

Statistical Physics Exam

17th February 2015

Name	Student Number

Problem 1	Problem 2	Problem 3	Problem 4	Total	Percentage	Mark

Useful constants

gas constant R	$8.31 J / (K \cdot mol)$
Boltzmann constant k_B	$1.38 \cdot 10^{-23} J / K$
Avogadro number N_A	$6.02 \cdot 10^{23} mol^{-1}$
speed of light c	$300 \cdot 10^6 m / s$
Planck constant h	$6.63 \cdot 10^{-34} J \cdot s$

(25P) Problem 1

1. **(1P)** Write down the relation between entropy and partition function for a microcanonical ensemble. $S = k_B \ln \Omega(N, V, E)$
2. **(3P)** Find the entropy in a grand-canonical ensemble from the probability for a microstate in that ensemble.

$$S = -k_B \sum_r P_r \ln P_r$$

$$\begin{aligned} S &= -k_B \sum_r \frac{\exp(-\beta(E_r - \mu N_r))}{\Xi} \ln \frac{\exp(-\beta(E_r - \mu N_r))}{\Xi} \\ &= -k_B \sum_r \frac{\exp(-\beta(E_r - \mu N_r))}{\Xi} [-\beta(E_r - \mu N_r) - \ln \Xi] \\ &= \beta k_B \sum_r \frac{(E_r - \mu N_r) \exp(-\beta(E_r - \mu N_r))}{\Xi} + \frac{k_B}{\Xi} \ln \Xi \sum_r \exp(-\beta(E_r - \mu N_r)) \\ &= \frac{\langle E_r - \mu N_r \rangle}{T} + k_B \ln \Xi \end{aligned} \tag{1}$$

3. **(1P)** Consider a system of N Fermions. How many energy levels are occupied at temperature $T=0K$ if energy does not depend on spin? $N/2$, one spin up, one spin down per energy state
4. **(2P)** Consider the thermodynamic quantities energy, temperature, pressure, volume, chemical potential, number of particles. Which of them fluctuate in a
 - (a) canonical ensemble ? energy, pressure, chemical potential
 - (b) grand-canonical ensemble ? energy, pressure, number of particles
5. **(2P)** How does the entropy of a closed system change in
 - (a) a reversible process? $\Delta S = 0$
 - (b) an irreversible process ? $\Delta S > 0$
6. **(2P)** Which of the following quantities are extensive: entropy, Gibbs free energy, pressure, chemical potential? entropy, Gibbs free energy
7. **(1P)** What is the value of the chemical potential of photons? $\mu = 0$
8. **(1P)** What happens to the heat capacity during a phase transition? The heat capacity has a discontinuity.
9. **(4P)** Under which conditions is classical Boltzmann statistics a good approximation and how is this justified? Boltzmann statistics is a good approximation for dilute systems of heavy particles at high temperature. There must be sufficient many one-particle energy states such that the particles can occupy one each, independent of each other (not like Fermions that occupy each level at most by two, due to the Pauli principle). If the thermal wave length $\lambda = \left(\frac{h^2}{2\pi m k_B T}\right)$ is approximately the same as the average distance, quantum statistics become important.

10. **(3P)** Derive the Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$. You can assume the number of particles N to be fixed (S : entropy, V : volume, T : temperature, P : pressure). Starting from Helmholtz free energy at equilibrium $dA = 0$. Since $A = A(V, T)$ for constant number of particles

$$\begin{aligned} dA &= \left(\frac{\partial A}{\partial V}\right)_T dV + \left(\frac{\partial A}{\partial T}\right)_V dT \\ &= -PdV - SdT \end{aligned}$$

which one can see from

$$\begin{aligned} dA &= dE - d(TS) \\ &= TdS - PdV - TdS - SdT \\ &= -PdV - SdT \end{aligned}$$

The Helmholtz free energy is a state function, hence

$$\begin{aligned} \left(\frac{\partial^2 A}{\partial V \partial T}\right) &= \left(\frac{\partial^2 A}{\partial T \partial V}\right) \\ -\left(\frac{\partial P}{\partial T}\right)_V &= -\left(\frac{\partial S}{\partial V}\right)_T \end{aligned}$$

11. **(2P)** What does the equipartition theorem state for an ideal, monoatomic gas? What does this mean for the heat capacity at constant volume, C_V ? Each degree of freedom contributes to the total energy by $\frac{1}{2}k_B T$ such that $E = \frac{3}{2}Nk_B T$. The heat capacity is therefore constant $C_V = \left(\frac{\partial E}{\partial T}\right)_V = \frac{3}{2}Nk_B$
12. **(3P)** What happens to an ideal quantum gas in the limit temperature $T \rightarrow 0$
- if the particles are fermions? Fermions will occupy the lowest energy levels in pairs up to the Fermi energy.
 - if the particles are bosons? A macroscopic number of bosons will occupy the ground state (condensate)
 - if the particles are photons (which are also boson, but without mass)? Since the number of photons is not conserved, all photons will disappear (up to vacuum fluctuations)

