NTNU

Institutt for fysikk

Fakultet for fysikk, informatikk og matematikk

Solution to the exam in
TFY4230 STATISTICAL PHYSICS
Wednesday december 21, 2011

This solution consists of 8 pages.

Problem 1. Qualitative explanations

Explain the following topics briefly

a) Central limit theorem.

In a simple form the central limit theorem states that the probability distribution of a sum (or average) of N *independent*, identically distributed random variables with finite mean and variance will approach a normal distribution (gaussian or bell-curve) when N becomes large. The condition of identical distributed variables may be relaxed, provided the sums of mean values and variances behave "properly" (like remaining finite).

One consequence of the central limit theorem is that the average of a large sample of N independent outcomes, drawn from a distribution with finite mean μ and variance σ^2, becomes normal distributed around μ with a variance σ^2/N.

Remark: There are extensions of the central limit theorem to cases where the limiting distribution is different from a gaussian.

b) Ergodic hypothesis.

The ergodic hypothesis postulates that the time average of physical quanties in a closed Hamiltonian system is equal to a phase space average,

$$\langle f \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T \mathrm{d}t \, f(\boldsymbol{q}, \boldsymbol{p}) = \Omega(E)^{-1} \int \prod_n \mathrm{d}q_n \mathrm{d}p_n \, f(\boldsymbol{q}, \boldsymbol{p}) \, \delta(H(\boldsymbol{q}, \boldsymbol{p}) - E). \tag{1}$$

Remark 1: Here $\boldsymbol{q}$ denote the collection of all position variables, and $\boldsymbol{p}$ the collection of all momentum variables. The normalization constant $\Omega(E)$, the microcanonical partition function, is chosen so that the equality is valid for $f = 1$. The right hand side says that the phase space average should be taken with respect to the Liouville measure (i.e. $\prod_n \mathrm{d}q_n \mathrm{d}p_n$) restricted to the constant energy surface.

Remark 2: The great success of statistical mechanics applied to physical systems in thermal equilibrium provides strong empirical support for the ergodic hypothesis, even for quite short times T. At least for large systems, and a restricted class of functions f.

c) Equipartition theorem.

Loosely speaking the equipartition theorem says that each quadratic term in the Hamiltonian contributes $\frac{1}{2}k_B$ to the heat capacity of a *classical* system.

Caveats: (i) The counting of terms assumes that the quadratic Hamiltonian has been brought to diagonal form by a canonical transformation. (ii) Terms occuring in the (diagonalized) quadratic Hamiltonian must not occur in the rest of the Hamiltonian.

d) Classical diamagnetism.

According to the Bohr – van Leeuwen theorem classical diamagnetism does not exist. The theorem is easily proven by shifting integration variables, $\boldsymbol{p}'_n = \boldsymbol{p}_n - q\boldsymbol{A}(\boldsymbol{x}_n)$, in the momentum integrals of the canonical partition function.

Remark 1: Why say that classical *diamagnetism* does not exist? We could equally well say that classical *magnetism* does not exist. Period. The chosen formulation is presumably due to the fact that the correponding quantum systems are weakly diamagnetic.

Although one often model magnetic materials using "classical" spins, it seems difficult to model such spins themselves in terms of classical particles in such a way that the Bohr – van Leeuwen theorem does not apply.

Remark 2: In *diamagnetic* materials there will be induced a magnetic field opposite to the external field; such materials will have a relative magnetic permeability less than 1. The opposite are *paramagnetic* materials where the induced magnetic field is aligned with the external field; such materials will have a relative magnetic permeability greater than 1. One also talks about *ferromagnetic* materials; they may be said to be extremely paramagnetic, with a non-linear response and may magnetize spontaneously. The opposite are *anti-ferromagnetic* materials which may exhibit *staggered magnetism* (i.e., with a spontaneous magnetic field pointing in one directions on even sites of a bipartite lattice, and in the opposite direction on odd sites).

e) Thermal de Broglie wavelength.

