus} = \sqrt{\frac{R_{\odot}}{2d}} T_{\odot} = 290 \text{ K}. \quad (35)$$

(b) Because the radius of Earth is much smaller than its distance from Sun, we can estimate the force directly from

$$\mathcal{F} = \frac{F_{\oplus}}{c} = \frac{R_s^2 \sigma T_{\odot}^4 \pi R_{\oplus}^2}{c} = 6 \times 10^8 \text{ N}.$$

(c) In this case we can use the same equation as derived above,

$$T = 290 \text{ K}, \quad \mathcal{F} = 1.7 \times 10^{-11} \text{ N}.$$

13. Harmonic oscillator

Determine eigenvectors of linear harmonic oscillator in coordinate representation.

Solution: We will use creation and annihilation operators. Let us remind that $\hat{a}|0\rangle = 0|0\rangle$. We will determine the coordinate representation of this vector

$$\langle q|\hat{a}|0\rangle = \langle q|0|0\rangle.$$

Because the annihilation operator can be written in terms of \hat{x} and \hat{p}_x as

$$\hat{a} = \frac{1}{\sqrt{2}}(\hat{q} + i\hat{p}),$$

where the dimensionless operators are

$$\hat{q} = \sqrt{\frac{m\omega}{\hbar}}\hat{x}, \quad \hat{p} = \sqrt{\frac{1}{m\hbar\omega}}\hat{p}_x.$$

We shall substitute in a previous equation obtaining

$$\langle q|\hat{a}|0\rangle = \left\langle q \left| \frac{1}{\sqrt{2}}(\hat{q} + i\hat{p}) \right| 0 \right\rangle = \frac{1}{\sqrt{2}}(\langle q|\hat{q}|0\rangle + i\langle q|\hat{p}|0\rangle).$$

The operator can act on the left state,

$$\frac{1}{\sqrt{2}}(\langle q|\hat{q}|0\rangle + i\langle q|\hat{p}|0\rangle) = \frac{1}{\sqrt{2}}q\langle q|0\rangle + \frac{1}{\sqrt{2}}\frac{d}{dq}\langle q|0\rangle = \frac{1}{\sqrt{2}}qh_0(q) + \frac{1}{\sqrt{2}}\frac{d}{dq}h_0(q) = 0.$$

We obtain equation for the eigenfunction of a given state $|0\rangle$ as

$$qh_0(q) + \frac{d}{dq}h_0(q) = 0. \quad (36)$$

Solution is

$$h_0(x) = C \exp\left(-\frac{m\omega}{2\hbar}x^2\right).$$

C constant can be determined from the norm of eigenvector

$$\int dx [h_0(x)]^2 = 1.$$

Then

$$C^2 = \sqrt{\frac{m\omega}{\pi\hbar}}. \quad (37)$$

The final eigenfunction is

$$h_0(x) = \sqrt[4]{\frac{m\omega}{\pi\hbar}} \exp\left(-\frac{m\omega x^2}{\hbar}\right). \quad (38)$$

To determine the coordinate representation of eigenstate with nonzero n , we shall use the identity $\hat{a}^\dagger |n\rangle = \sqrt{n+1} |n+1\rangle$. Fro $n = 1$ we have

$$\langle q | \hat{a}^\dagger | 0 \rangle = \langle q | 0 \rangle,$$

then

$$\left\langle q \left| \frac{1}{\sqrt{2}} (\hat{q} - i\hat{p}) \right| 1 \right\rangle = \langle q | 0 \rangle.$$

We shall rewrite the left hand side

$$\frac{1}{\sqrt{2}} q \langle q | 0 \rangle + \frac{1}{\sqrt{2}} \frac{d}{dq} \langle q | 0 \rangle = \langle q | 1 \rangle,$$

from which

$$h_1(q) = \frac{1}{\sqrt{2}} \left(q h_0(q) + \frac{d}{dq} h_0(q) \right). \quad (39)$$

The eigenfunction $h_n(q)$ can be written in terms of recursion formula

$$h_n(q) = \frac{1}{\sqrt{2}} \left[q h_{n-1}(q) + \frac{d}{dq} h_{n-1}(q) \right]. \quad (40)$$

14. System of harmonic oscillators

Determine thermodynamic properties of the system of N distinguishable classical harmonic oscillators with frequency ω .

Solution: The energy of a system of harmonic oscillators is

$$E = \sum_{n=1}^N \left(\frac{p_n^2}{2m} + \frac{1}{2} m \omega^2 q_n^2 \right). \quad (41)$$

We will calculate the statistical sum first,

$$\begin{aligned} Z &= \frac{1}{h^N} \int_{\mathbb{R}^{2N}} d^N q \cdot d^N p \cdot \exp \left[- \sum_{n=1}^N \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) \right] = \\ &= \frac{1}{h^N} \int_{\mathbb{R}^{2N}} d^N p \cdot d^N q \cdot \prod_{n=1}^N \exp \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) = \\ &= \frac{1}{h^N} \prod_{n=1}^N \int_{\mathbb{R}} dp_n \cdot dq_n \cdot \exp \left(\frac{p_n^2}{2mk_B T} + \frac{m\omega^2 q_n^2}{2k_B T} \right) = \\ &= \frac{1}{h^N} \left[\int_0^\infty dp \cdot \exp \left(\frac{p^2}{2mk_B T} \right) \right]^N \left[\int_0^\infty dq \exp \left(\frac{m\omega^2 q^2}{2k_B T} \right) \right]^N = \\ &= \frac{1}{h^N} \left(\sqrt{2mk_B T \pi} \cdot \frac{2\pi k_B T}{m\omega^2} \right)^N = \left(\frac{2\pi k_B T}{h\omega} \right)^N = \left(\frac{k_B T}{\hbar\omega} \right)^N. \quad (42) \end{aligned}$$

Helmholtz free energy can be determined from

$$F = -k_B T \ln(Z) = -k_B T \ln \left(\frac{k_B T}{\hbar\omega} \right)^N = -N k_B T \ln \left(\frac{k_B T}{\hbar\omega} \right). \quad (43)$$

The pressure and entropy are

$$p = - \left(\frac{\partial F}{\partial V} \right)_T = 0, \quad (44)$$

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = Nk_B \left[\ln \left(\frac{k_B T}{\hbar \omega} \right) + 1 \right]. \quad (45)$$

Energy of the system is

$$E = F + TS = Nk_B T.$$

15. Density distribution in an atmosphere

Determine the density distribution in a gas column with a cross-section A in homogeneous gravitational field. Let us assume that the gas is composed from indistinguishable particles with mass m .

Solution: We will start with calculation of the canonical partition function, which can be written as

$$Z = \frac{1}{N!(2\pi\hbar)^3} \int_{\mathbb{R}^{3N} \times \Omega} d^{3N}p \cdot d^{3N}q \cdot \exp \left[- \sum_n \left(\frac{\mathbf{p}_n^2}{2mk_B T} + \frac{mg\mathbf{q}}{k_B T} \right) \right],$$

where $\Omega = \{[x, y, z]; x \in [-L, L], y \in [-L, L], z \in [0, \infty), L \in \mathbb{R}^+\}$. One-particle partition function is

$$Z = \frac{1}{(2\pi\hbar)^3} \left[\int_{\mathbb{R}} dp \cdot \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \int_{\Omega} dq \cdot \exp \left(- \frac{mg\mathbf{q}}{k_B T} \right) \right];$$

the first integral leads to Gaussian function,

$$\int_{\mathbb{R}} dp \cdot \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) = \sqrt{(2\pi mk_B T)^3}.$$

The second integral gives

$$\int_{\Omega} dq \cdot \exp \left(- \frac{mg\mathbf{q}}{k_B T} \right) = \underbrace{\int_{-L}^L dx \int_{-L}^L dy}_{A} \underbrace{\int_0^{\infty} dz}_{\frac{k_B T}{mg}} \exp \left(- \frac{mgz}{k_B T} \right) = A \frac{k_B T}{mg}.$$

Consequently,

$$Z = \frac{1}{(2\pi\hbar)^3} (2\pi mk_B T)^{\frac{3}{2}} A \frac{k_B T}{mg}. \quad (46)$$

The probability of finding the particle in a phase space $d^3p \cdot d^3q$ is given by

$$dw_n = \frac{1}{Z} \frac{d^3p \cdot d^3q}{(2\pi\hbar)^3} \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \exp \left(- \frac{mg\mathbf{q}}{k_B T} \right) = \frac{mg}{(2\pi mk_B T)^{\frac{3}{2}} Ak_B T} \exp \left(- \frac{\mathbf{p}^2}{2mk_B T} \right) \exp \left(- \frac{mg\mathbf{q}}{k_B T} \right) d^3p \cdot d^3q.$$

Our aim is to obtain the probability density in real space \mathbf{q} , therefore we shall integrate w_n over the momentum space,

$$\int_{\mathbf{p}} dw_n = \underbrace{\frac{mg}{Ak_B T} \exp \left(- \frac{mgq_3}{k_B T} \right)}_{\mathcal{P}} \cdot d^3q,$$

where \mathcal{P} denotes the probability density of finding the particle at the position \mathbf{q} . The particle number density is

$$n = \frac{Nmg}{Ak_B T} \exp \left(- \frac{mgq_3}{k_B T} \right). \quad (47)$$

The mass density is

$$\rho(z) = \rho(0) \cdot \exp \left(- \frac{mgq_3}{k_B T} \right). \quad (48)$$

16. Heat capacity of a gas I

Let us study a gas composed of diatomic molecules. We shall calculate heat capacity per molecule. We shall account just vibrational motion of molecules with energy given by

$$E_n = \hbar\omega \left(n + \frac{1}{2} \right). \quad (49)$$

Calculate the partition function, determine the Helmholtz free energy, and the heat capacity. Determine the approximate behaviour at low and high temperatures.

Solution: The partition function is

$$Z = \sum_{n=0}^{\infty} \exp\left(-\frac{E_n}{k_B T}\right) = \sum_{n=0}^{\infty} \exp\left[-\frac{\hbar\omega \left(n + \frac{1}{2}\right)}{k_B T}\right] = \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \sum_{n=0}^{\infty} \exp\left(-\frac{\hbar\omega}{k_B T} n\right). \quad (50)$$

Using the sum of a geometric sequence we derive

$$Z = \frac{\exp\left(-\frac{\hbar\omega}{2k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} = \frac{2}{2 \left[\exp\left(\frac{\hbar\omega}{2k_B T}\right) - \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \right]} = \frac{1}{2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right)}. \quad (51)$$

From the partition function we determine the Helmholtz free energy

$$F = -k_B T \ln(Z) = k_B T \ln \left[2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right) \right].$$

We will estimate the energy first,

$$E = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V.$$

After substitution and differentiation

$$E = k_B T \ln \left[2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right) \right] - k_B T \ln \left[2 \sinh\left(\frac{\hbar\omega}{2k_B T}\right) \right] + \frac{\hbar\omega}{2} \operatorname{coth}\left(\frac{\hbar\omega}{2k_B T}\right) = \frac{\hbar\omega}{2} \operatorname{coth}\left(\frac{\hbar\omega}{2k_B T}\right).$$

From this for the heat capacity follows

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\hbar\omega}{2T} \right)^2 \frac{1}{k_B \sinh^2\left(\frac{\hbar\omega}{2k_B T}\right)}. \quad (52)$$

The limiting behaviour at low and high temperatures is

- **low-temperature approximation:** we will approximate the sinh function using exponentials

$$c_V = \left(\frac{\partial E}{\partial T} \right)_V = \left(\frac{\hbar\omega}{T} \right)^2 \frac{1}{k_B \left[\exp\left(\frac{\hbar\omega}{2k_B T}\right) - \exp\left(-\frac{\hbar\omega}{2k_B T}\right) \right]^2}.$$

The first term dominates, therefore

$$c_V \approx \frac{1}{k_B} \left(\frac{\hbar\omega}{T} \right)^2 \exp\left(-\frac{\hbar\omega}{2k_B T}\right). \quad (53)$$

- **high-temperature approximation:** We perform first-order Taylor expansion of sinh, from which

$$c_V \approx \left(\frac{\hbar\omega}{T} \right)^2 \frac{1}{k_B \left(\frac{\hbar\omega}{k_B T} \right)^2} = k_B. \quad (54)$$

17. Heat capacity of a gas II

Let us study a gas composed from diatomic molecules. Calculate heat capacity per mole of a given gas. You may account just rotational movement of the molecules with energy given by

$$E_{j,m} = \frac{\hbar^2 j(j+1)}{2I}, \quad (55)$$

where I is molecular moment of inertia. The partition function cannot be calculated analytically, therefore express this quantity in the limit of high and low temperatures.