(25P) Problem 2

Consider a system of N classical gas atoms in a box of volume V . The walls of the box are covered with a coating such that the gas atoms can bind to the surface. Once bound, the atoms do not move any more. There are in total N_B binding sites and $N \leq N_B$. When bound to the surface, the atoms have an energy that is lower by ϵ than in the unbound state. Gas atoms do not interact with each other, neither in the bound nor in the unbound state. The particles cannot be distinguished.

1. **(2P)** Write down the number of possibilities of distributing the N gas particles over the N_B binding site. $\Omega = \frac{N_B!}{N_s!(N_B - N_s)!}$
2. **(1P)** Give an estimate of the energy fluctuations for the surface-bound particles (no calculation needed). **No kinetic energy, all have same binding energy, hence no fluctuations and $\langle E \rangle = E$**
3. **(4P)** Find the energy contribution E and the entropic contribution TS to the Helmholtz free energy for the N_s particles bound to the surface (T : temperature, S : entropy). $E = -N_s \epsilon$
 $S = k_B \ln \frac{N_B!}{N_s!(N_B - N_s)!}$; $A_s = E_s - TS_s$
4. **(5P)** Assuming a continuous momentum space, show that the canonical partition function for the gas particles is given by:

$$Z_{N_{gas}} = \frac{1}{N_{gas}!} \left(\frac{\sqrt{8}V}{h^3} (\pi m k_B T)^{\frac{3}{2}} \right)^{N_{gas}} \quad (2)$$

with k_B : Boltzmann constant, h : Planck constant, m : mass of particle, T : temperature, and $N_{gas} = N - N_s$

We can use the classical ideal gas here

$$Z_{total} = \frac{Z^{N_{gas}}_{\text{one particle}}}{N_{gas}!} \quad (3)$$

$$Z(1, V, T) = \frac{1}{h^3} \int d^3q \exp(-\beta U(q)) \int d^3p \exp\left(-\beta \frac{p^2}{2m}\right) \quad (4)$$

The integral over the positions is simply the volume since

$$\exp(-\beta U(q)) \begin{cases} 1 & \text{inside } V = L^3 \\ 0 & \text{otherwise} \end{cases} \quad (5)$$

and $\int d^3q = V$. We therefore have to deal only with the momenta

$$Z(1, V, T) = \frac{V}{h^3} \int d^3p \exp\left(-\beta \frac{p^2}{2m}\right) \quad (6)$$

Since the momenta in all three directions p_x, p_y, p_z are all equivalent and independent of each other, they factorise and we can integrate individually

$$Z(1, V, T) = \frac{V}{h^3} \cdot \int dp_x \exp\left(-\beta \frac{p_x^2}{2m}\right) \cdot \int dp_y \exp\left(-\beta \frac{p_y^2}{2m}\right) \cdot \int dp_z \exp\left(-\beta \frac{p_z^2}{2m}\right) \quad (7)$$

With the substitution $a^2 = \beta \frac{p^2}{2m}$ we can transform the integrals over the momenta into

$$\begin{aligned} \int dp \exp\left(-\beta \frac{p^2}{2m}\right) &= \sqrt{\frac{2m}{\beta}} \int da \exp(-a^2) \\ &= \sqrt{\frac{2m}{\beta}} \pi \end{aligned}$$

and therefore the partition function becomes

$$Z(1, V, T) = \frac{V}{h^3} \cdot \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \quad (8)$$

and using the notation with temperature, i.e. $\beta = \frac{1}{k_B T}$

$$Z(1, V, T) = \frac{V}{h^3} \cdot (2\pi m k_B T)^{\frac{3}{2}} \quad (9)$$

which is for N_{gas} particles and rearranged

$$Z_{N_{gas}} = \frac{1}{N_{gas}!} \left(\frac{\sqrt{8}V}{h^3} (\pi m k_B T)^{\frac{3}{2}} \right)^{N_{gas}} = \frac{1}{N_{gas}!} \left(\frac{V}{\lambda^3} \right)^{N_{gas}} \quad (10)$$

with

$$\lambda = \frac{h}{\sqrt{2\pi m k_B T}} \quad (11)$$

1. **(4P)** Write down the canonical partition function for the whole system of N particles in an equilibrium where N_s particles are bound to the surface.