Quantum particles with momentum p are associated with a de Broglie wavelength $\lambda = h/p$. Crudely speaking the thermal de Broglie wavelength is the average λ of particles in thermal equilibrium. Such particles with mass m have kinetic energy $\langle K(\boldsymbol{p}) \rangle = \langle \frac{1}{2m}\boldsymbol{p}^2 \rangle = \frac{3}{2}k_B T$ (nonrelativistically). This provides an estimate $\lambda_{\mathrm{dB}}^{-2} \sim mk_B T/h^2$. A suitable precise definition is to say that

$$\lambda_{\mathrm{dB}}^{-3} \equiv \int \frac{\mathrm{d}^3 p}{h^3} \, \mathrm{e}^{-K(\boldsymbol{p})/k_B T}, \tag{2}$$

which gives $\lambda_{\mathrm{dB}} = h/\sqrt{2\pi m k_B T}$ for nonrelativistic particles.

Problem 2. Python code

Listing 1: Python code fragment

```
1    nPoints = 50000
2    nBins = 1000
3    qValues = numpy.linspace(0, 0.5*numpy.pi, nPoints)[1:nPoints]
4    omega = numpy.sqrt( 4*numpy.sin(qValues)**2 + 2*numpy.sin(2*qValues)**2)
5    [weights, bins] = numpy.histogram(omega, bins=nBins)
6    normalizedWeights = weights/numpy.sum(weights)
```

a) Explain what is done by the six lines of Python code above.

- The first two lines create two variables `nPoints` and `nBins`. We could have inserted their values directly in the code below, but that would make the code more difficult to change consistently.

- In the third line we first create an array of exactly `nPoints` equally spaced points, starting with 0 and ending with $\frac{1}{2}\pi$, and next (with the clause `[n:nPoints]`) define a "view" `qValues` to all these points q except the first one ($q = 0$).

- In the fourth line we create an array `omega` of values

$$\omega = \sqrt{4\sin^2 q + 2\sin^2 2q} \tag{3}$$

This array have `nPoints-1` elements.

- In the fifth line we use the `histogram` function in `numpy` to construct a histogram of the values occuring in `omega`. This function find the smallest and largest value occuring, divides this interval into `nBins` subintervals, and finally counts the number of ω-values in each subintervals. These values are returned in the array `weights` of length `nBins`. The `nBins+1` boundaries of the subintervals are returned in the array `bin`.

- In the sixt line we normalize the histogram so that the value of each bin can be interpreted as the probability that ω falls in that bin.

In summary the code calculates the normalized density of states, $g(\omega)$, for a system with dispersion relation (3).

Problem 3. Statistical mechanics of 3-level systems

Consider a system which can be in three different energy states, $\{E_0, E_1, E_2\}$, in thermal equilibrium with a reservoir at temperature T.

a) Write down the partition function for this system.

$$Z = e^{-\beta F} = \sum_{k=0}^{2} e^{-\beta E_k} = e^{-\beta E_0} \left(1 + e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}\right), \tag{4}$$

where $\varepsilon_k = E_k - E_0$.

b) Calculate the internal energy of this system.

$$U = \langle E \rangle = -\frac{\partial}{\partial \beta} \log Z = E_0 + \frac{\varepsilon_1 e^{-\beta \varepsilon_1} + \varepsilon_2 e^{-\beta \varepsilon_2}}{1 + e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}}. \tag{5}$$

c) Calculate the entropy of this system.