Solution: The partition function can be written as

$$Z = \sum_j g_j \exp\left(-\frac{E_j}{k_B T}\right), \quad (56)$$

where g_j is the degeneracy factor of a given energy level. After substitution (55) we derive

$$Z = \sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{\hbar^2 j(j+1)}{2Ik_B T}\right). \quad (57)$$

The sum cannot be evaluated analytically, therefore we express the quantity in the limit of high and low temperatures. the degeneracy factor,

- **high-temperature limit:** in this case

$$\frac{\hbar^2}{2Ik_B T} \ll 1,$$

therefore (57) is in fact left Riemann sum. Therefore, we can approximate

$$\sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{\hbar^2 j(j+1)}{2Ik_B T}\right) \approx \int_0^{\infty} dj (2j+1) \exp\left(-\frac{\hbar^2 j(j+1)}{2Ik_B T}\right) = \int_0^{\infty} dz \exp\left(-\frac{\hbar^2 z}{2Ik_B T}\right) = \frac{2Ik_B T}{\hbar^2}.$$

From this the Helmholtz free energy is

$$F = -k_B T \ln\left(\frac{2Ik_B T}{\hbar^2}\right),$$

energy

$$E = k_B T,$$

and heat capacity

$$c_V = k_B. \quad (58)$$

- **low-temperature limit:** for low temperatures

$$\frac{\hbar^2}{2Ik_B T} \gg 1;$$

the exponential tends quickly to zero, and we can account just limited number of summands. Let us take just tow; in this case the partition function can be approximated as

$$\sum_{j=0}^{\infty} (2j+1) \exp\left(-\frac{\hbar^2 j(j+1)}{2Ik_B T}\right) \approx 1 + 3 \exp\left(-\frac{\hbar^2}{Ik_B T}\right).$$

We shall proceed as previously estimating the Helmholtz free energy, energy, and heat capacity. The energy is

$$E = \frac{3\hbar^2}{I} \frac{1}{3 + \exp\left(\frac{\hbar^2}{Ik_B T}\right)},$$

and heat capacity is

$$c_V = \frac{3\hbar^4}{k_B T^2 I^2} \frac{1}{\left[3 \exp\left(-\frac{\hbar^2}{2k_B T I}\right) + \exp\left(\frac{\hbar^2}{2k_B T I}\right)\right]^2}. \quad (59)$$

18. Unit testing

Show that pressure and energy density share the same unit.

Solution: we shall proceed from definition

$$[p] = \frac{[F]}{[S]} = \frac{\text{kg} \cdot \text{m} \cdot \text{s}^{-2}}{\text{m}^2} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2},$$

$$[e] = \frac{[E]}{[V]} = \frac{\text{kg} \cdot \text{m}^2 \cdot \text{s}^{-2}}{\text{m}^3} = \text{kg} \cdot \text{m}^{-1} \cdot \text{s}^{-2}.$$

19. Relativistic particles

Calculate density of states of relativistic particles and find the limiting formulae for classical and ultra-relativistic particles.

Solution: The density of states is given by

$$\rho(E) = \frac{gV}{\pi^d} \frac{1}{2^d} \text{Vol}(S^{d-1}) \frac{[k(E)]^{d-1}}{\left| \frac{dE}{dk} \right|}, \quad (60)$$

where g is the degeneracy factor, d is the dimension of space, and $\text{Vol}(S^{d-1})$ surface area of $d-1$ dimensional sphere. In our case $d = 3$. Dispersion relation $E(k)$ is given by

$$E = \sqrt{m^2 c^4 + \hbar^2 k^2 c^2},$$

from which

$$k = \frac{\sqrt{E^2 - m^2 c^4}}{\hbar c}.$$

We substitute in 60) obtaining

$$\rho(E) = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} E \sqrt{E^2 - m^2 c^4}. \quad (61)$$

- Classical limit: Energy is given by

$$E_{\text{cl}} \approx E - mc^2 = \sqrt{m^2 c^4 + \hbar^2 k^2 c^2} - mc^2 = mc^2 \sqrt{1 + \frac{\hbar^2 k^2}{m^2 c^2}} - mc^2 \approx mc^2 \left(1 + \frac{1}{2} \frac{\hbar^2 k^2}{m^2 c^2} \right) - mc^2 = \frac{\hbar^2 k^2}{2m}. \quad (62)$$

- Ultra-relativistic limit – in this case $E \gg mc^2$ and we can neglect the second term in square root

$$\rho(E) = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} E^2.$$

20. Maxwell–Boltzmann distribution

Show that it is possible to derive Maxwell–Boltzmann distribution of velocities from the grand-canonical distribution.

Solution: The number of bosons in energy interval $(E, E + dE)$ is

$$dN = \frac{\rho(E) dE}{\exp\left(\frac{E - \mu}{k_B T}\right) + 1}.$$

In a classical case

$$\exp\left(-\frac{E - \mu}{k_B T}\right) \ll 1,$$

therefore we can neglect one in the denominator. After the substitution of $\rho(E)$ we arrive at

$$dN = \frac{4\pi gV}{(2\pi\hbar)^3} \sqrt{2m^3 E} \exp\left(\frac{E - \mu}{k_B T}\right) dE.$$

The expression can be transformed into velocity space

$$dE = \frac{\partial E}{\partial v} dv = mv dv,$$

using classical expression for kinetic energy $E = 0.5 \cdot mv^2$

$$dw = \frac{4\pi gV}{(2\pi\hbar)^3} \sqrt{2m^3} \sqrt{\frac{m}{2}} \exp\left(\frac{0.5mv^2 - \mu}{k_B T}\right) mv^2 dv = \frac{4\pi gV}{(2\pi\hbar)^3} m^3 v^2 \exp\left(-\frac{v^2}{2mk_B T}\right) \exp\left(-\frac{\mu}{k_B T}\right) dv.$$

The chemical potential can be derived from the equation for one particle

$$1 = N = \frac{gV}{(2\pi\hbar)^3} (2\pi mk_B T)^{\frac{3}{2}} F_{\frac{3}{2}}\left(\frac{\mu}{k_B T}\right) = \frac{gV}{(2\pi\hbar)^3} (2\pi mk_B T)^{\frac{3}{2}} \frac{1}{\Gamma\left(\frac{3}{2}\right)} \int_0^\infty dx \frac{x^{\frac{1}{2}}}{\exp\left(x - \frac{\mu}{k_B T}\right) + 1}.$$

The exponential is significantly higher than one, therefore we can approximate

$$\int_0^\infty dx x^{\frac{1}{2}} \exp\left(-x + \frac{\mu}{k_B T}\right) \approx \exp\left(\frac{\mu}{k_B T}\right) \int_0^\infty dx x^{\frac{1}{2}} \exp(-x) = \exp\left(\frac{\mu}{k_B T}\right) \Gamma\left(\frac{3}{2}\right).$$

We substitute in the previous formula

$$\frac{gV}{(2\pi\hbar)^3} \exp\left(\frac{\mu}{k_B T}\right) = (2\pi mk_B T)^{-\frac{3}{2}}.$$

This gives

$$dw = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} v^2 \exp\left(-\frac{v^2}{2k_B T}\right) dv. \quad (63)$$

21. Derivation of the Planck's law

Show that the Planck's law can be derived from grandcanonical distribution of particles with $\mu = 0$.

Solution: The number of bosons in energy interval is

$$dN = \frac{\rho(E)dE}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1}.$$

For photons $\mu = 0$ holds and their energy is equal to $E = h\nu$. Transforming to frequencies, we derive the energy density

$$E dN = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{\exp\left(\frac{h\nu}{k_B T}\right) - 1}. \quad (64)$$

22. Bosonic a Fermionic integral

Prove that

$$I_f(m) = \int_0^\infty dx \cdot \frac{x^{m-1}}{\exp(x) + 1} = (1 - 2^{1-m}) \zeta(m) \cdot \Gamma(m), \quad (65)$$

and

$$I_b(m) = \int_0^\infty dx \cdot \frac{x^{m-1}}{\exp(x) - 1} = \zeta(m) \cdot \Gamma(m), \quad (66)$$

where $\zeta(m)$ is the Riemann function

$$\zeta(m) = \sum_{k=1}^\infty \frac{1}{k^m}.$$

Solution: We can manipulate $I_f(m)$ to

$$\int_0^{\infty} dx \frac{x^{m-1}}{\exp(x)+1} = \int_0^{\infty} dx x^{m-1} \exp(-x) \frac{1}{1+\exp(-x)};$$

the fraction can be expanded as

$$\frac{1}{1 \pm x} = 1 \mp x + x^2 \mp \dots, \quad (67)$$

which gives

$$\begin{aligned} \int_0^{\infty} dx x^{m-1} \exp(-x) \frac{1}{1+\exp(-x)} &= \int_0^{\infty} dx x^{m-1} \exp(-x) \sum_{k=0}^{\infty} (-1)^k \exp(-kx) = \\ &= \sum_{k=0}^{\infty} \int_0^{\infty} dx (-1)^k \exp[-(1+k)x] x^{m-1}. \end{aligned}$$

In sum we substitute $k' = k + 1$, take out terms that do not depend on variable x , and perform a substitution $y = k'x$

$$\sum_{k'=0}^{\infty} \int_0^{\infty} dx (-1)^{k'} \exp[-(1+k')] x^{m-1} = \sum_{k'=1}^{\infty} \int_0^{\infty} dx (-1)^{k'-1} \exp(-k'x) x^{m-1} = \sum_{k'=1}^{\infty} \frac{(-1)^{k'-1}}{k'^m} \int_0^{\infty} dy \exp(-y) y^{m-1}.$$

Because the integral does not depend on k' , the sum can be evaluated separately. We can separate positive and negative contributions to the sum, which gives

$$\sum_{k'=1}^{\infty} \frac{(-1)^{k'-1}}{(k')^m} = \sum_{l=1}^{\infty} \frac{1}{(2l-1)^m} - \sum_{l=1}^{\infty} \frac{1}{(2l)^m}.$$