$$Z_{total} = Z_{N_{gas}} \cdot Z_{N_s}$$

with $Z_{N_{gas}}$ from above. There is only one energy state for bound particles but Ω many possibilities for realising it. Hence $Z = \exp\left(\frac{\epsilon}{k_B T}\right)^{N_s} \cdot \Omega$

2. **(4P)** Find the chemical potential for the gas particles μ_g and for the surface-bound particles μ_s . The chemical potential can be found as the derivative of the Helmholtz free energy $\mu = \left(\frac{\partial A}{\partial N}\right)_{V, T}$. The Helmholtz free energy is either $A = E - TS$ or $A = -k_B T \ln Z$. We obtain for the gas particles

$$\begin{aligned} \mu_g &= -k_B T \frac{\partial}{\partial N} \ln \left(\frac{1}{N_{gas}!} \left(\frac{V}{\lambda^3} \right)^{N_{gas}} \right) \\ &= k_B T \frac{\partial}{\partial N} \left[\ln(N_{gas}!) + N_{gas} \ln \left(\frac{\lambda^3}{V} \right) \right] \\ &\approx k_B T \frac{\partial}{\partial N} \left[N_{gas} \ln(N_{gas}) - N_{gas} + N_{gas} \ln \left(\frac{\lambda^3}{V} \right) \right] \\ &= k_B T \left[\ln(N_{gas}) + N_{gas} \frac{1}{N_{gas}} - 1 + \ln \left(\frac{\lambda^3}{V} \right) \right] \\ &= k_B T \left[\ln(N_{gas}) + \ln \left(\frac{\lambda^3}{V} \right) \right] \\ \mu_g &= k_B T \ln \left(\frac{N_{gas} \lambda^3}{V} \right) \end{aligned}$$

and for the surface-bound particles

$$\begin{aligned}
\mu_s &= -k_B T \frac{\partial}{\partial N_s} \left[N_s \left(\frac{\epsilon}{k_B T} \right) + \ln \frac{N_B!}{N_s! (N_B - N_s)!} \right] \\
&= -\epsilon - k_B T \frac{\partial}{\partial N_s} \ln \left[\frac{N_B!}{N_s! (N_B - N_s)!} \right] \\
&= -\epsilon - k_B T \frac{\partial}{\partial N_s} [\ln N_B! - \ln N_s! - \ln (N_B - N_s)] \\
&\approx -\epsilon - k_B T \frac{\partial}{\partial N_s} [-N_s \ln N_s + N_s - (N_B - N_s) \ln (N_B - N_s) + (N_B - N_s)] \\
&= -\epsilon - k_B T [-\ln N_s - 1 + 1 - (-1) \ln (N_B - N_s) - 1 + (-1)] \\
&= -\epsilon - k_B T [-\ln N_s + \ln (N_B - N_s)] \\
&= -\epsilon - k_B T \ln \frac{(N_B - N_s)}{N_s}
\end{aligned}$$

3. **(5P)** Find an expression for the relation between number of particles bound to the surface and total number of particles as a function of temperature. Hint: the bound particles and the gas particles are in chemical equilibrium. In chemical equilibrium the two chemical potentials must equal

$$\begin{aligned}
\mu_s &= \mu_g \\
-\epsilon - k_B T \ln \frac{(N_B - N_s)}{N_s} &= k_B T \left[\ln (N_{gas}) + \ln \left(\frac{\lambda^3}{V} \right) \right] \\
\frac{\epsilon}{k_B T} &= \ln \frac{(N_B - N_s)}{N_s} + \ln (N_{gas}) + \ln \left(\frac{\lambda^3}{V} \right) \\
\frac{\epsilon}{k_B T} + \ln \left(\frac{V}{\lambda^3} \right) &= \ln \frac{(N_B - N_s)}{N_s} + \ln N_{gas}
\end{aligned}$$

(25P) Problem 3

Consider an ideal, non-relativistic Bose gas of particles with spin zero in a symmetric d -dimensional Volume $V = L^d$ with energy levels

$$\varepsilon_p = \frac{p^2}{2m} \quad (12)$$

where p : momentum, m : mass of gas particle. The grand partition function

$$\Xi = \prod_p \frac{1}{1 - \xi \cdot \exp[-\varepsilon_p/(k_B T)]}. \quad (13)$$