Since $k_B \log Z = -k_B \beta F = S - k_B \beta U$ we find
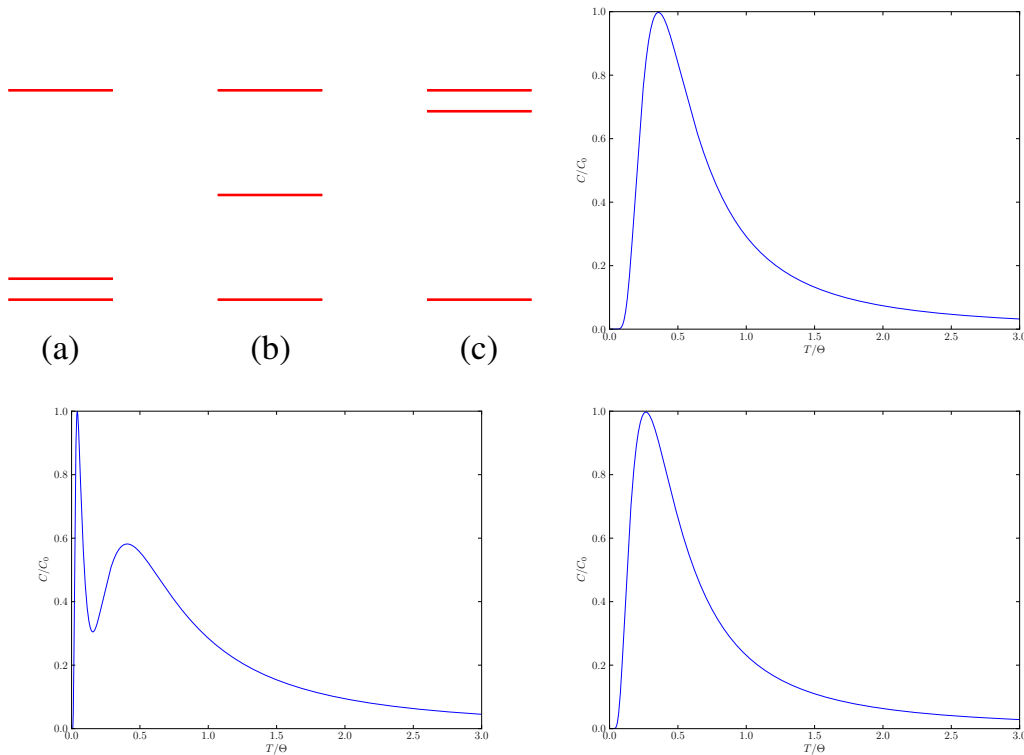
$$S = k_B \left(\log Z + \beta U\right) \tag{6}$$

$$= k_B \left(1 - \beta \frac{\partial}{\partial \beta}\right) \log Z$$

$$= k_B \left[\log \left(1 + e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}\right) + \frac{\beta \varepsilon_1 e^{-\beta \varepsilon_1} + \beta \varepsilon_2 e^{-\beta \varepsilon_2}}{1 + e^{-\beta \varepsilon_1} + e^{-\beta \varepsilon_2}}\right]. \tag{7}$$

Remark 1: Note that the thermodynamic expression (6) is equivalent to the formula

$$S = -k_B \langle \log \mathcal{P} \rangle, \tag{8}$$

where $\mathcal{P}_k = Z^{-1} e^{-\beta E_k}$ is the probability of being in state k.

Remark 2: Note that $\left(1 - \beta \frac{\partial}{\partial \beta}\right) \log e^{-\beta E_0} = 0$.

In the upper left figure above three possible orderings of the energy levels are listed. The three other figures show the corresponding heat capacities in random order. The temperature scale Θ is the same in all three cases (but C_0 is not).

d) Which heat capacity correspond to which level ordering? Explain your choices.

To obtain a significant heat capacity C the thermal energy $k_B T$ must be large enough to excite the system over an energy gap ΔE, but not much larger (when $k_B T \gg \Delta E$ the states on both sides of the gap is already populated with equal probability; hence a further increase in temperature will not lead to a change in the internal energy from this part of the system).

For the case **(a)** we can first excite over a small energy gap and next over a large energy gap (with increasing temperature). This will lead to a double hump in the heat capacity, and must correspond to the lower left figure. (The case **(c)** also has a small and a large energy gap, but for temperatures suitable for the small energy gap the state E_1 is not yet populated; hence there are no particles available to cross the gap.)

For the cases **(b)** and **(c)** we start to excite the system when $k_B T$ is comparable to the largest energy gap, hence we get a single hump in the heat capacity. The relevant energy gap is almost twice as large for case **(c)** than for case **(b)**, hence excitation should start at about twice the temperature, which corresponds to the upper right figure.