This can be manipulated in the following way

$$\begin{aligned} \sum_{l=1}^{\infty} \frac{1}{(2l-1)^m} - \sum_{l=1}^{\infty} \frac{1}{(2l)^m} &= \\ \frac{1}{1^m} + \frac{1}{3^m} + \frac{1}{5^m} + \dots + \frac{1}{(2l-1)^m} + \dots - \frac{1}{2^m} - \frac{1}{4^m} - \frac{1}{6^m} - \dots - \frac{1}{(2l)^m} - \dots &= \\ \frac{1}{1^m} + \frac{1}{2^m} + \frac{1}{3^m} + \frac{1}{4^m} + \dots + \frac{1}{k^m} - 2 \left(\frac{1}{2^m} + \frac{1}{4^m} + \dots + \frac{1}{(2l)^m} + \dots \right) &= \sum_{k=1}^{\infty} \frac{1}{k^m} - 2 \sum_{l=1}^{\infty} \frac{1}{(2l)^m} = \\ \sum_{k=1}^{\infty} \frac{1}{k^m} - 2^{1-m} \sum_{l=1}^{\infty} \frac{1}{l^m} &= (1 - 2^{1-m}) \sum_{k=1}^{\infty} \frac{1}{k^m}. \quad (68) \end{aligned}$$

The function is then

$$\sum_{k'=1}^{\infty} \frac{(-1)^{k'-1}}{k'^m} \int_0^{\infty} dy \exp(-y) y^{m-1} = (1 - 2^{1-m}) \sum_{k=1}^{\infty} \frac{1}{k^m} \int_0^{\infty} dy \exp(-y) y^{m-1} = (1 - 2^{1-m}) \zeta(m) \Gamma(m). \quad (69)$$

The equality can be proven analogously – we expand according to (67)

$$\begin{aligned} I_b(m) &= \int_0^{\infty} dx \cdot \frac{x^{m-1}}{\exp(x)-1} = \\ &= \sum_{k=0}^{\infty} \int_0^{\infty} dx x^{m-1} \exp[-x(1+k)] = \sum_{k=1}^{\infty} \int_0^{\infty} dx x^{m-1} \exp(-kx) = \\ &= \sum_{k=1}^{\infty} \frac{1}{k^m} \int_0^{\infty} dy y^{m-1} \exp(-y) = \zeta(m) \Gamma(m). \quad (70) \end{aligned}$$

23. Properties of functions

We shall define

$$B_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) - 1}, \quad (71)$$

and

$$F_n(y) = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) + 1}. \quad (72)$$

Prove that

$$\frac{dB_{n+1}(y)}{dy} = B_n(y),$$

and

$$\frac{dF_{n+1}(y)}{dy} = F_n(y).$$

Solution: We will start with

$$\frac{dB_{n+1}(y)}{dy} = \frac{d}{dy} \left[\frac{1}{\Gamma(n+1)} \int_0^\infty dx \frac{x^n}{\exp(x-y) - 1} \right] = \frac{1}{\Gamma(n+1)} \int_0^\infty dx x^n \frac{d}{dy} \frac{1}{\exp(x-y) - 1}.$$

Because the following identity holds

$$\frac{d}{dy} \frac{1}{\exp(x-y) - 1} = -\frac{d}{dx} \frac{1}{\exp(x-y) - 1},$$

we can substitute into the integral and integrate by parts

$$-\frac{1}{\Gamma(n+1)} \int_0^\infty dx x^n \frac{d}{dx} \frac{1}{\exp(x-y) - 1} = \frac{1}{\Gamma(n+1)} \left\{ \underbrace{\left[-\frac{x^n}{\exp(x-y) - 1} \right]_0^\infty}_0 + \int_0^\infty dx \frac{n \cdot x^{n-1}}{\exp(x-y) - 1} \right\}.$$

Using $\Gamma(n+1) = n\Gamma(n)$ we derive

$$\frac{dB_{n+1}(y)}{dy} \frac{d}{dy} = \frac{1}{\Gamma(n)} \int_0^\infty dx \frac{x^{n-1}}{\exp(x-y) - 1} = B_n(y). \quad (73)$$

The fermionic relations can be proven analogously.

24. Bose–Einstein condensate in 2D?

Prove that in there is no Bose–Einstein condensate in $d = 2$.

Solution: We shall estimate the density of states in 2d:

$$\rho(E) = \frac{2\pi gSm}{(2\pi\hbar)^2}.$$

Landau potential is

$$\Omega = - \int_0^\infty dE \left[\int_0^\infty dE' \rho(E') \right] \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1},$$

where

$$\int_0^\infty dE' \rho(E') = \frac{2\pi gSmE}{(2\pi\hbar)^2}.$$

The potential Ω is equal to

$$\Omega = \frac{2\pi gSm}{(2\pi\hbar)^2} \int_0^\infty dE \frac{E}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1}.$$

Number of particles is in the 2D case equal to (taking into account $\mu \rightarrow 0$)

$$N = \int_0^\infty dE \frac{\rho(E)}{\exp\left(\frac{E-\mu}{k_B T}\right) - 1} = \frac{2\pi gmS}{(2\pi\hbar)^2} k_B T \int_0^\infty dx \frac{1}{\exp(x) - 1} = \frac{2\pi gmS}{(2\pi\hbar)^2} k_B T \zeta(1) \Gamma(1).$$

Because $\zeta(1) \rightarrow \infty$, any number of particles can appear in the state with $E = 0$, and there is no Bose-Einstein condensate.

25. Electron-positron gas

At temperatures $k_B T \approx m_e c^2$ electron-positron pairs are created. Determine equilibrium number of e^- and e^+ . **Solution:** We shall start with.

$$\sum_i \gamma_i \mu_i = 0. \quad (74)$$

From the equation that describes the reaction follows that the number of electrons and positrons is the same, therefore

$$\mu_- + \mu_+ = 0 = 2\mu,$$

that is, the chemical potential is equal zero. For ultra-relativistic fermions

$$dN_E = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} \frac{E^2 dE}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1},$$

therefore the number of particles is

$$N_E = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{1}{c^3} \int dE \frac{E^2}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} = \frac{4\pi gV}{(2\pi\hbar)^3} \frac{(k_B T)^3}{c^3} \Gamma(3) F_3\left(\frac{\mu}{k_B T}\right).$$

For the case $\mu = 0$ we derive

$$F_3\left(\frac{\mu}{k_B T}\right) = (1 - 2^{-2}) \zeta(3) = \frac{3}{4} \cdot \zeta(3).$$

Number of particles is

$$N_+ = N_- = \frac{3\pi gV}{4(\pi\hbar)^3} \frac{(k_B T)^3}{c^3} \zeta(3).$$

For $g = 2$ in particular

$$N_+ = N_- = \frac{3V}{2\pi^2} \left(\frac{k_B T}{\hbar c}\right)^3 \zeta(3). \quad (75)$$

26. Number of particles of bosonic gas

From the Landau potential of nonrelativistic bosonic gas

$$\Omega = -k_B T \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} B_{\frac{5}{2}}\left(\frac{\mu}{k_B T}\right), \quad (76)$$

determine number of particles N .

Solution: The number of particles is given by

$$N = - \left(\frac{\partial \Omega}{\partial \mu} \right)_{T,V},$$

substituting from (76) we obtain

$$N = -k_B T \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} \frac{\partial}{\partial \mu} B_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right).$$

From the previous problem can use the identity

$$\frac{dB_{n+1}(y)}{dy} = B_n(y),$$

from which

$$\frac{dB_{n+1} \left(\frac{\mu}{k_B T} \right)}{d\mu} = \frac{1}{k_B T} B_n \left(\frac{\mu}{k_B T} \right).$$

The number of particles is then

$$N = \frac{gV}{(2\pi\hbar)^3} (2\pi m k_B T)^{\frac{3}{2}} B_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right). \quad (77)$$

27. Adiabatic process equation for photon gas

Determine the adiabatic process equation for photon gas in terms of p and V .

Solution: Helmholtz free energy of photon gas is

$$F = -\frac{4}{3c} \sigma T^4 V,$$

the following relations hold

$$\left(\frac{\partial F}{\partial V} \right)_T = -p, \quad \left(\frac{\partial F}{\partial T} \right)_V = -S.$$

From these equations the entropy is

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

and the temperature is

$$T = \sqrt[4]{\frac{3cp}{4\sigma}},$$

after the substitution

$$S = \frac{4^{\frac{5}{4}}}{3^{\frac{1}{4}}} c^{\frac{3}{4}} p^{\frac{3}{4}} \sigma^{\frac{1}{4}} V = \text{const.}$$

After using more suitable constant, we derive $p^{\frac{3}{4}} V = \text{const.}$, what can be manipulated into the form

$$pV^{\frac{4}{3}} = \text{const.} \quad (78)$$

28. Fermi gas degeneration

Rewrite the degeneracy condition of Fermi gas $k_B T \ll \varepsilon_F$ in terms of wavelength of the de Broglie wave corresponding to the thermal motion and Fermi wavelength.

Solution: We substitute into the formula for λ_T

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \gg \sqrt{\frac{2\pi\hbar^2}{m\varepsilon_F}}.$$

The Fermi wavelength is

$$\lambda_F = \frac{2\pi\hbar}{p_F} = \frac{2\pi\hbar}{\sqrt{2m\varepsilon}} = \sqrt{\frac{4\pi^2\hbar}{2m\varepsilon}},$$

The inequality can be rewritten as

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} \gg \sqrt{\frac{2\pi\hbar^2}{m\varepsilon_F}} \approx \lambda_F.$$

From this follows

$$\lambda_T \gg \lambda_F. \quad (79)$$

29. Heat capacity III

Determine the heat capacity c_V of fermionic gas and prove the validity of classical limit for c_V/N .