1. **(3P) For a dilute gas at high-temperature**, expand the partition function in ξ . Find the chemical potential to leading order of ξ . **Expansion in a power series**

$$\sum_{n=0}^{\infty} x^n = 1 + x + x^2 + \dots = \frac{1}{1-x} \quad (14)$$

with $x = \xi \cdot \exp[-\beta\varepsilon_p]$

$$\Xi = \prod_p \sum_{n=0}^{\infty} (\xi \cdot \exp[-\beta\varepsilon_p])^n$$

We can also expand the logarithm since we need it later in that form

$$\ln \Xi = - \sum_p \xi \cdot \exp[-\beta\varepsilon_p] \mp \frac{1}{2} \xi^2 \cdot \exp[-2\beta\varepsilon_p] + \dots \quad (15)$$

In leading order we have

$$\ln \Xi \approx -\xi \cdot \sum_p \exp[-\beta\varepsilon_p] \quad (16)$$

To replace the sum we can use the canonical partition function of an ideal gas (given in problem 2)

$$\Xi(\mu, V, T) = \sum_{N=0}^{\infty} Z(N, V, T) \cdot \xi^N \quad (17)$$

$$\begin{aligned} \Xi(\mu, V, T) &= \sum_{N=0}^{\infty} \frac{V^N}{N! \lambda^{3N}} \cdot \xi^N \\ &= \sum_{N=0}^{\infty} \frac{1}{N!} \left(\frac{\xi \cdot V}{\lambda^3} \right)^N \\ &= \exp\left(\frac{\xi \cdot V}{\lambda^3} \right) \end{aligned}$$

where in the last line we have used another series. Using now for the leading order, classical term

$$\ln \Xi = \frac{pV}{k_B T} = N \quad (18)$$

with $\xi = \exp[\beta\mu]$ we obtain

$$\mu = k_B T \ln \left(N \frac{\lambda^3}{V} \right) \quad (19)$$

2. **(9P)** Assuming a continuous momentum space, write down the grand-canonical partition function of the non-relativistic quantum Bose gas in logarithmic and integral form (over p) for dimensions $d = 1, 2$, and 3. For a quantum gas we need the full expansion and we further have to single out the first term $-\ln[1 - \exp[\beta(\varepsilon_0 - \mu)]]$ which for $\varepsilon = 0$ becomes $-\ln[1 - \exp[\beta\mu]]$. Expanding

$$\ln \Xi = -\ln[1 - \exp[\beta(\varepsilon_0 - \mu)]] - \sum_{p \neq 0} \sum_{l=1}^{\infty} \frac{1}{l} [\exp[\beta(\varepsilon_p - \mu)]]^l \quad (20)$$

$$\ln \Xi = -\ln[1 - \xi] - \sum_p \sum_{l=1}^{\infty} \frac{1}{l} (\xi \cdot \exp[-\beta\varepsilon_p])^l$$

Case $d = 3$ in integral form

$$\ln \Xi = -\ln[1 - \xi] - \sum_{l=1}^{\infty} \frac{1}{l} \frac{V}{h^3} \xi^l \cdot \int_{-\infty}^{\infty} d^3p \exp\left(-\frac{p^2 l}{2mk_B T}\right) \quad (21)$$

We know (or find from doing enough powers of l)

$$\ln \Xi = -\frac{V}{\lambda^3} \sum_{l=1}^{\infty} \frac{1}{l} \frac{\xi^l}{l^{\frac{3}{2}}} - \ln[1 - \xi]$$

with

$$\lambda = \left(\frac{h^2}{2\pi mk_B T}\right)^{\frac{1}{2}}$$

Case $d = 2$ in integral form

$$\ln \Xi = -\ln[1 - \xi] - \sum_{l=1}^{\infty} \frac{1}{l} \frac{L^2}{h^2} \xi^l \cdot \int_{-\infty}^{\infty} d^2p \exp\left(-\frac{p^2 l}{2mk_B T}\right) \quad (22)$$

We now substitute $x^2 = \frac{p^2}{2mk_B T}$ and obtain

$$\ln \Xi = -\ln[1 - \xi] - \sum_{l=1}^{\infty} \frac{L^2}{h^2} \frac{1}{l} \xi^l \cdot (2mk_B T) \int_{-\infty}^{\infty} d^2x \exp(-x^2 l) \quad (23)$$

which assuming again isotropy of the momenta is

$$\ln \Xi = -\ln[1 - \xi] - \sum_{l=1}^{\infty} \frac{L^2}{h^2} \frac{1}{l} \xi^l \cdot (2mk_B T) 2\pi \int_0^{\infty} dx x \cdot \exp(-x^2 l) \quad (24)$$

