

Statistical Mechanics

Exam

3/4-2017

For this exam no books, tablets, or smartphones are allowed.

Location: 5161.0151, Time: 9:00-12:00.

Correct answers are given in blue

Norm:

The answers must be given in English.

The table below shows the number of points to be given for each of the questions. For the exam score the total score, M , is converted to the mark using the max score ($M_{\max}=54$) according to the formula $\frac{9M}{M_{\max}} + 1$. If 1/2 bonus point was earned during the problem solving session this is added and if the resulting mark is above 10 the final mark will be 10.

Subquestion	Q1	Q2	Q3	Q4
A	2	4	4	2
B	4	2	2	4
C	4	4	2	4
D	2	4	4	2
E	-	-	-	4

1 The Ideal Gas

Consider two ideal gasses each consisting of N molecules contained in their own volume V at identical temperature T . The internal energy of each gas is U_1 and U_2 and the masses are m_1 and m_2 , respectively.

A. What is the entropy of each individual gas?

This is given by the Sackur-Tetrode equation (provided on the equation sheet). The proper value of U must be used for each gas.

$$S_1 = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m_1 U_1}{3h^2} \frac{1}{N} \right)^{3/2} \right] + \frac{5}{2} \right)$$
$$S_2 = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m_2 U_2}{3h^2} \frac{1}{N} \right)^{3/2} \right] + \frac{5}{2} \right)$$

B. Derive the expression for the change in entropy when the two gasses are mixed assuming that they are different.

We thus have N_1 and N_2 both equal to N . The initial and final volumes are V and $2V$ and the temperature does not change. The internal energy, U may be different (U_1 and U_2). Before mixing the gasses the entropy is the sum of the individual values.

$$S_{\text{before}} = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m_1 U_1}{3h^2} \frac{1}{N} \right)^{3/2} \right] + \log \left[\frac{V}{N} \left(\frac{4\pi m_2 U_2}{3h^2} \frac{1}{N} \right)^{3/2} \right] + 5 \right).$$

After mixing the volume for each gas is doubled, but the gasses do not interact as they are assumed ideal. The entropy is then

$$S_{\text{after}} = k_B N \left(\log \left[\frac{2V}{N} \left(\frac{4\pi m_1 U_1}{3h^2} \frac{1}{N} \right)^{3/2} \right] + \log \left[\frac{2V}{N} \left(\frac{4\pi m_2 U_2}{3h^2} \frac{1}{N} \right)^{3/2} \right] + 5 \right).$$

The change is given by $\Delta S = S_{\text{after}} - S_{\text{before}}$

$$\Delta S = 2k_B N \log \left[\frac{2V}{V} \right] \quad (1)$$

C. Derive the expression for the change in entropy when the two gasses are mixed assuming that they are identical.

In this case $U_1 = U_2$ and $m_1 = m_2$. The entropy before is twice that of one gas in one container

$$S_{\text{before}} = 2k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2} \frac{1}{N} \right)^{3/2} \right] + \frac{5}{2} \right).$$

After mixing the volume doubled, but also the number of particles doubled, and the internal energy doubled, but we only have one container.

$$S_{\text{after}} = k_B 2N \left(\log \left[\frac{2V}{2N} \left(\frac{4\pi m}{3h^2} \frac{2U}{2N} \right)^{3/2} \right] + \frac{5}{2} \right).$$

The difference between these two expressions is

$$\Delta S = 0$$

as all the factors of 2 cancel with each other.

D. Explain the difference between the result of question B and C.

In the second case essentially nothing happened as we cannot distinguish the gas molecules of the identical gasses, while in the other case the entropy increased as the different gas molecules are allowed to mix.

2 The quantum harmonic oscillator

Consider an ensemble of independent one-dimensional quantum mechanical harmonic oscillators with the energy of each quantum level given by $E_n = \hbar\omega(n + 1/2)$. They all have the same fundamental frequency, ω .

A. Derive the expression for the partition function for one independent quantum mechanical harmonic oscillators.

$$\begin{aligned} Q_1 &= \sum_{n=0}^{\infty} e^{-\beta E_n} \\ &= \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n + 1/2)} \\ &= e^{-\beta \hbar \omega / 2} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n \end{aligned}$$

Using the geometric series (equation sheet) we get

$$Q_1 = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

B. Now consider a collection of N non-interacting harmonic oscillators. Derive the partition function.

$$Q_N = (Q_Z)^N = \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^N$$

C. Derive the Helmholtz free energy for the system.

$$\begin{aligned} A &= -k_B T \log Q_N \\ &= -k_B T \log \left(\frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}} \right)^N \\ &= \frac{N\hbar\omega}{2} + Nk_B T \log(1 - e^{-\beta\hbar\omega}) \end{aligned}$$