To summarize:

(a) corresponds to the lower left figure,

(b) corresponds to the lower right figure,

(c) corresponds to the upper right figure.

Problem 4. Ideal bose gas

The grand partition function of an ideal gas of nonrelativistic spin-0 bosons in a volume $V = L^3$ is

$$\Xi = \prod_{\boldsymbol{k}} \left(1 - e^{\beta(\mu - E_{\boldsymbol{k}})} \right)^{-1}, \quad \text{where } E_{\boldsymbol{k}} = \frac{\hbar^2 \boldsymbol{k}^2}{2m}. \tag{9}$$

With periodic boundary conditions the allowed values for $k_x = \frac{2\pi n_x}{L}$ with $n_x = 0, \pm 1, \pm 2, \cdots$, and similar for k_y and k_z. Assume the limit of large V, so that summations over $\boldsymbol{k}$ can be replaced by integrals.

a) Calculate the pressure βPV of this gas to second order in the parameter $z \equiv e^{\beta\mu}$.

We have

$$\beta PV = \log \Xi = -\sum_{\boldsymbol{k}} \log \left(1 - e^{\beta(\mu - E_{\boldsymbol{k}})} \right)$$

$$\underset{\text{large } V}{=} -V \int \frac{d^3 k}{(2\pi)^3} \log \left(1 - z\, e^{-\beta E_{\boldsymbol{k}}} \right)$$

$$= V \sum_{L=1}^{\infty} \frac{z^L}{L} \int \frac{d^3 k}{(2\pi)^3}\, e^{-L\beta E_{\boldsymbol{k}}} = V \lambda_{\text{dB}}^{-3} \sum_{L=1}^{\infty} \frac{z^L}{L^{5/2}}$$

$$\equiv V \lambda_{\text{dB}}^{-3} \operatorname{Li}_{5/2}(z) = V \lambda_{\text{dB}}^{-3} \left(z + 2^{-5/2} z^2 + \cdots \right). \tag{10}$$

Remark 1: Here we have used the fact that the integral of $\boldsymbol{k}$ is equal to λ_{dB}^{-3} at a temperature $T_M = T/L$, essentially by definition of the thermal de Broglie wavelength, and that this wavelength scales like $T^{-1/2}$ in the non-relativistic case, thereby leading to an additional factor $L^{-3/2}$ in the sum.

Remark 2: For those who enjoy integration, or have forgotten about the slick definition of the thermal wavelength, we may compute the integral by first introducing a scaled coordinate $\boldsymbol{x}$ so that $L\beta E_{\boldsymbol{k}} = L\beta\hbar^2\boldsymbol{k}^2/2m = \boldsymbol{x}^2/2$. This gives

$$I_L \equiv \int \frac{d^3 k}{(2\pi)^3}\, e^{-L\beta E_{\boldsymbol{k}}} = \left(\frac{mk_B T}{L\hbar^2} \right)^{3/2} \int \frac{d^3 x}{(2\pi)^3}\, e^{-\boldsymbol{x}^2/2} \equiv \left(\frac{mk_B T}{L\hbar^2} \right)^{3/2} C^3 \quad \text{with } C = \int_{-\infty}^{\infty} \frac{dx}{2\pi}\, e^{-x^2/2},$$

which provides the most important information, like how I_L depends on temperature T and the factor $L^{-3/2}$. A simple way to compute C is to consider

$$C^2 = \frac{1}{(2\pi)^2} \int_{-\infty}^{\infty} dx \int_{-\infty}^{\infty} dy\, e^{-(x^2 + y^2)/2} = \frac{1}{(2\pi)^2} \underbrace{\int_0^{\infty} r dr\, e^{-r^2/2}}_{1} \underbrace{\int_0^{2\pi} d\phi}_{2\pi} = \frac{1}{2\pi}.$$

Hence we find that $C = 1/\sqrt{2\pi}$, and

$$I_L = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} L^{-3/2} \equiv \lambda_{\text{dB}}^{-3} L^{-3/2}. \tag{11}$$

b) Calculate the mean particle number $\langle N \rangle$ of this gas to second order in the parameter z.