Using the given integral

$$\int_0^{\infty} x \exp(-lx^2) dx = \frac{1}{2l} \quad (25)$$

we arrive at

$$\ln \Xi = -\ln[1 - \xi] - \frac{L^2}{h^2} (2\pi mk_B T) \sum_{l=1}^{\infty} \frac{1}{l} \cdot \frac{\xi^l}{l} \quad (26)$$

$$\ln \Xi = -\ln[1 - \xi] - \frac{L^2}{\lambda^2} \sum_{l=1}^{\infty} \frac{1}{l} \cdot \frac{\xi^l}{l} \quad (27)$$

$$= -\ln[1 - \xi] - \frac{L^2}{\lambda^2} g_{\frac{3}{2}+1}(\xi) \quad (28)$$

Case $d = 1$ in integral form

$$\ln \Xi = -\ln [1 - \xi] - \sum_{l=1}^{\infty} \frac{L}{h} \frac{1}{l} \xi^l \cdot \int_{-\infty}^{\infty} dp \exp\left(-\frac{p^2 l}{2mk_B T}\right) \quad (29)$$

We now substitute $x^2 = \frac{p^2}{2mk_B T}$ and obtain

$$\ln \Xi = -\ln [1 - \xi] - \sum_{l=1}^{\infty} \frac{L}{h} \frac{1}{l} \xi^l \cdot (2mk_B T)^{\frac{1}{2}} \int_{-\infty}^{\infty} dx \exp(-x^2 l) \quad (30)$$

or

$$\ln \Xi = -\ln [1 - \xi] - \sum_{l=1}^{\infty} \frac{L}{h} \frac{1}{l} \xi^l \cdot (2mk_B T)^{\frac{1}{2}} 2 \int_0^{\infty} dx \exp(-x^2 l) \quad (31)$$

using the given integral

$$\int_0^{\infty} \exp(-lx^2) dx = \frac{1}{2} \left(\frac{\pi}{l}\right)^{\frac{1}{2}} \quad (32)$$

we arrive at

$$\ln \Xi = -\ln [1 - \xi] - \frac{L}{h} (2mk_B T)^{\frac{1}{2}} 2 \sum_{l=1}^{\infty} \frac{1}{l} \cdot \frac{\xi^l}{2} \left(\frac{\pi}{l}\right)^{\frac{1}{2}} \quad (33)$$

$$\ln \Xi = -\ln [1 - \xi] - \frac{L}{\lambda} \sum_{l=1}^{\infty} \frac{1}{l^{\frac{3}{2}}} \cdot \frac{\xi^l}{l} \quad (34)$$

$$= -\ln [1 - \xi] - \frac{L}{\lambda} g_{\frac{3}{2}+1}(\xi) \quad (35)$$

3. **(9P)** Use these partition functions to show that to leading order for dimensions $d = 1, 2$, and 3.

$$\frac{P}{k_B T} = \frac{1}{\lambda^d} g_{\frac{d}{2}+1}(\xi) - \frac{1}{L^d} \ln(1 - \xi) \quad (36)$$

$$\frac{N}{L^d} = \frac{1}{\lambda^d} g_{\frac{d}{2}}(\xi) + \frac{1}{L^d} \frac{\xi}{1 - \xi} \quad (37)$$

$$\frac{E}{L^d} = \frac{d}{2} \frac{k_B T}{\lambda^d} g_{\frac{d}{2}+1}(\xi) \quad (38)$$

where $\xi = \exp\left(\frac{\mu}{k_B T}\right)$ with k_B : Boltzmann's constant, T : temperature, μ : chemical potential, and P : pressure, N : number of particles, E : total energy, λ : thermal wave length. For the pressure we use $PV = k_B T \ln \Xi$. Therefore we have for the three cases $d=3$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{\frac{3}{2}+1}(\xi) - \frac{1}{V} \ln [1 - \xi]$$

$d=2$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{\frac{3}{2}+1}(\xi) - \frac{1}{L^2} \ln [1 - \xi]$$

$d=1$

$$\frac{P}{k_B T} = \frac{1}{\lambda^3} g_{\frac{1}{2}}(\xi) - \frac{1}{L^1} \ln [1 - \xi]$$

The number of particles is

$$\begin{aligned}
N &= \langle n_0 \rangle + \sum_{p \neq 0} \langle n_p \rangle \\
&= \langle n_0 \rangle + \sum_{p \neq 0} \langle n_p \rangle
\end{aligned} \tag{39}$$