D. Derive the entropy of the system of non-interacting quantum mechanical harmonic oscillators.

$$\begin{aligned} S &= -\frac{\partial A}{\partial T} \\ &= Nk_B \log(1 - e^{-\beta\hbar\omega}) + Nk_B T \frac{\hbar\omega e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \left(\frac{1}{k_B T^2} \right) \\ &= Nk_B \left[-\log(1 - e^{-\beta\hbar\omega}) + \frac{\hbar\omega\beta e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}} \right] \\ &= Nk_B \left[-\log(1 - e^{-\beta\hbar\omega}) + \frac{\hbar\omega\beta}{e^{\beta\hbar\omega} - 1} \right] \end{aligned}$$

3 Phase Transitions

A. Consider a system described with the grand partition function

$$\mathcal{Q}(z, V) = (1 + z)^V (1 + z^{\alpha V}) (1 + 2z^{\beta V}), \quad (2)$$

where α and β are positive constants, z is the fugacity and V the volume. Write down the equation of state for this system (present equations for P/kT and $1/v$).

$$\begin{aligned} \frac{P}{kT} &= V^{-1} \log(\mathcal{Q}(z, V)) = \log(1 + z) + \frac{1}{V} (\log(1 + z^{\alpha V}) + \log(1 + 2z^{\beta V})) \\ \frac{1}{v} &= V^{-1} z \frac{\partial}{\partial z} \log(\mathcal{Q}(z, V)) = \frac{z}{1 + z} + \frac{\alpha z^{\alpha V}}{1 + z^{\alpha V}} + \frac{2\beta z^{\beta V}}{1 + 2z^{\beta V}} \end{aligned}$$

B. What are the roots of this grand partition function?

We have five roots: $z = -1$, $z = \exp(\pm i\pi/\alpha V)$, and $z = \exp(\pm i\pi/\beta V)/2^{1/\beta V}$.

C. In which limit will this system exhibit a phase transition and for which values of the fugacity does it happen?

When the volume goes to infinity four of the solutions will be at the real axis for $z = 1$. There will then be a phase transition when the fugacity z is 1.

D. What is the order of the phase transition(s)? Motivate your answer.

There is one first-order phase transition as the density ($1/v$) goes from from $1/2$ to $1/2 + \alpha + \beta$ passing through $z = 1$.

4 Fermi systems

Consider an ideal Fermi gas, with spin 1/2 particles. All particles have the same mass, m .

A. Give the internal energy for the gas at low temperature. The expression should explicitly give the dependence on the degeneracy.

The degeneracy of the system is 2, which enter in the expression for the Fermi energy (taken from the equation sheet).

$$U = \frac{3}{5} N \epsilon_F \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right)$$

$$U_{1/2} = \frac{3}{5}N \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2v} \right)^{2/3} \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\frac{\hbar^2}{2m} \left(\frac{6\pi^2}{2v} \right)^{2/3}} \right)^2 + \dots \right) \quad (3)$$

B. Use the Helmholtz energy of the Fermi gas to derive the pressure of the Fermi gas at low temperature. The Helmholtz energy is given as:

$$A_{1/2} = \frac{3}{5}N\epsilon_F \left(1 - \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right) \quad (4)$$

What is the pressure of the Fermi gas?

The pressure can be determined from the Maxwell equation $P = - \left(\frac{\partial A}{\partial V} \right)_T$ and $v = \frac{V}{N}$.

$$\begin{aligned} A_{1/2} &= \frac{3}{5}N \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V} \right)^{2/3} \left(1 - \frac{5\pi^2}{12} \left(\frac{k_B T}{\frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V} \right)^{2/3}} \right)^2 + \dots \right) \\ P_{1/2} &= \frac{2}{5}N \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V} \right)^{2/3} \frac{1}{V} \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V} \right)^{2/3}} \right)^2 + \dots \right) \\ P_{1/2} &= \frac{2}{5}N\epsilon_F \frac{1}{V} \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\epsilon_F} \right)^2 + \dots \right) \end{aligned}$$

C. Consider two containers, one with the spin 1/2 gas and one with a classical ideal gas connected with a freely moving piston. The number of particles, N , in the two containers is the same. Write the equation determining the volume of the Fermi gas, V_{Fermi} , given that the total volume is V_{Total} . (You do not need to isolate V_{Fermi} in the equation, but it may not explicitly depend on the volume of the classical ideal gas.)

The pressure in the two containers must be identical. We thus have

$$\begin{aligned} P_{1/2} &= \frac{2}{5}N \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V_{\text{Fermi}}} \right)^{2/3} \frac{1}{V_{\text{Fermi}}} \left(1 + \frac{5\pi^2}{12} \left(\frac{k_B T}{\frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{2V_{\text{Fermi}}} \right)^{2/3}} \right)^2 + \dots \right) \\ &= \frac{NRT}{V_{\text{Total}} - V_{\text{Fermi}}} \end{aligned}$$

D. What happens if the temperature goes to zero?

The volume of the ideal gas will be reduced to zero. (Which is unrealistic for a real physical gas.)