Solution: The energy of classical fermionic gas is

$$E = \frac{3}{2} \frac{gV}{\lambda_T^3} k_B T F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right), \quad (80)$$

and number of particles is

$$N = \frac{gV}{\lambda_T^3} F_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right), \quad (81)$$

where

$$\lambda_T = \sqrt{\frac{2\pi\hbar^2}{mk_B T}}. \quad (82)$$

From this the energy could be written as

$$E = \frac{3}{2} N k_B T \frac{F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right)}{F_{\frac{3}{2}} \left(\frac{\mu}{k_B T} \right)}.$$

We denote

$$F_n \left(\frac{\mu}{k_B T} \right) = F_n.$$

Heat capacity is

$$c_V = \left(\frac{\partial E}{\partial T} \right)_{N,V} = \frac{3}{2} N k_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} + \frac{3}{2} N k_B T \frac{\frac{\partial F_{\frac{5}{2}}}{\partial T} F_{\frac{3}{2}} - F_{\frac{5}{2}} \frac{\partial F_{\frac{3}{2}}}{\partial T}}{\left(F_{\frac{3}{2}} \right)^2},$$

where the differentiation of F_n with respect to T is

$$\left(\frac{\partial F_n}{\partial T} \right)_{V,N} = \frac{\partial}{\partial T} \left(\frac{\mu}{k_B T} \right) F_n' = \left[\left(\frac{\partial \mu}{\partial T} \right)_{V,N} \frac{1}{k_B T} - \frac{\mu}{k_B T^2} \right] F_{n-1}.$$

Substituting into the formula for c_V

$$c_V = \frac{3}{2} N k_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} + \frac{3}{2} N \left[\left(\frac{\partial \mu}{\partial T} \right)_{V,N} - \frac{\mu}{T} \right] \left[1 - \frac{F_{\frac{5}{2}} F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}} \right)^2} \right].$$

The number of particles does not depend on temperature,

$$\left(\frac{\partial N}{\partial T} \right)_{V,N} = \frac{3}{2} F_{\frac{3}{2}} + \left[\frac{1}{k_B} \left(\frac{\partial \mu}{\partial T} \right)_{V,N} - \frac{\mu}{k_B T} \right] F_{\frac{1}{2}} = 0.$$

From this the temperature derivative of chemical potential is

$$\left(\frac{\partial \mu}{\partial T} \right)_{V,N} = \frac{\mu}{T} - \frac{3}{2} k_B \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}}. \quad (83)$$

After substitution

$$c_V = \frac{3}{2} N \left[1 - \frac{F_{\frac{5}{2}} F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}} \right)^2} \right] \left(-\frac{3}{2} k_B \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} \right) + \frac{3}{2} N k_B \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} = \frac{3}{2} N k_B \left\{ \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} - \frac{3}{2} N \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} \left[1 - \frac{F_{\frac{5}{2}} F_{\frac{1}{2}}}{\left(F_{\frac{3}{2}} \right)^2} \right] \right\}.$$

In a classical case we can approximate F_n by

$$F_n \approx \exp\left(\frac{\mu}{k_B T}\right), \quad (84)$$

then all ratios of F functions are equal to one and we derive the classical limit

$$c_V \approx \frac{3}{2} N k_B. \quad (85)$$

Another approach: We shall calculate $c_{V,N}$ first. In

$$c_{V,\mu} = T \left(\frac{\partial S}{\partial T} \right)_{V,\mu},$$

we express entropy as $S = S(N(\mu, V, T), V, T)$, therefore

$$T \left(\frac{\partial S}{\partial T} \right)_{V,\mu} = T \left(\frac{\partial S(N(\mu, V, T), V, T)}{\partial T} \right)_{V,\mu} = T \left(\frac{\partial S}{\partial N} \right)_{V,\mu} \left(\frac{\partial N}{\partial T} \right)_{V,\mu} + T \left(\frac{\partial S}{\partial T} \right)_{V,N}.$$

We shall use Maxwell's relation that follows from the Helmholtz free energy

$$dF = -SdT - pdV + \mu dN,$$

from which

$$\left(\frac{\partial S}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{N,V}.$$

Because the number of particles is constant

$$dN = \left(\frac{\partial N}{\partial \mu} \right)_{T,V} + \left(\frac{\partial N}{\partial T} \right)_{\mu,V} = 0,$$

we derive

$$\left(\frac{\partial \mu}{\partial T} \right)_{N,V} = - \left(\frac{\partial \mu}{\partial N} \right)_{T,V} \left(\frac{\partial N}{\partial T} \right)_{\mu,V}.$$

We substitute partial derivatives into $c_{V,\mu}$

$$c_{V,\mu} = T \left(\frac{\partial N}{\partial \mu} \right)_{T,V}^{-1} \left(\frac{\partial N}{\partial T} \right)_{\mu,V}^2 + T \underbrace{\left(\frac{\partial S}{\partial T} \right)_{V,N}}_{c_{V,N}}.$$

This gives for the heat capacity

$$c_{V,N} = c_{V,\mu} - T \frac{\left(\frac{\partial N}{\partial T} \right)_{\mu,V}^2}{\left(\frac{\partial N}{\partial \mu} \right)_{T,V}}. \quad (86)$$

Now we can substitute results from the statistical physics for fermionic gas. Landau potential is

$$\Omega = - \frac{gV}{\lambda_T^3} k_B T F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right). \quad (87)$$

The entropy is from (87)

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V,\mu} = \frac{-gV k_B}{\lambda_T^3} \left(\frac{5}{2} F_{\frac{5}{2}} - \frac{\mu}{k_B T} F_{\frac{3}{2}} \right).$$

From this the heat capacity $c_{V,\mu}$ is

$$c_{V,\mu} = T \left(\frac{\partial S}{\partial T} \right)_{V,\mu} = - \frac{gV k_B}{\lambda_T^3} \left(\frac{15}{4} F_{\frac{5}{2}} - 3 \frac{\mu}{k_B T} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^2} F_{\frac{1}{2}} \right).$$

We calculate derivative from (81)

$$\left(\frac{\partial N}{\partial T}\right)_{V,\mu} = \frac{gV}{\lambda_T^3} \left(\frac{3}{2T} F_{\frac{3}{2}} - \frac{\mu}{k_B T^2} F_{\frac{1}{2}} \right).$$

Finally,

$$\left(\frac{\partial N}{\partial \mu}\right)_{V,T} = \frac{gV}{\lambda_T^3} \frac{1}{k_B T} F_{\frac{1}{2}}.$$

We substitute this into (86)

$$c_{V,N} = \frac{gV k_B}{\lambda_T^3} \left[\left(\frac{15}{4} F_{\frac{5}{2}} - 3 \frac{\mu}{k_B T} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^2} F_{\frac{1}{2}} \right) - T^2 \left(\frac{9}{4T^2} \frac{F_{\frac{3}{2}}^2}{F_{\frac{1}{2}}} - \frac{3\mu}{k_B T^3} F_{\frac{3}{2}} + \frac{\mu^2}{k_B^2 T^4} F_{\frac{1}{2}} \right) \right].$$

We divide by $k_B N$ and substitute (81)

$$\frac{c_{V,N}}{k_B N} = \frac{15}{4} \frac{F_{\frac{5}{2}}}{F_{\frac{3}{2}}} - 3 \frac{\mu}{k_B T} + \frac{\mu^2}{k_B^2 T^2} \frac{F_{\frac{1}{2}}}{F_{\frac{3}{2}}} - \frac{9}{4} \frac{F_{\frac{3}{2}}}{F_{\frac{1}{2}}} + \frac{3\mu}{k_B T} - \frac{\mu^2}{k_B^2 T^2} \frac{F_{\frac{1}{2}}}{F_{\frac{3}{2}}}.$$

In a classical case one can approximate F_n by (84), therefore

$$\frac{c_{V,N}}{k_B N} = \frac{15}{4} - 3 \frac{\mu}{k_B T} + \frac{\mu^2}{k_B^2 T^2} - \frac{9}{4} + 3 \frac{\mu}{k_B T} - \frac{\mu^2}{k_B^2 T^2}.$$

All terms except 3/2 cancel out and we finally arrive at

$$\frac{c_{V,N}}{k_B N} = \frac{3}{2}, \quad (88)$$

what is the same result as in previous case.

30. Classical limit

Prove the validity of the classical limit

$$E = \frac{3}{2} N k_B T,$$

Solution: We use (80) and (81) once again. We approximate F_n as (84). Then the energy is

$$E = \frac{3}{2} \frac{gV}{\lambda_T^3} k_B T F_{\frac{5}{2}} \left(\frac{\mu}{k_B T} \right) \approx \frac{3}{2} \frac{gV}{\lambda_T^3} k_B T F_{\frac{5}{2}} \exp \left(\frac{\mu}{k_B T} \right),$$

and analogously for the number of particles

$$N \approx \frac{gV}{\lambda_T^3} \exp \left(\frac{\mu}{k_B T} \right).$$

This gives for $E \cdot N/N$,

$$E = \frac{3}{2} k_B T N. \quad (89)$$

31. Relativistic fully degenerate fermionic gas

Calculate:

- density of states,
- Fermi energy, Fermi momentum,
- number of particles,
- energy,
- Landau potential,
- equation of state

for relativistic (in case 31f ultra-relativistic) fully degenerated fermionic gas. Evaluate number of particles, energy, and the Landau potential in terms of Fermi energy.

Solution: The assumption of fully degenerated fermionic gas means for temperature $T \rightarrow 0$. In this case

$$\lim_{T \rightarrow 0^+} \frac{1}{\exp\left(\frac{E-\mu}{k_B T}\right) + 1} = \begin{cases} 1 & E < \mu \\ \frac{1}{2} & E = \mu \\ 0 & E > \mu. \end{cases}$$

(a) Density of states can be derived from

$$n(\mathbf{p})d\mathbf{p} = \frac{V}{(2\pi\hbar)^3} g d\mathbf{p},$$

in this case

$$n(p)dp = \frac{V}{\pi^2\hbar^3} p^2 dp.$$

(b) Because fully degenerated fermionic gas populates levels up to state with Fermi energy or momentum p_F , we obtain after integration of density of states

$$N = \frac{V}{\pi^2\hbar^3} \frac{p_F^3}{3}.$$

From this the Fermi momentum follows as

$$p_F = (3\pi^2)^{\frac{1}{3}} \left(\frac{N}{V}\right)^{\frac{1}{3}} \hbar.$$

The Fermi energy is

$$\varepsilon_F = \sqrt{p_F^2 c^2 + m_0^2 c^4}.$$

(c) We will express the density of states in terms of energy,

$$n(\varepsilon)d\varepsilon = \frac{V}{\pi^2\hbar^3} \frac{\sqrt{\varepsilon^2 - m^2 c^4}}{c^3} \varepsilon d\varepsilon.$$

After substitution $\varepsilon \rightarrow mc^2 t$ we obtain

$$n(t)dt = \frac{V (mc^2)^3}{\pi^2\hbar^3 c^3} \sqrt{t^2 - 1} dt.$$

The number of particles can be obtained by integration with respect to t from 1 to ε_F/mc^2 (which corresponds to from mc^2 to ε_F before substitution) and by multiplying by the above term,

$$N = \frac{V (mc^2)^3}{\pi^2\hbar^3 c^3} \int_1^{\frac{\varepsilon_F}{mc^2}} dt \sqrt{t^2 - 1},$$

what gives

$$N = \frac{V}{3\pi^2\hbar^3 c^3} (\varepsilon_F^2 - m^2 c^4)^{\frac{3}{2}}.$$

(d) The energy is given by

$$U = \int_{mc^2}^{\infty} dNE = \frac{V}{\pi^2\hbar^3} \int_{mc^2}^{\varepsilon_F} d\varepsilon \varepsilon^2 \frac{\sqrt{\varepsilon^2 - m^2 c^4}}{c^3} = \frac{V (mc^2)^4}{\pi^2\hbar^3 c^3} \int_1^{\frac{\varepsilon_F}{mc^2}} dt (t^2 - 1)^{\frac{1}{2}} t^2.$$

The integral can be evaluated using substitution $t = \cosh(x)$, which, after some manipulation gives

$$\frac{V (mc^2)^4}{\pi^2 \hbar^3 c^3} \int_1^{\frac{\epsilon_F}{mc^2}} dt (t^2 - 1)^{\frac{1}{2}} t^2 = \frac{V (mc^2)^4}{8\pi^2 \hbar^3 c^3} \left[t (2t^2 - 1) \sqrt{t^2 - 1} - \ln \left(t + \sqrt{t^2 - 1} \right) \right]_{t=1}^{t=\frac{\epsilon_F}{mc^2}}.$$

The result can be cast in the form of

$$U = \frac{V (mc^2)^4}{8\pi^2 \hbar^3 c^3} \left[\frac{\epsilon_F}{mc^2} \left(2 \frac{\epsilon_F^2}{(mc^2)^2} - 1 \right) \sqrt{\frac{\epsilon_F^2}{(mc^2)^2} - 1} - \ln \left(\frac{\epsilon_F}{mc^2} + \sqrt{\frac{\epsilon_F^2}{(mc^2)^2} - 1} \right) \right].$$

- (e) We can proceed analogously as in previous case to determine the Landau potential Ω . We will evaluate

$$\Omega = -\frac{V (mc^2)^4}{3\pi^2 \hbar^3 c^3} \int_1^{\frac{\epsilon_F}{mc^2}} dt (t^2 - 1)^{\frac{3}{2}}.$$

We integrate as in previous problem obtaining

$$\Omega = -\frac{V (mc^2)^4}{8\pi^2 \hbar^3 c^3} \left[\frac{\epsilon_F}{mc^2} \left(\frac{2}{3} \frac{\epsilon_F^2}{(mc^2)^2} - 1 \right) \sqrt{\frac{\epsilon_F^2}{(mc^2)^2} - 1} + \ln \left(\frac{\epsilon_F}{mc^2} + \sqrt{\frac{\epsilon_F^2}{(mc^2)^2} - 1} \right) \right].$$

- (f) We shall rewrite the formulae obtained above in the case of ultra-relativistic gas. Number of particles is

$$N = \frac{V (mc^2)^3}{3\pi^2 \hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^3,$$

Landau potential is

$$\Omega = -\frac{V (mc^2)^4}{12\pi^2 \hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^4,$$

and energy

$$U = \frac{V (mc^2)^4}{4\pi^2 \hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^4.$$

From the identity $\Omega = -PV$ follows

$$P = \frac{(mc^2)^4}{12\pi^2 \hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^4,$$

or, in terms of number of particles,

$$P = \frac{3^{\frac{1}{3}}}{4} \left(\frac{N}{V} \right)^{\frac{4}{3}} \pi^{\frac{2}{3}} \hbar.$$

This gives $P \propto \rho^{\frac{4}{3}}$.

32. Fluctuations

Determine fluctuation of number of particles in the case of grandcanonical distribution $(\Delta N^2 = \langle N^2 \rangle - \langle N \rangle^2)$. Evaluate in the case of nonrelativistic bosonic and fermionic gas.

Solution: We shall start manipulating the formula for $\langle N \rangle$

$$\langle N \rangle = \sum_{n,N} N w_{n,N} = \sum_{n,N} N \frac{\exp\left(-\frac{E_{n,N} - \mu N}{k_B T}\right)}{\Xi}$$

Now we differentiate the exponential with respect to the chemical potential

$$\frac{\partial \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right)}{\partial \mu} = \frac{N}{k_B T} \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right).$$

Then

$$\sum_{n,N} N \frac{\exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right)}{\Xi} = \frac{k_B T}{\Xi} \sum_{n,N} \frac{\partial}{\partial \mu} \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right),$$

the differentiation can be taken out of the sum,

$$\frac{k_B T}{\Xi} \frac{\partial}{\partial \mu} \sum_{n,N} \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right) = \frac{k_B T}{\Xi} \frac{\partial \Xi}{\partial \mu}.$$

We proceed analogously to evaluate $\langle N^2 \rangle$

$$\langle N^2 \rangle = \sum_{n,N} N^2 w_{n,N} = \sum_{n,N} N^2 \frac{\exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right)}{\Xi}.$$

Then

$$\sum_{n,N} N^2 \frac{\exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right)}{\Xi} = \frac{k_B T}{\Xi} \sum_{n,N} N \frac{\partial}{\partial \mu} \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right),$$

the differentiation can be taken out of the sum and we can expand Ξ

$$\frac{k_B T}{\Xi} \frac{\partial}{\partial \mu} \sum_{n,N} N \exp\left(-\frac{E_{n,N}-\mu N}{k_B T}\right) \frac{\Xi}{\Xi} = \frac{k_B T}{\Xi} \frac{\partial}{\partial \mu} (\langle N \rangle \Xi) = \frac{k_B T}{\Xi} \frac{\partial \langle N \rangle}{\partial \mu} \Xi + \frac{k_B T}{\Xi} \langle N \rangle \frac{\partial \Xi}{\partial \mu}.$$

Because we have already determined $\langle N \rangle$, we can rewrite

$$k_B T \frac{\partial \langle N \rangle}{\partial \mu} + \frac{k_B T}{\Xi} \langle N \rangle \frac{\partial \Xi}{\partial \mu} = k_B T \frac{\partial \langle N \rangle}{\partial \mu} + \langle N \rangle^2.$$

From this follows

$$\langle N^2 \rangle - \langle N \rangle^2 = k_B T \frac{\partial \langle N \rangle}{\partial \mu}.$$

We apply this to the case of bosonic gas; the number of particles is

$$\langle N \rangle = \frac{gV}{\lambda_T^3} B_{\frac{3}{2}}\left(\frac{\mu}{k_B T}\right),$$

then

$$(\Delta N)^2 = \frac{gV}{\lambda_T^3} B_{\frac{1}{2}}\left(\frac{\mu}{k_B T}\right).$$

This can be written as

$$\frac{(\Delta N)^2}{N^2} = \frac{1}{N} \frac{B_{\frac{1}{2}}\left(\frac{\mu}{k_B T}\right)}{B_{\frac{3}{2}}\left(\frac{\mu}{k_B T}\right)}.$$

A similar equation can be written also for fermionic gas except the fact that we shall replace B by F . Therefore, the resulting formula is

$$\frac{(\Delta N)^2}{N^2} = \frac{1}{N} \frac{F_{\frac{1}{2}}\left(\frac{\mu}{k_B T}\right)}{F_{\frac{3}{2}}\left(\frac{\mu}{k_B T}\right)}.$$

33. Virial theorem

Derive the virial theorem from the classical mechanics.

Solution: The virial theorem can be derived for the movement of particles in central force field. Let us study

$$G = \sum_i \mathbf{p}_i \cdot \mathbf{r}_i,$$

where we sum over all particles of the system. Total derivative is

$$\frac{dG}{dt} = \sum_i \dot{\mathbf{r}}_i \cdot \mathbf{p}_i + \sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i. \quad (90)$$

We can manipulate the first term on the right hand side in the following way

$$\sum_i \dot{\mathbf{r}}_i \cdot \mathbf{p}_i = \sum_i m_i \dot{\mathbf{r}}_i \cdot \dot{\mathbf{r}}_i = \sum_i m_i v_i^2 = 2T.$$

The second term can be rewritten as

$$\sum_i \dot{\mathbf{p}}_i \cdot \mathbf{r}_i = \sum_i \mathbf{F}_i \cdot \mathbf{r}_i.$$

Equation (90) then takes the form of

$$\frac{d}{dt} \sum_i \mathbf{p}_i \cdot \mathbf{r}_i = 2T + \sum_i \mathbf{F}_i \cdot \mathbf{r}_i. \quad (91)$$

Taking the mean value by integrating from 0 to τ and divide by τ

$$\frac{1}{\tau} \int_0^\tau dt \frac{dG}{dt} \equiv \frac{d\langle G \rangle}{dt} = 2\langle T \rangle + \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle.$$

Left hand side can be rewritten as

$$\frac{1}{\tau} [G(\tau) - G(0)] = 2\langle T \rangle + \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle. \quad (92)$$

Left hand side tends to zero for periodic motion or for spatially confined system (in this case also G is bounded from above), therefore for large τ we obtain

$$\langle T \rangle = -\frac{1}{2} \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle. \quad (93)$$

We can rewrite the right hand term. The force acting on a given particle is given by the mutual interaction of particles and by pressure,

$$-\frac{1}{2} \left\langle \sum_i \mathbf{F}_i \cdot \mathbf{r}_i \right\rangle = -\frac{1}{2} \left(- \left\langle \sum_i \mathbf{r}_i \cdot \nabla \Pi \right\rangle - P \left\langle \oint_S d\mathbf{A} \cdot \mathbf{r} \right\rangle \right).$$

The diversion: Euler's homogeneous function theorem

A function f of N variable is homogeneous of degree k if

$$f(tx_1, tx_2, \dots, tx_N) = t^k f(x_1, x_2, \dots, x_N).$$

The Euler's theorem states that the sum of product of the partial derivatives of homogeneous function and the variables is equal to the given function multiplied by the degree,

$$\sum_{n=1}^N x_n \frac{\partial f(x_1, x_2, \dots, x_N)}{\partial x_n} = k f(x_1, x_2, \dots, x_N). \quad (94)$$

End of the diversion.

Let us assume that the potential energy Π is a homogeneous function of coordinates of degree n . In this case

$$-\frac{1}{2} \left(- \left\langle \sum_i \mathbf{r}_i \cdot \nabla \Pi \right\rangle - P \left\langle \oint_S dA \mathbf{n} \cdot \mathbf{r} \right\rangle \right) = \frac{1}{2} (n \langle \Pi \rangle - 3PV).$$

We substitute this to the right hand side of (93), what gives the virial theorem in the form of

$$2 \langle T \rangle - n \langle \Pi \rangle - 3PV = 0. \quad (95)$$

34. Application of the virial theorem

Determine the equation of state using the virial theorem.

Solution: The mean kinetic energy is from the equipartition theorem equal to

$$\langle T \rangle = \frac{3}{2} k_B T.$$

We shall evaluate the right hand side term of (93). From the definition of the perfect gas follows that the mutual interaction of particle is rare in comparison with interaction with walls of the vessel. This is why we can replace summation with integral over the gas surface. The differential of the force is

$$d\mathbf{F}_i = -P \mathbf{n} dA,$$

or

$$\frac{1}{2} \sum_i \mathbf{F}_i \cdot \mathbf{r}_i = -\frac{P}{2} \int dA \mathbf{n} \cdot \mathbf{r},$$

where P is a pressure due to the particle flux, \mathbf{n} is vector of the normal and dA is surface element. This can be rewritten using the divergence theorem as

$$\int dA \mathbf{n} \cdot \mathbf{r} = \int dV \nabla \cdot \mathbf{r} = 3V.$$

We substitute the expression for kinetic energy and potential into (93)

$$\frac{3}{2} N k_B T = \frac{3}{2} PV, \quad (96)$$

from which follows

$$N k_B T = PV, \quad (97)$$

This is the state equation. The same result can be derived from (95).

35. Application of the virial theorem II

Studied system contains N weakly interacting particle and its temperature is high enough to use classical mechanics. Each particle has mass of m and oscillates around the equilibrium position. Determine the heat capacity for the following cases:

- The return force is proportional to deviation x from the equilibrium position.
- The return force is proportional to x^3 .

Calculate without evaluating the corresponding integrals.

Solution: We will use (95) without surface forces, that is with $P = 0$.