We use further

$$\begin{aligned}
\langle n_p \rangle &= \frac{1}{\xi \cdot \exp[-\beta \varepsilon_p]} \\
&= \frac{\xi \cdot \exp[-\beta \varepsilon_p]}{1 - \xi \cdot \exp[-\beta \varepsilon_p]}
\end{aligned}$$

and for $\varepsilon_0 = 0$

$$\langle n_0 \rangle = \frac{\xi}{1 - \xi}$$

Replacing the sum by integrals and expanding in powers of the exponential series like we did for the partition function

$$N = \frac{L^3}{h^3} \sum_{l=1}^{\infty} \xi^l \int d^3 p \exp\left(-\frac{p^2 l}{2mk_B T}\right) + \frac{\xi}{1 - \xi} \tag{40}$$

$$N = \frac{L^2}{h^2} \sum_{l=1}^{\infty} \xi^l \int d^2 p \exp\left(-\frac{p^2 l}{2mk_B T}\right) + \frac{\xi}{1 - \xi} \tag{41}$$

$$N = \frac{L}{h} \sum_{l=1}^{\infty} \xi^l \int dp \exp\left(-\frac{p^2 l}{2mk_B T}\right) + \frac{\xi}{1 - \xi} \tag{42}$$

The integrals are the same as for the partition function such that

$$N = \frac{L^3}{\lambda^3} \sum_{l=1}^{\infty} \frac{\xi^l}{l^{\frac{3}{2}}} + \frac{\xi}{1 - \xi} \tag{43}$$

$$N = \frac{L^2}{\lambda^2} \sum_{l=1}^{\infty} \frac{\xi^l}{l^{\frac{2}{2}}} + \frac{\xi}{1 - \xi} \tag{44}$$

$$N = \frac{L}{\lambda} \sum_{l=1}^{\infty} \frac{\xi^l}{l^{\frac{1}{2}}} + \frac{\xi}{1 - \xi} \tag{45}$$

as requested. The energy can be obtained from

$$E = \sum_p \varepsilon_p \langle n_p \rangle \tag{46}$$

$$= \frac{L^d}{h^d} \sum_{l=1}^{\infty} \xi \int d^d p \frac{p^2}{2m} \exp\left(-\frac{p^2 l}{2mk_B T}\right) \tag{47}$$

and doing the same exercise to solve the integrals again or, considering that the Bose gas is ideal and according to the equipartition theorem $E = \frac{d}{2} N k_B T$ With

$$\frac{N}{L^d} = \frac{1}{\lambda^d} g_{\frac{d}{2}}(\xi) \quad (48)$$

we directly have

$$\frac{E}{L^d} = \frac{d}{2} \frac{k_B T}{\lambda^d} g_{\frac{d}{2}}(\xi) \quad (49)$$

where we do not need a special extra term for the first term in energy that is zero anyway.

4. **(4P)** Is a Bose-Einstein condensation possible at finite temperature ($T > 0$) for one or two dimensions? Justify your answer. The total number of particles is a finite number. Thus

$$N = \frac{L^d}{\lambda^d} \sum_{l=1}^{\infty} \frac{\xi^l}{l^{\frac{d}{2}}} + \frac{\xi}{1-\xi} \quad (50)$$

has to remain finite also for $\xi \rightarrow 1$ or $\mu \rightarrow 0$ (this is when Bose Einstein condensation occurs). In one dimension we have $g_\nu(1) = \zeta(\nu)$ and $\zeta(\frac{1}{2}) = \infty$. So the first term for the number of particles diverges. Also for two dimensions there is divergence of the first term because also $\zeta(1)$ diverges.

You may need the function

$$g_\nu(\xi) = \sum_{l=1}^{\infty} \frac{\xi^l}{l^\nu} \quad (51)$$

with the following values for Riemann's zeta function for $g_\nu(1) = \zeta(\nu)$

$$\zeta(\nu) \approx \begin{cases} \infty & \nu = \frac{1}{2} \\ 2.6124 & \nu = \frac{3}{2} \\ 1.3415 & \nu = \frac{5}{2} \end{cases} \quad (52)$$

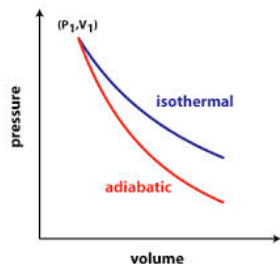
and following integrals

$$\int_0^{\infty} x \exp(-lx^2) dx = \frac{1}{2l} \quad (53)$$

$$\int_0^{\infty} \exp(-lx^2) dx = \frac{1}{2} \left(\frac{\pi}{l} \right)^{\frac{1}{2}} \quad (54)$$