E. Now consider two containers, one with the spin 1/2 gas and one with a classical van der Waals gas connected with a freely moving piston. The number of particles, N , in the two containers is the same and the temperature is 0 K. What is the volume of the Fermi gas, V_{Fermi} , given that the total volume is V_{Total} ?

The pressure in the two containers must be identical. However, the pressure of the van der Waals gas at zero temperature is negative. The volume of the van der Waals gas is therefore derived

$$\left[P + a \left(\frac{N}{V_{\text{vdW}}} \right)^2 \right] \left(\frac{V_{\text{vdW}}}{N} - b \right) = RT = 0 \Leftrightarrow \\ V_{\text{vdW}} = bN$$

The volume of the Fermi gas is the:

$$V_{\text{Fermi}} = V_{\text{Total}} - bN$$

This exam has been drafted by T. L. C. Jansen and verified by T. A. Schlathölter.

Date: 24/3-2017

Signature T. L. C. Jansen:



Date: 24/3-2017

Signature T. A. Schlathölter:



Potentially useful equations

Maxwell relations:

$$P = - \left(\frac{\partial A}{\partial V} \right)_T$$

$$P = - \left(\frac{\partial U}{\partial V} \right)_S$$

$$V = \left(\frac{\partial H}{\partial P} \right)_S$$

$$V = \left(\frac{\partial G}{\partial P} \right)_T$$

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

$$S = - \left(\frac{\partial G}{\partial T} \right)_P$$

$$T = \left(\frac{\partial H}{\partial S} \right)_P$$

$$T = \left(\frac{\partial U}{\partial S} \right)_V$$

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

$$\mu = \left(\frac{\partial G}{\partial N} \right)_{P,T}$$

The thermal wavelength:

$$\lambda = \sqrt{2\pi\hbar^2/mkT}$$

The Ideal gas law:

$$PV = nRT \quad (5)$$

The van der Waas equation:

$$\left[P + a \left(\frac{n}{V} \right)^2 \right] \left(\frac{V}{n} - b \right) = RT$$

The Sacktur-Tetrode equation:

$$S = k_B N \left(\log \left[\frac{V}{N} \left(\frac{4\pi m U}{3h^2 N} \right)^{3/2} \right] + \frac{5}{2} \right)$$

The functions for the ideal Fermi gas including the low-fugacity expansions:

$$f_{5/2}(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{5/2}}$$

$$f_{3/2}(z) = \sum_{l=1}^{\infty} \frac{(-1)^{l+1} z^l}{l^{3/2}} \approx z - \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} - \frac{z^4}{4^{3/2}} + \dots$$

$$z = \frac{\lambda^3}{v} + \frac{1}{2^{3/2}} \left(\frac{\lambda^3}{v} \right)^2 + \dots$$

$$\epsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2}{gv} \right)^{2/3}$$

$$U = \frac{3}{5} N \epsilon_F \left[1 + \frac{5}{12} \pi^2 \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \right]$$

The functions for the ideal Bose gas including the low-fugacity expansions

$$g_{5/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{5/2}}$$

$$g_{3/2}(z) = \sum_{l=1}^{\infty} \frac{z^l}{l^{3/2}} \approx z + \frac{z^2}{2^{3/2}} + \frac{z^3}{3^{3/2}} + \frac{z^4}{4^{3/2}} + \dots$$

$$g_{5/2}(1) = \zeta(5/2) = 1.342 \dots$$

$$g_{3/2}(1) = \zeta(3/2) = 2.612 \dots$$

Scaling laws

Fisher: $\gamma = \nu(2 - \eta)$

Rushbrooke: $\alpha + 2\beta + \gamma = 2$

Widom: $\gamma = \beta(\delta - 1)$

Josephson: $\nu d = 2 - \alpha$

5 Mathematical relations

Geometric series valid for $x < 1$:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x}$$

$$\exp(-ax) = \sum_{n=0}^{\infty} \frac{(-ax)^n}{n!}$$

With $\log()$ the natural logarithm is considered. For $-1 < x < 1$:

$$\log(1+x) = \sum_{n=1}^{\infty} \frac{(-x)^{n+1}}{n}$$

Potentially useful constants

$$m_e = 9.10938356 \times 10^{-31} \text{ kg}$$

$$N_A = 6.022140857 \times 10^{23} \text{ 1/mol}$$

$$\hbar = 1.0545718 \times 10^{-34} \text{ Js}$$

$$k_B = 1.38064852 \times 10^{23} \text{ J/K}$$

$$c = 2.99792458 \times 10^8 \text{ m/s}$$