The probability $\mathcal{P}_N$ for N particles in the system is in general

$$\mathcal{P}_N = \Xi^{-1} e^{\beta\mu N}\, Z_N,$$

which gives

$$\langle N \rangle = \Xi^{-1} \sum_{N=0}^{\infty} N e^{\beta\mu N}\, Z_N = \left(\frac{\partial \log \Xi}{\beta \partial \mu} \right)_{\beta, V} = z \left(\frac{\partial \log \Xi}{\partial z} \right)_{\beta, V} = z \left(\frac{\partial \beta PV}{\partial z} \right)_{\beta, V}.$$

In this case we find $\langle N \rangle = V \int \frac{d^3 k}{(2\pi)^3} \frac{z}{e^{\beta E_{\boldsymbol{k}}} - z}$, or by inserting the expansion (10),

$$\langle N \rangle = V \lambda_{\text{dB}}^{-3} \sum_{L=1}^{\infty} \frac{z^L}{L^{3/2}} \equiv V \lambda_{\text{dB}}^{-3} \operatorname{Li}_{3/2}(z) = V \lambda_{\text{dB}}^{-3} \left(z + 2^{-3/2} z^2 + \cdots \right). \tag{12}$$

c) Calculate the fluctuations in particle number, $\mathrm{Var}\,N = \langle N^2 \rangle - \langle N \rangle^2$, to second order in the parameter z.

We have in general

$$\mathrm{Var}N = \langle N^2 \rangle - \langle N \rangle^2 = \left(\frac{\partial^2 \log \Xi}{\beta^2 \partial \mu^2} \right)_{\beta,V} = \left(\frac{\partial \langle N \rangle}{\beta \partial \mu} \right)_{\beta,V} = z \left(\frac{\partial \langle N \rangle}{\partial z} \right)_{\beta,V}.$$

In this case we find, by inserting the expansion (12)

$$\mathrm{Var}N = V\lambda_{\mathrm{dB}}^{-3/2} \sum_{L=1}^{\infty} \frac{z^L}{L^{1/2}} = V\lambda_{\mathrm{dB}}^{-3/2} \left(z + 2^{-1/2}z^2 + \cdots \right). \qquad (13)$$

d) Calculate the internal energy, $U = \langle E \rangle$, to second order in the parameter z.

The fast way to solve this problem is to make use of the fact that $pV = \frac{2}{3}U$ for nonrelativistic ideal quantum gases. Hence we have that

$$U = \frac{3}{2}k_B T V \lambda_{\mathrm{dB}}^{-3} \sum_{L=1}^{\infty} \frac{z^L}{L^{5/2}} \equiv \frac{3}{2}k_B T V \lambda_{\mathrm{dB}}^{-3} \, \mathrm{Li}_{5/2}(z) = \frac{3}{2}k_B T V \lambda_{\mathrm{dB}}^{-3} \left(z + 2^{-5/2}z^2 + \cdots \right).$$
$$(14)$$

Remark 1: Referring to obscure relations feels almost like cheating; hence we prefer to also go through the probabilistic argument in some detail. In general the probability density for finding N particles with total energy E in the system is

$$\mathcal{P}_N(E) = \Xi^{-1}\, \mathrm{e}^{\beta\mu N}\, \mathrm{e}^{-\beta E}\, g_N(E), \qquad (15)$$

where $g_N(E)$ is the density of states per energy in the N-particle system. It is related to the canonical partition function by

$$Z_N = \int \mathrm{d}E\, g_N(E)\, \mathrm{e}^{-\beta E}.$$

It follows that

$$\langle\, E \,\rangle = \Xi^{-1} \sum_{N=0}^{\infty} \mathrm{e}^{\beta\mu N} \int \mathrm{d}E\, g_N(E)\, E\, \mathrm{e}^{-\beta E} = -\left(\frac{\partial \log \Xi}{\partial \beta} \right)_{\beta\mu} = -\left(\frac{\partial \log \Xi}{\partial \beta} \right)_{z}.$$

For fixed z the temperature dependence of $\log \Xi = \beta PV$ only occurs in the factor $\lambda_{\mathrm{dB}}^{-3}$. We find

$$\frac{\partial}{\partial \beta}\lambda_{\mathrm{dB}}^{-3} = \frac{3}{2\beta}\lambda_{\mathrm{dB}}^{-3} = \frac{3}{2}k_B T\lambda_{\mathrm{dB}}^{-3},$$

which verifies the relation $PV = \frac{2}{3}U$.

e) Calculate the heat capacity at constant volume, C_V, to second order in the parameter z.