(25P) Problem 4

1. (3P) Sketch the pressure, volume -diagramm for the expansion of an ideal gas from volume V_1 to



volume V_2 for

- isothermic expansion
 - adiabatic expansion
 - Is the temperature after adiabatic expansion lower, higher, or equal to that after isothermic expansion? **Temperature is lower after adiabatic expansion.**
2. (6P) How does the temperature change in a free expansion (at constant energy) $\left(\frac{dT}{dV}\right)_E$ of
- an ideal gas? **We start with the first law of thermodynamics $dE = TdS - PdV$ and further use the definition of the heat capacity and Maxwell relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ proven in Problem1:**

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV \\ &= C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \end{aligned}$$

Inserting this in the first law

$$\begin{aligned} dE &= T \left[C_V dT + \left(\frac{\partial P}{\partial T}\right)_V dV \right] - PdV = 0 \\ dE &= C_V dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV = 0 \end{aligned}$$

From this we can solve for

$$\left(\frac{dT}{dV}\right)_E = -\frac{T \left(\frac{\partial P}{\partial T}\right)_V - P}{C_V}$$

We know that for ideal gases, the energy does not depend on volume, $U = \frac{3}{2}Nk_B T$, hence $\frac{\partial U}{\partial V} = 0$ Hence $\left(\frac{dT}{dV}\right)_U = 0$ But we can see this again inserting $P = \frac{Nk_B T}{V}$

$$\begin{aligned} \left(\frac{dT}{dV}\right)_E &= -\frac{T \left(\frac{\partial P}{\partial T}\right)_V - \frac{Nk_B T}{V}}{C_V} \\ &= -\frac{T \frac{Nk_B}{V} - \frac{Nk_B T}{V}}{C_V} = 0 \end{aligned}$$

- a van-der-Waals gas? The van der Waals gas equation is

$$\left(P + a\frac{N^2}{V^2}\right)(V - bN) = Nk_B T \quad (55)$$

which solved for pressure

$$P = \frac{Nk_B T}{(V - bN)} - a \frac{N^2}{V^2} \quad (56)$$

and

$$\frac{\partial P}{\partial T} = \frac{Nk_B}{(V - bN)}$$

hence

$$\begin{aligned} \left(\frac{dT}{dV}\right)_E &= -\frac{T \frac{Nk_B}{(V-bN)} - \frac{Nk_B T}{(V-bN)} + a \frac{N^2}{V^2}}{C_V} \\ &= -\frac{a \frac{N^2}{V^2}}{C_V} \end{aligned}$$

(Hint: Use $dU = TdS - pdV$, the definition of the heat capacity C_v and Maxwell relations)

3. **(6P)** Which expansion of a gas will produce a larger amount of cooling, adiabatic expansion (with constant entropy S) $\Delta T_{Ad} = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial p}\right)_S dP$, or Joule-Thomson expansion (with constant enthalpy H) $\Delta T_{JT} = \int_{P_1}^{P_2} \left(\frac{\partial T}{\partial p}\right)_H dP$? (Hint: Use $dH = TdS + VdP$, the definition of the heat capacity C_p and Maxwell relations.) For the adiabatic expansion we start from

$$dH = TdS + VdP$$

which reduces because of $dS = 0$ to

$$dH = VdP$$

Then

$$\begin{aligned} \frac{dH}{dT} &= V \frac{dP}{dT} \\ C_P &= V \left(\frac{dP}{dT}\right)_S \end{aligned}$$

from the definition of the heat capacity. Hence

$$\left(\frac{dT}{dP}\right)_S = \frac{V}{C_P}$$

and

$$\begin{aligned} \Delta T_{Ad} &= \int_{P_1}^{P_2} \frac{V}{C_P} dP \\ &= \frac{V}{C_P} (P_2 - P_1) < 0 \end{aligned}$$

For the Joule-Thomson expansion we use the relations from below

$$\left(\frac{dT}{dp}\right)_H = \frac{T \left(\frac{\partial V}{\partial T}\right)_p - V}{C_p} \quad (57)$$

such that

$$\begin{aligned}\Delta T_{JT} &= \int_{P_1}^{P_2} \frac{T \left(\frac{\partial V}{\partial T}\right)_p - V}{C_P} dP \\ &= \frac{T \left(\frac{\partial V}{\partial T}\right)_p - V}{C_P} (P_2 - P_1) \\ &= \frac{T \left(\frac{\partial V}{\partial T}\right)_p}{C_P} (P_2 - P_1) - \frac{V}{C_P} (P_2 - P_1)\end{aligned}$$

We can use a Maxwell relation

$$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p$$

The entropy change is positive in this irreversible process, the pressure decreases, hence $\left(\frac{\partial V}{\partial T}\right)_p > 0$ and $\Delta T_{JT} = \frac{T \left(\frac{\partial V}{\partial T}\right)_p}{C_P} (P_2 - P_1) - \frac{V}{C_P} (P_2 - P_1) < 0$ It is more negative, that means more cooling by $\frac{T \left(\frac{\partial V}{\partial T}\right)_p}{C_P} (P_2 - P_1)$ compared to the adiabatic process.