- Because the force is proportional to r , the potential is proportional to $\Pi \propto r^2$. Consequently, the potential is a homogeneous function of second order. Therefore, the virial theorem is

$$2 \langle T \rangle - 2 \langle \Pi \rangle = 0,$$

and

$$\langle T \rangle = \langle \Pi \rangle.$$

We insert this result into the law of conservation of energy $U = \langle T \rangle + \langle \Pi \rangle$

$$U = 2 \langle T \rangle = 3Nk_B T,$$

from which

$$U = 3Nk_B T.$$

(b) In this case $\Pi \propto r^4$, therefore

$$2 \langle T \rangle - 4 \langle \Pi \rangle = 0,$$

from which

$$U = \frac{9}{4} Nk_B T.$$

36. Lattice vibrations

Determine the heat capacity due to the lattice vibrations for

(a) Debye model,

(b) Einstein model

of the lattice.

Solution: The energy of vibrations is

$$u = \frac{1}{V} \frac{\sum_i E_i \exp(-\beta E_i)}{\sum_i \exp(-\beta E_i)}. \quad (98)$$

Let us assume harmonic lattice composed of N ions, which can be regarded as a system of $3N$ oscillators. The contribution of ordinary mode with frequency $\omega_s(\mathbf{k})$ to the energy is quantized,

$$E_n = \left(n_{\mathbf{k}s} + \frac{1}{2} \right) \hbar \omega_s(\mathbf{k}), \quad (99)$$

where $n_{\mathbf{k}s} \in 0, 1, 2, \dots$. The total energy is given by a sum of energies of individual modes,

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

Let us define f

$$f = \frac{1}{V} \ln \left(\sum_i \exp(-\beta E_i) \right).$$

We can easily prove that

$$u = -\frac{\partial f}{\partial \beta}.$$

Substituting for E_n , we obtain

$$\begin{aligned} f &= \frac{1}{V} \ln \left\{ \sum_{n_{\mathbf{k}s}} \exp \left[-\beta \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) \left(n_{\mathbf{k}s} + \frac{1}{2} \right) \right] \right\} = \frac{1}{V} \ln \left\{ \prod_{\mathbf{k}s} \sum_{n_{\mathbf{k}s}} \exp \left[-\beta \hbar \omega_s(\mathbf{k}) \left(n_{\mathbf{k}s} + \frac{1}{2} \right) \right] \right\} \\ &= \frac{1}{V} \ln \left\{ \prod_{\mathbf{k}s} \frac{\exp \left[-\frac{\beta \hbar \omega_s(\mathbf{k})}{2} \right]}{1 - \exp[-\beta \hbar \omega_s(\mathbf{k})]} \right\} = \frac{1}{V} \sum_{\mathbf{k}s} \left\{ \left[-\frac{\beta \hbar \omega_s(\mathbf{k})}{2} \right] - \ln [1 - \exp(-\beta \hbar \omega_s(\mathbf{k}))] \right\}. \end{aligned}$$

The energy is given by the expression above

$$u = -\frac{1}{V} \sum_{\mathbf{k}s} \left[-\frac{\hbar \omega_s(\mathbf{k})}{2} - \frac{\hbar \omega_s(\mathbf{k}) \exp(-\beta \hbar \omega_s(\mathbf{k}))}{1 - \exp(-\beta \hbar \omega_s(\mathbf{k}))} \right] = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) \left[\frac{1}{2} + \frac{1}{\exp(\beta \hbar \omega_s(\mathbf{k})) - 1} \right].$$

This can be rewritten as

$$u = \frac{1}{V} \sum_{\mathbf{k}s} \hbar \omega_s(\mathbf{k}) \left(n_{\mathbf{k}s} + \frac{1}{2} \right), \quad (100)$$

where

$$n_{\mathbf{k}s} = \frac{1}{\exp(\beta\hbar\omega_s(\mathbf{k})) - 1}.$$

From the comparison with (99) follows that $n_{\mathbf{k}s}$ excitational number of ordinary mode $\mathbf{k}s$ at temperature T . The classical energy of lattice is

$$u = u^{\text{eq}} + \frac{1}{V} \sum_{\mathbf{k}s} \frac{1}{2} \hbar\omega_s(\mathbf{k}) + \frac{1}{V} \sum_{\mathbf{k}s} \frac{\hbar\omega_s(\mathbf{k})}{\exp(\beta\hbar\omega_s(\mathbf{k})) - 1}.$$

The specific heat capacity is then

$$c_V = \frac{1}{V} \sum_{\mathbf{k}s} \frac{\partial}{\partial T} \frac{\hbar\omega_s(\mathbf{k})}{\exp(\beta\hbar\omega_s(\mathbf{k})) - 1}. \quad (101)$$

(a) Within Debye model we assume

$$\omega_s(\mathbf{k}) = c_s(\mathbf{k}^0)k.$$

Sum in (101) can be replaced by integral (across the first Brillouin zone)

$$c_V = \frac{\partial}{\partial T} \sum_s \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hbar\omega_s(\mathbf{k})}{\exp(\beta\hbar\omega_s(\mathbf{k})) - 1}.$$

This integral can be replaced by an integral across the sphere with radius k_D chosen in such a way that it contains exactly N allowed vectors, where N is the number of ions in the lattice. Volume of k -space corresponding to one wavevector is $(2\pi)^3/V$, what requires volume of k -space to fill the volume $(2\pi)^3 N/V$ to fill $4\pi k_D^3/3$, so k_D is

$$n = \frac{k_D^3}{6\pi^2}.$$

We substitute

$$c_V = \sum_s \frac{\partial}{\partial T} \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{\hbar c_s k}{\exp(\beta\hbar c_s k) - 1} = \sum_s \frac{\partial}{\partial T} \int_0^{2\pi} d\Omega \int_0^{k_D} \frac{dk}{(2\pi)^3} \frac{\hbar c_s k^3}{\exp(\beta\hbar c_s k) - 1}$$

and perform a substitution

$$x = \frac{\hbar c_s k}{k_B T},$$

obtaining

$$\sum_s \frac{\partial}{\partial T} \int_0^{2\pi} d\Omega \int_0^{k_D} \frac{dk}{(2\pi)^3} \frac{\hbar c_s k^3}{\exp(\beta\hbar c_s k) - 1} = \frac{1}{8\pi^3} \left(\frac{k_B T}{\hbar} \right)^3 \sum_s \int d\Omega \frac{1}{c_s^3(\Omega)} \int_0^{\frac{\hbar c_s k_D}{k_B T}} dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2}.$$

We denote

$$\frac{1}{c^3} = \frac{1}{4\pi} \sum_s \int d\Omega \frac{1}{c_s^3} \quad (102)$$

and for k_D holds

$$\omega_D = k_D c,$$

for Debye temperature Θ_D

$$k_B \Theta_D = \hbar \omega_D = \hbar c k_D.$$

After substitution,

$$c_V = 9nk_B \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\frac{\Theta_D}{T}} dx \frac{x^4 \exp(x)}{(\exp(x) - 1)^2}. \quad (103)$$

The derived equation depends just on Θ_D . Debye temperature can be derived using low-temperature limit. At low temperatures, the heat capacity is

$$c_V = \frac{2\pi^2}{5} k_B \left(\frac{k_B T}{\hbar c} \right)^3,$$

where we substitute equation for Debye temperature,

$$k_B \Theta_D = \hbar c k_D = \hbar c \sqrt{6\pi^2 n},$$

after the substitution of $\hbar c/k_B$

$$c_V = \frac{12\pi^4}{5} n k_B \left(\frac{T}{\Theta_D} \right)^3.$$

(b) Einstein model is more suitable for optical branch and assumes that

$$\omega_s(\mathbf{k}) = \omega_E.$$

The heat capacity can be derived from (101), where we substitute the dispersion relation

$$c_V = \frac{\partial}{\partial \beta} \frac{1}{V} \hbar \omega_E N \frac{1}{\exp\left(\frac{\hbar \omega_E}{k_B T}\right) - 1} = n k_B \left(\frac{\hbar \omega_E}{k_B T} \right)^2 \frac{\exp\left(\frac{\hbar \omega_E}{k_B T}\right)}{\left[\exp\left(\frac{\hbar \omega_E}{k_B T}\right) - 1 \right]^2}.$$

37. Free particle I

Determine the mean coordinate in the case of 1D movement of free particle confined in the region $x \in [0, L]$, the density matrix operator is

$$\rho(x, x', \beta) = \frac{1}{L} \exp\left(-\frac{\pi(x-x')^2}{\lambda_T^2}\right). \quad (104)$$

Solution: The mean value can be determined from

$$\langle \hat{x} \rangle = \text{Tr}(\hat{\rho} \hat{x}).$$

The trace is

$$\text{Tr}(\hat{\rho} \hat{x}) = \int_0^L dx' \langle x' | \hat{\rho} \hat{x} | x' \rangle = \int_0^L dx' \int_{-\infty}^{\infty} dx \langle x' | \hat{\rho} | x \rangle \langle x | \hat{x} | x' \rangle,$$

The first matrix element correspond to the density matrix, and the second element is

$$\langle x | \hat{x} | x' \rangle = x \langle x | x' \rangle = x \delta(x - x').$$

We obtain

$$\langle \hat{x} \rangle = \int_0^L dx' \int_{-\infty}^{\infty} dx \frac{1}{L} \exp\left(-\frac{\pi(x-x')^2}{\lambda_T^2}\right) x \delta(x - x') = \frac{1}{L} \int_0^L dx' x' = \frac{L}{2}.$$

38. Free particle II

Determine matrix elements of the density operator of free particle in the momentum representation.

Solution: Density operator is

$$\hat{\rho} = \frac{\exp(-\beta \hat{H})}{\text{Tr}(-\beta \hat{H})}. \quad (105)$$

We shall start with the partition function. Free particle Hamiltonian is $\hat{H} = \hat{\mathbf{p}}^2/(2m)$:

$$Z(T, V, 1) = \text{Tr} \exp(-\beta \hat{H}) = \sum_{\mathbf{p}} \langle \phi_{\mathbf{p}} | \exp(-\beta \hat{H}) | \phi_{\mathbf{p}} \rangle = \sum_{\mathbf{p}} \exp\left(-\frac{\beta \mathbf{p}^2}{2m}\right).$$

We can approximate the sum by an integral

$$Z(T, V, 1) = \frac{V}{(2\pi)^3} \int d\mathbf{p} \exp\left(-\frac{\beta \mathbf{p}^2}{2m}\right) = \frac{V}{(2\pi)^3} \left(\frac{2m\pi}{\beta \hbar^2}\right)^{\frac{3}{2}} = \frac{V}{\lambda^3}.$$

From this the matrix elements of the density operator are

$$\langle \phi_{\mathbf{p}'} | \hat{\rho} | \phi_{\mathbf{p}} \rangle = \frac{\lambda^3}{V} \exp\left(\frac{-\beta \mathbf{p}^2}{2m}\right) \delta_{\mathbf{p}\mathbf{p}'}$$

39. Free particle III

Determine the mean value of the Hamiltonian of a free particle using a direct calculation in the momentum representation from

$$\langle \hat{\mathcal{H}} \rangle = \text{Tr}(\hat{\rho} \hat{\mathcal{H}}). \quad (106)$$

Solution: We will write the trace as

$$\text{Tr}(\hat{\rho} \hat{\mathcal{H}}) = \sum_{\mathbf{p}} \langle \mathbf{p} | \hat{\rho} \hat{\mathcal{H}} | \mathbf{p} \rangle = \sum_{\mathbf{p}, \mathbf{p}'} \langle \mathbf{p} | \hat{\rho} | \mathbf{p}' \rangle \langle \mathbf{p} | \hat{\mathcal{H}} | \mathbf{p} \rangle = \sum_{\mathbf{p}, \mathbf{p}'} \left[\frac{\lambda^3}{V} \exp\left(\frac{-\beta \mathbf{p}^2}{2m}\right) \delta_{\mathbf{p}\mathbf{p}'} \right] \left(\frac{\mathbf{p}^2}{2m} \delta_{\mathbf{p}\mathbf{p}'} \right).$$

We approximate the summation by an integral and rewrite the integral in the spherical coordinates

$$\frac{1}{\hbar^2} \frac{\hbar^2}{2m} \frac{\lambda^3}{V} \frac{V}{(2\pi)^3} \int d\mathbf{p} \mathbf{p}^2 \exp\left(\frac{-\beta \mathbf{p}^2}{2m}\right) = \frac{1}{2m} \lambda^2 \frac{2}{(2\pi)^2} \int_0^\infty dk k^4 \exp\left(\frac{-\beta p^2}{2m}\right).$$

After the substitution we have

$$\langle \hat{H} \rangle = \frac{\hbar^2 \lambda^3}{m} \frac{1}{(2\pi)^2} \frac{1}{2} \left(\frac{2m}{\beta \hbar^2}\right)^{\frac{5}{2}} \int_0^\infty dx x^{\frac{3}{2}} \exp(-x).$$

From this follows

$$\langle \hat{H} \rangle = \frac{3}{2} k_B T.$$

40. Free particle IV

Calculate the mean value of the Hamiltonian of a free particle from the partition function (in a framework of quantum physics)

$$Z = \frac{V}{\lambda_1^3}. \quad (107)$$

Solution: The mean value of the Hamiltonian is

$$\langle H \rangle = \frac{\text{Tr}[\exp(-\beta \hat{H}) \hat{H}]}{\text{Tr}[\exp(-\beta \hat{H})]} = -\frac{\partial}{\partial \beta} \ln[\text{Tr}(\exp(-\beta \hat{H}))] = -\frac{\partial}{\partial \beta} \ln(Z),$$

now we can substitute

$$-\frac{\partial}{\partial \beta} \ln(Z) = 3 \frac{\partial}{\partial \beta} \lambda_1^{-3} = 3 \frac{1}{2} \frac{\partial}{\partial \beta} (\ln \beta) = \frac{3}{2} \frac{1}{\beta} = \frac{3}{2} k_B T.$$

41. Two fermions

Calculate the matrix elements of density operator and the partition function for two noninteracting fermions.

Solution: The wave function should be antisymmetric with respect to interchange of particles, therefore

$$|p_1, p_2\rangle = \frac{1}{\sqrt{2}} (|p_1, p_2\rangle - |p_2, p_1\rangle).$$

The matrix elements of density operator are according to (105)

$$\begin{aligned}
\langle p'_1, p'_2 | \hat{\rho} | p_1, p_2 \rangle &= \frac{1}{2Z} (\langle p'_1, p'_2 | - \langle p'_2, p'_1 |) \exp\left(-\frac{\hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2}{2mk_B T}\right) (|p_1, p_2\rangle - |p_2, p_1\rangle) \\
&= \frac{1}{2Z} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) (\langle p'_1, p'_2 | p_1, p_2\rangle - \langle p'_1, p'_2 | p_2, p_1\rangle - \langle p'_2, p'_1 | p_1, p_2\rangle + \langle p'_2, p'_1 | p_2, p_1\rangle) \\
&\quad \frac{1}{2Z} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) [\delta(\mathbf{p}'_1 - \mathbf{p}_1) \delta(\mathbf{p}'_2 - \mathbf{p}_2) - \delta(\mathbf{p}'_1 - \mathbf{p}_2) \delta(\mathbf{p}'_2 - \mathbf{p}_1) - \\
&\quad \delta(\mathbf{p}'_2 - \mathbf{p}_1) \delta(\mathbf{p}'_1 - \mathbf{p}_2) + \delta(\mathbf{p}'_2 - \mathbf{p}_2) \delta(\mathbf{p}'_1 - \mathbf{p}_1)] \\
&= \frac{1}{Z} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) [\delta(\mathbf{p}'_1 - \mathbf{p}_1) \delta(\mathbf{p}'_2 - \mathbf{p}_2) - \delta(\mathbf{p}'_1 - \mathbf{p}_2) \delta(\mathbf{p}'_2 - \mathbf{p}_1)].
\end{aligned}$$

The partition function is

$$\begin{aligned}
Z = \text{Tr}[\exp(-\beta\hat{H})] &= \frac{1}{2} \sum_{\mathbf{p}_1, \mathbf{p}_2} (\langle p_1, p_2 | - \langle p_2, p_1 |) \exp\left(-\frac{\hat{\mathbf{p}}_1^2 + \hat{\mathbf{p}}_2^2}{2mk_B T}\right) (|p_1, p_2\rangle - |p_2, p_1\rangle) \\
&= \frac{1}{2} \sum_{\mathbf{p}_1, \mathbf{p}_2} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) (2 - 2\langle p_1, p_2 | p_2, p_1\rangle) = \frac{1}{2} \sum_{\mathbf{p}_1, \mathbf{p}_2} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) [2 - 2\delta(\mathbf{p}_1 - \mathbf{p}_2)] \\
&= \frac{1}{2} \sum_{\mathbf{p}_1, \mathbf{p}_2} \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) - \frac{1}{2} \sum_{\mathbf{p}} \exp\left(-\frac{\mathbf{p}^2}{2mk_B T}\right)
\end{aligned}$$

Approximating the sum by the integral

$$\begin{aligned}
\frac{1}{2} \frac{V^2}{(2\pi\hbar)^6} \int d\mathbf{p}_1 d\mathbf{p}_2 \exp\left(-\frac{\mathbf{p}_1^2 + \mathbf{p}_2^2}{2mk_B T}\right) - \frac{1}{2} \frac{V}{(2\pi\hbar)^3} \int d\mathbf{p} \exp\left(-\frac{\mathbf{p}^2}{2mk_B T}\right) \\
= \frac{1}{2} \frac{V^2}{(2\pi\hbar)^6} (2\pi mk_B T)^3 - \frac{1}{2} \frac{V}{(2\pi\hbar)^3} (2\pi mk_B T)^{\frac{3}{2}}. \quad (108)
\end{aligned}$$

This can be rewritten as

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}},$$

and finally

$$Z = \frac{1}{2} \frac{V^2}{\lambda^6} \left(1 - \frac{1}{2^{\frac{3}{2}}} \frac{\lambda^3}{V}\right).$$

42. White dwarf

We will study a star made of electron degenerate gas.

- Denoting the number of nucleons N estimate the number of electrons (assume ^{12}C a ^{16}O composition).
- Determine energy per electron assuming
 - relativistic gas,
 - nonrelativistic gas.
- Determine energy per nucleon.
- Find the minimum energy as a function of radius and show that in ultra-relativistic case the minimum appears for $R \rightarrow 0$.
- Determine the limiting mass for ultra-relativistic case for zero total energy.

Solution:

- Carbon contains six electrons a twelve nucleons. Oxygen has eight electrons and sixteen nucleons. Consequently, the number of electrons is half the number of nucleons in both cases.

(b) In the case of nonrelativistic gas we obtain (see problem 31)

$$E = \frac{p_F^5}{10m_e\pi^2\hbar^3}, N = \frac{Vp_F^3}{3\pi^2\hbar^3}.$$

Dividing these results

$$\frac{E}{N} = \frac{3}{10m_e} \left(\frac{N}{V} 3\pi^2\hbar^3 \right),$$

we substitute volume of a sphere

$$\frac{E}{N} = \frac{3}{10m_e} \left(\frac{9}{4}\pi\hbar^3 \right)^{\frac{2}{3}} \frac{N_e^{\frac{2}{3}}}{R^2}.$$

For ultra-relativistic case

$$E = \frac{V(mc^2)^4}{4\pi^2\hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^4.$$

$$N = \frac{V(mc^2)^3}{3\pi^2\hbar^3} \left(\frac{\epsilon_F}{mc^2} \right)^3.$$

Energy per particle can be derived in a similar way as in previous case

$$\frac{E}{N} = \frac{3}{4}m_e c^2 = \frac{3}{4}m_e c^2 \left(\frac{N_e}{V} 3\pi^2 \frac{\hbar^3}{(m_e c^2)^3} \right)^{\frac{1}{3}} = \frac{3}{4}m_e c^2 \left(\frac{9}{4}\pi \right)^{\frac{1}{3}} \frac{\hbar}{m_e c^2} \frac{N_e^{\frac{1}{3}}}{R}.$$

(c) Gravitational potential energy is

$$E_G = -\frac{Gm^2}{R}.$$

Mass is

$$m = Nu,$$

then

$$\frac{E_G}{N} = -\frac{GNu^2}{R}.$$

(d) The total energy is given by a sum of kinetic and potential energy.

$$\frac{E}{N_e} = \frac{E_k}{N_e} + \frac{E_G}{N_e} = \frac{3}{10m_e} \left(\frac{9}{4}\pi\hbar^3 \right)^{\frac{2}{3}} \frac{N_e^{\frac{2}{3}}}{R^2} - \frac{4GN_e u^2}{R}.$$

The necessary condition of extreme is

$$\frac{dE}{dR} = 0 = \frac{3}{5m_e} \left(\frac{9}{4}\pi\hbar^3 \right)^{\frac{2}{3}} \frac{N_e^{\frac{2}{3}}}{R^3} - \frac{4GN_e u^2}{R^2},$$

which gives

$$R = \frac{3\hbar^2}{20m_e G u^2} \left(\frac{9}{4}\pi \right)^{\frac{2}{3}} N_e^{-\frac{1}{3}},$$

from which follows

$$R \sim N^{-\frac{1}{3}}.$$

The energy in extremely relativistic case is

$$\frac{E}{N_e} = \frac{E_k}{N_e} + \frac{E_G}{N_e} = \frac{3}{4}m_e c^2 = \frac{3}{4}m_e c^2 \left(\frac{N_e}{V} 3\pi^2 \frac{\hbar^3}{(m_e c^2)^3} \right)^{\frac{1}{3}} - \frac{4GN_e u^2}{R}.$$

From this follows that the derivative with respect to radius is proportional to R^{-2} and minimum energy appears for $R \rightarrow 0$, when $E \rightarrow -\infty$.

(e) For $N_e > N_{Cr}$ and $E = 0$ we obtain from the formula above

$$N_{cr} = \left(\frac{3hc}{16G} \right)^{\frac{3}{2}} \frac{3}{2} \sqrt{\pi} \frac{1}{u^3},$$

and the critical mass is

$$m_{cr} = 2N_{cr}u = \left(\frac{3hc}{16G} \right)^{\frac{3}{2}} \frac{3\sqrt{\pi}}{u^2}.$$

43. Equation for the chemical potential

Determine the equation for the chemical potential for a matter in spherically symmetric gravitational field. Assume that

$$\mu + ku\varphi = \mu' + mc^2 + ku\varphi = \text{konst.},$$

where k is number of nucleons per electrons and u is the nucleon mass. Explain the equation. You can neglect the pressure of nondegenerate matter and electron mass.

Solution: From the instructions follows that

$$\varphi = \frac{\text{konst.}}{ku} - \frac{\mu}{ku},$$

or

$$\varphi = \frac{\text{konst.}}{ku} - \frac{\mu'}{ku} - \frac{mc^2}{ku}.$$

For spherically symmetric case

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \varphi}{\partial r} \right) = 4\pi G\rho.$$

We substitute φ from previous equation. Only the chemical potential depends on radius. After substitution and some manipulation we arrive at

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \mu}{\partial r} \right) = -4\pi Gk^2 u^2 n.$$

We can obtain the same equation after substitution of equation with μ' .

44. Equation for chemical potential in integral form

Integrate the equation for chemical potential assuming

$$\left. \frac{d\mu}{dr} \right|_{r=0} = 0,$$

where R is radius of a star. Express the result using total mass of the star.

Solution: We shall start with the equation from the previous problem multiplied by r^2

$$\frac{\partial}{\partial r} \left(r^2 \frac{\partial \mu}{\partial r} \right) = -4\pi Gk^2 u^2 nr^2.$$

After integration

$$\int_0^R dr \frac{\partial}{\partial r} \left(r^2 \frac{\partial \mu}{\partial r} \right) = - \int_0^R dr 4\pi Gk^2 u^2 nr^2.$$

The left hand side contains total differentiation and we obtain

$$\int_0^R dr \frac{\partial}{\partial r} \left(r^2 \frac{\partial \mu}{\partial r} \right) = r^2 \left. \frac{\partial \mu}{\partial r} \right|_{r=R} - r^2 \left. \frac{\partial \mu}{\partial r} \right|_{r=0} = r^2 \left. \frac{\partial \mu}{\partial r} \right|_{r=R}.$$

Right hand side gives

$$- \int_0^R dr 4\pi Gk^2 u^2 nr^2 = -4\pi Gku \int_0^R dr kunr^2 = -4\pi GkunM.$$

We obtain

$$r^2 \frac{\partial \mu}{\partial r} \Big|_{r=R} = -4\pi G k u n M.$$

45. Nondimensional form of equation for chemical potential

Rewrite the equation for chemical potential in nondimensional variables

$$\xi = \frac{r}{R}, \mu(r) = \frac{1}{\sqrt{\lambda R}} f(\xi),$$

where

$$\lambda = \frac{4 k^2}{3 \pi} \frac{6 u^2}{(\hbar c)^3},$$

and determine the boundary conditions.

Solution: Number density is

$$n = \frac{\mu^3}{(\hbar c)^3 3 \pi^2},$$

after the substitution

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \mu}{\partial r} \right) = -\frac{4\pi G k^2 u^2 \mu^3}{(\hbar c)^3 3 \pi^3} = -\lambda \mu^3,$$

and some manipulation gives

$$\frac{1}{\xi^2} \frac{\partial}{\partial \xi} \left(\xi^2 \frac{\partial f}{\partial \xi} \right) = -f^3.$$

46. Equation of continuity

Derive equation of continuity from the Boltzmann transport equation. Assume that the force is independent of momentum.

Solution: Boltzmann transport equation is

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{p}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll.}}$$

Integrating over momentum

$$m \int_{\Gamma} d\mathbf{p} \frac{\partial f}{\partial t} + m \int_{\Gamma} d\mathbf{p} \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \int_{\Gamma} d\mathbf{p} \mathbf{F} \cdot \nabla_{\mathbf{p}} f = m \frac{\partial}{\partial t} \int_{\Gamma} d\mathbf{p} f + m \nabla_{\mathbf{r}} \cdot \int_{\Gamma} d\mathbf{p} \mathbf{v} f + m \mathbf{F} \cdot \int_{\Gamma} d\mathbf{p} \nabla_{\mathbf{p}} f.$$

We use Stokes theorem to manipulate the third term

$$\int_{\Gamma} d\mathbf{p} \nabla_{\mathbf{p}} f = \int_{\partial \Gamma} d\mathbf{S}_{\mathbf{p}} f = 0,$$

assuming that f tends to zero faster than p^2 . From

$$f(\mathbf{r}, t) = m \cdot n(\mathbf{r}, t) = m \int_{\Gamma} d\mathbf{p} \frac{f(\mathbf{r}, \mathbf{p}, t)}{(2\pi\hbar)^3}.$$

Mean velocity is

$$\mathbf{u}(\mathbf{r}, t) = \langle \mathbf{v} \rangle = \frac{\int_{\Gamma} d\mathbf{p} \mathbf{v} f}{\int_{\Gamma} d\mathbf{p} f} = \frac{\int_{\Gamma} d\mathbf{p} \mathbf{v} f}{(2\pi\hbar)^3 m n(\mathbf{r}, t)}.$$

After the substitution we derive

$$m \frac{\partial n}{\partial t} + m \nabla_{\mathbf{r}} \cdot (n \mathbf{u}) = 0.$$

Equivalently,

$$\frac{\partial \rho}{\partial t} + \nabla_{\mathbf{r}} \cdot (\rho \mathbf{u}) = 0.$$

47. Thermal transpiration

Determine the heat flux from the Boltzmann transport equation due to temperature gradient

$$\alpha = -\frac{dT}{dy}, T = T_0 - \alpha y. \quad (109)$$

Solution: The hydrostatic equilibrium holds due to the subsonic motion

$$p = n_0 k_B T_0 = n k_B (T_0 - \alpha y),$$

from which

$$n = n_0 \frac{T_0}{T_0 - \alpha y}.$$

In the Boltzmann transport equation

$$\frac{\partial f}{\partial t} + \mathbf{v} \cdot \nabla_{\mathbf{r}} f + \frac{\mathbf{F}}{m} \cdot \nabla_{\mathbf{p}} f = \left(\frac{\partial f}{\partial t} \right)_{\text{coll}},$$

we shall assume the stationary state. We further assume $\mathbf{F} = \mathbf{0}$ and

$$\left(\frac{\partial f}{\partial t} \right)_{\text{coll}} = -\frac{f - f_0}{\tau},$$

where f_0 is equilibrium distribution function, which is assumed to take the form of

$$f_0 = n \left(\frac{2\pi\hbar^2}{mk_B T} \right)^{\frac{3}{2}} \exp\left(-\frac{p^2}{2mk_B T}\right) = n_0 \left(\frac{2\pi\hbar^2}{mk_B} \right)^{\frac{3}{2}} \frac{T_0}{(T_0 - \alpha y)^{\frac{5}{2}}} \exp\left(-\frac{p^2}{2mk_B(T_0 - \alpha y)}\right).$$

This simplifies the Boltzmann transport equation substantially

$$\mathbf{v} \cdot \nabla_{\mathbf{r}} f = \frac{f - f_0}{\tau},$$

where we shall approximate the gradient of f by the gradient of f_0 . This gives form f

$$f = f_0 - \tau \mathbf{v} \cdot \nabla_{\mathbf{r}} f_0 = f_0 - \tau v_y \frac{\partial f_0}{\partial y}.$$

We substitute into the distribution function,

$$f = f_0 + \alpha \tau v_y \frac{T_0}{2(T_0 - \alpha y)^{\frac{7}{2}}} \left[\frac{p^2}{mk_B(T_0 - \alpha y)} - 5 \right] n_0 \left(\frac{2\pi\hbar^2}{mk_B} \right)^{\frac{3}{2}} \exp\left(-\frac{p^2}{2mk_B(T_0 - \alpha y)}\right).$$

Finally, we can focus on the heat transport flux, which is

$$q_y = \int \frac{d^3 p}{(2\pi\hbar)^3} \frac{p^2}{2m} v_y f.$$

Because f_0 is an eve function, the integral is equal to zero. Within an approximation $T_0 - \alpha y \approx T_0$ the heat flux is

$$q_y = \frac{\alpha \tau}{2T_0} \frac{1}{2m} n_0 \left(\frac{2\pi\hbar^2}{mk_B T_0} \right)^{\frac{3}{2}} \int \frac{d^3 p}{(2\pi\hbar)^3} p^2 v_y^2 \left(\frac{p^2}{mk_B T_0} - 5 \right) \exp\left(-\frac{p^2}{2mk_B T_0}\right).$$

We shall introduce the spherical coordinates with north pole unusually in the direction of y axis, that is

$$v_y = v \cos(\theta)$$

$$\begin{aligned} & \frac{1}{m^2} \frac{1}{(2\pi\hbar)^3} \int_0^{2\pi} d\phi \int_0^\pi d\theta \int_0^\infty dp \left(\frac{p^2}{mk_B T_0} - 5 \right) p^6 \cos^2 \theta \sin \theta \exp\left(-\frac{p^2}{2mk_B T_0}\right) \\ &= \frac{1}{m^2} \frac{1}{(2\pi\hbar)^3} \cdot 2\pi \cdot \left[-\frac{1}{3} \cos^3 \theta \right]_0^\pi \cdot \left[\frac{1}{mk_B T_0} \frac{1}{2} (2mk_B T_0)^{\frac{9}{2}} \int_0^\infty dt t^{\frac{7}{2}} \exp(-t) - \frac{5}{2} (2mk_B T_0)^{\frac{7}{2}} \int_0^\infty dt t^{\frac{5}{2}} \exp(-t) \right] \\ &= \frac{5}{2} \alpha \frac{n_0 k_B^2 T_0 \beta}{m}. \end{aligned}$$

We derive for the heat transfer

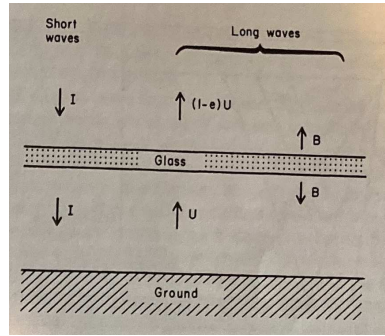
$$q = -\kappa \frac{dT}{dr} = \kappa \alpha,$$

where

$$\kappa = \frac{5 n_0 k_B^2 T_0 \beta}{2 m}.$$

48. **Greenhouse effect**

Consider a greenhouse formed by placing a horizontal sheet of glass above the ground. The glass is transparent to radiation with wavelengths below $4 \mu\text{m}$, but absorbs a fraction ϵ of radiation at longer wavelengths. Suppose a downward flux I of solar radiation. Assume that both earth and glass radiate according to the Stefan-Boltzmann law. Determine the change of earth temperature due to presence of glass.



Solution The ground warms up to a temperature T_g and emits long-wavelength radiation with upward flux given by

$$U = \sigma T_g^4.$$

Part of this flux is absorbed by the glass and reflected back. Equilibrium is reached when the upward fluxes balance the downward fluxes, that is,

$$I = (1 - \epsilon)U + B = U - B,$$

where B is a flux emitted by the glass. Solving for B gives $B = \epsilon U / 2$ and

$$\sigma T_g^4 = U = \frac{I}{1 - \frac{\epsilon}{2}}, \quad T_g = \left(\frac{I}{\sigma (1 - \frac{\epsilon}{2})} \right)^{1/4}$$

Therefore, T_g is higher by up to 19% (for $\epsilon = 1$) higher than it would be in the absence of glass (for $\epsilon = 0$).