As it stands this question is not completely defined. Should we increase the temperature with a fixed particle number $\langle\, N \,\rangle$, or with a fixed chemical potential μ, or with a fixed fugacity z, or some combination of these possibilities? (In an exam solution – but only there – any of these choices would be acceptable.)

For a general analysis one may write

$$\left(\frac{\partial U}{\partial T} \right)_V = \underbrace{\left(\frac{\partial \beta}{\partial T} \right)}_{-k_B\beta^2} \left[\left(\frac{\partial U}{\partial \beta} \right)_{V,z} + \left(\frac{\partial U}{\partial z} \right)_{V,\beta} \left(\frac{\partial z}{\partial \beta} \right)_V \right]. \qquad (16)$$

For fixed V and z the only T-dependence in U occurs in the prefactor $\beta^{-1}\lambda_{\mathrm{dB}}^{-3} \propto \beta^{-5/2}$,

$$\frac{\partial}{\partial \beta} \beta^{-1}\lambda_{\mathrm{dB}}^{-3} = -\frac{5}{2\beta^2}\lambda_{\mathrm{dB}}^{-3}.$$

Hence we find

$$\left(\frac{\partial U}{\partial T} \right)_{V,z} = \frac{15}{4}k_B\, V\lambda_{\mathrm{dB}}^{-3} \sum_{L=1}^{\infty} \frac{z^L}{L^{5/2}} \equiv \frac{15}{4}k_B\, V\lambda_{\mathrm{dB}}^{-3}\, \mathrm{Li}_{5/2}(z)$$

$$= \frac{15}{4}k_B\, V\lambda_{\mathrm{dB}}^{-3} \left(z + 2^{-5/2}z^2 + \cdots \right). \qquad (17)$$

For fixed V and μ we find $\partial z/\partial\beta = \mu z = -\beta^{-1}\log(1/z)\,z$, and

$$\left(\frac{\partial U}{\partial z}\right)_{z,V}\left(\frac{\partial z}{\partial\beta}\right) = -\frac{3}{2\beta^2}V\lambda_{\mathrm{dB}}^{-3}\,\log\frac{1}{z}\sum_{L=1}^{\infty}\frac{z^N}{L^{3/2}}.$$

This gives

$$\left(\frac{\partial U}{\partial T}\right)_{V,\mu} = k_B\,V\lambda_{\mathrm{dB}}^{-3}\left[\frac{15}{4}\mathrm{Li}_{5/2}(z) + \frac{3}{2}\,\log\left(\frac{1}{z}\right)\mathrm{Li}_{3/2}(z)\right]. \tag{18}$$

The results (17, 18) correspond to unconventional definitions of heat capacity, since part of the change in U with temperature is due to an increase in particle number. A conventional definition is to see how the internal energy change with temperature at constant particle number or density. I.e., we require

$$d\rho = \left(\frac{\partial\rho}{\partial\beta}\right)_z d\beta + \left(\frac{\partial\rho}{\partial z}\right)_\beta dz = 0,$$

or

$$\frac{1}{z}\left(\frac{\partial z}{\partial\beta}\right) = -\frac{(\partial\rho/\partial\beta)_z}{(z\partial\rho/\partial z)_\beta} = \frac{3}{2\beta}\frac{\mathrm{Li}_{3/2}(z)}{\mathrm{Li}_{1/2}(z)}. \tag{19}$$