4. **(5P)** Show that the Joule-Thomson coefficient $\left(\frac{\partial T}{\partial p}\right)_H$ is zero for an ideal gas (You need relations from 3.) above). Give an explanation in your own words why there is no cooling in an ideal gas.

$$\begin{aligned}dH &= TdS + VdP = 0 \\ &= T \left[\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp \right] + Vdp\end{aligned}\tag{58}$$

From the Maxwell relations we know that

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p\tag{59}$$

which together with the definition for $C_p = T \left(\frac{\partial S}{\partial T}\right)_p$ yields

$$dH = C_p dT - T \left(\frac{\partial V}{\partial T}\right)_p dp + V dp = 0\tag{60}$$

For the isenthalpic process we get

$$C_p dT = \left[\left(T \frac{\partial V}{\partial T}\right)_p - V \right] dp\tag{61}$$

and

$$\left(\frac{dT}{dp}\right)_H = \frac{T \left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}\tag{62}$$

which can also be written in terms of the expansion coefficient $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_p$ as

$$\left(\frac{dT}{dp}\right)_H = \frac{V}{C_p} (T\alpha - 1)\tag{63}$$

For ideal gases there is no effect, i.e. no temperature change upon expansion, since $T \left(\frac{\partial V}{\partial T}\right)_p = V$ and $\alpha = \frac{1}{T}$. Ideal gases do not interact, they do not “benefit” from larger volume.

5. **(2P)** A Carnot engine, operating between a low temperature T_L and a high temperature T_H converts heat into work. Which change in temperature causes a larger increase in the efficiency η_{engine} of the Carnot engine: lower T_L or higher T_H ? Justify your answer.

$$\begin{aligned}\eta &= \frac{|W|}{|Q_2|} \\ &= \frac{(T_2 - T_1)(S_2 - S_1)}{T_2(S_2 - S_1)} \\ &= 1 - \frac{T_1}{T_2} < 1\end{aligned}\tag{64}$$

To see which change has more effect, we can take the derivative ($-dT_1$ for lowering T_1)

$$\frac{d\eta}{dT_2} = \frac{T_1}{T_2^2}$$

and

$$-\frac{d\eta}{dT_1} = \frac{1}{T_2}$$

Comparing the two

$$\frac{T_1}{T_2^2} - \frac{1}{T_2} = \frac{T_1 - T_2}{T_2^2}$$

This is < 0 since $T_1 < T_2$. Therefore $\frac{T_1}{T_2^2} < \frac{1}{T_2}$. Hence, lowering the lower temperature T_1 has the larger effect (increase) in the efficiency.

6. **(3P)** A Carnot fridge uses work to cool down the temperature T_L in a cool box against the temperature T_H around it. The cooling efficiency is

$$\begin{aligned}\eta_C &= \frac{|Q_1|}{|W|} \\ &= \frac{T_1(S_2 - S_1)}{(T_1 - T_2)(S_2 - S_1)} \\ &= \frac{T_1}{T_2 - T_1}\end{aligned}\tag{65}$$

- (a) Calculate the efficiency η_{fridge} for $T_L=280\text{K}$ and $T_H=300\text{K}$.

$$\begin{aligned}\eta_C &= \frac{T_1}{T_2 - T_1} \\ &= \frac{280\text{K}}{300\text{K} - 280\text{K}} \\ &= \frac{280\text{K}}{20\text{K}} = 14\end{aligned}\tag{66}$$

- (b) Now consider a 5K larger temperature difference, i.e. either $T_L=275\text{K}$; $T_H=300\text{K}$ or $T_L=280\text{K}$; $T_H=305\text{K}$. Which combination has a larger effect on η_{fridge} . How does η_{fridge} change (increase or decrease)?

$$\begin{aligned}\eta_{fridge}^{300 \rightarrow 275} &= \frac{T_1}{T_2 - T_1} \\ &= \frac{275\text{K}}{300\text{K} - 275\text{K}} \\ &= \frac{275\text{K}}{25\text{K}} = 11\end{aligned}\tag{67}$$

and

$$\begin{aligned}\eta_{fridge}^{305 \rightarrow 280} &= \frac{T_1}{T_2 - T_1} \\ &= \frac{280K}{305K - 280K} \\ &= \frac{280K}{25K} = 11.2\end{aligned}\tag{68}$$

The first combination has a larger effect, since the efficiency is more reduced (by 3 compared to 2.8 in the second combination).