We combine this with the relations

$$(\partial U/\partial\beta)_{V,z} = -\frac{15}{4\beta^2}\,V\lambda_{\mathrm{dB}}^{-3}\,\mathrm{Li}_{5/2}(z),$$

$$z\,(\partial U/\partial z)_{V,\beta} = \frac{3}{2\beta}\,V\lambda_{\mathrm{dB}}^{-3}\,\mathrm{Li}_{3/2}(z),$$

and equation (16) to find

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,\rho} = \frac{3}{4}k_B\,V\lambda_{\mathrm{dB}}^{-3}\left[5\mathrm{Li}_{5/2}(z) - 3\mathrm{Li}_{3/2}(z)^2\,\mathrm{Li}_{1/2}(z)^{-1}\right]$$

$$= \frac{3}{2}k_B\,V\lambda_{\mathrm{dB}}^{-3}\left(z + 5\cdot 2^{-7/2}z^2 + \cdots\right). \tag{20}$$

f) Use your result from point **b)** to express z in terms of the particle density,

$$\rho = \frac{\langle N\rangle}{V}, \tag{21}$$

up to second order in ρ.

We have the relation

$$\bar\rho \equiv \rho\lambda_{\mathrm{dB}}^3 = z + \sum_{L=2}^{\infty}L^{-3/2}z^L.$$

Or rewritten,

$$z = \bar\rho - \sum_{L=2}^{\infty}L^{-3/2}z^L. \tag{22}$$

This gives $z = \bar\rho$ to first order in z (or $\bar\rho$), which can be reinserted on the right hand side of (22) to find z to second order in $\bar\rho$,

$$z = \bar\rho - 2^{-3/2}\bar\rho^2 + \cdots. \tag{23}$$

Remark 1: With $\bar\rho$ expanded to second order in z one may find an expression for $z = z(\bar\rho)$ by solving the quadratic equation in z. But this is not the right way to proceed; it leads to an ugly expression which is anyway correct only to second order in $\bar\rho$ as found in (23).

Remark 2: We may again reinsert (23) on the right hand side of (22) to find z to third order in $\bar\rho$,

$$z = \bar\rho - 2^{-3/2}\bar\rho^2 + (2^{-2} - 3^{-3/2})\bar\rho^3 + \cdots,$$

which may be reinserted in (23) to give to fourth order,

$$z = \bar{\rho} - 2^{-3/2}\bar{\rho}^2 + \left(2^{-2} - 3^{-3/2}\right)\bar{\rho}^3 - \left(2^{-3} - 5 \cdot 6^{-3/2} + 5 \cdot 2^{-9/2}\right)\bar{\rho}^4 + \cdots,$$

and so on. . . .

Next one may insert these expressions for z into the pressure expansion,

$$\beta P \lambda_{\mathrm{dB}}^3 = \sum_{L=1}^{\infty} \frac{z^L}{L^{5/2}},$$

to obtain the *virial expansion* for the equation of state

$$\beta P \lambda_{\mathrm{dB}}^3 = \bar{\rho} - 2^{-5/2}\bar{\rho}^2 + \left(2^{-3} - 2 \cdot 3^{-5/2}\right)\bar{\rho}^3 - \left(3 \cdot 2^{-5} - 2 \cdot 12^{-1/2} + 5 \cdot 2^{-11/2}\right)\bar{\rho}^4 + \cdots.$$

Similar expansions in terms of density $\bar{\rho}$ can be obtained for other physical quantities, like those considered in points **c)**, **d)**, **e)**.
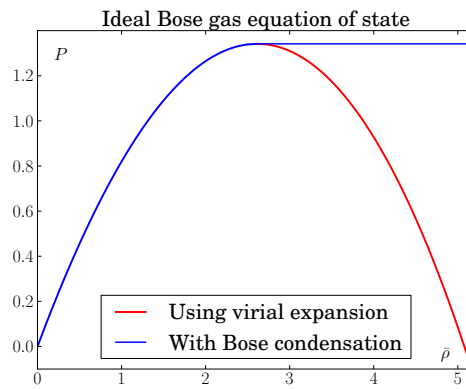

Figure 1: