UNIVERSITY OF OSLO

Faculty of Mathematics and Natural Sciences

Exam in: **Fys2160**

Exam date: **Wednesday January 17, 2024**

Exam time: **15.00 - 19.00**

Number of pages: **4**

Allowed material:

- **Electronic calculator**
- **K. Rottman: Matematisk formelsamling**
- **Øgrim and Lian or Angell and Lian: Fysiske størrelser og enheter**
- **One A4 sheet of notes (both sides can be used)**

Make sure that the exam set is complete before you begin to solve the problems. You must justify your answers in the solutions.

	water	ice
Density [kg/m^3]	1000	916.2
Speed of sound [m/s]	1500	3800
Latent heat of melting [kJ/kg]		334
Latent heat of vaporization [kJ/kg]	2260	
Heat capacity [kJ/kg K]	4.186	2.108
Thermal conductivity [W / m K]	0.54	2.22
	eV/K	J/K
Boltzmann constant	$8.62 \cdot 10^{-5}$	$1.38 \cdot 10^{-23}$

Table 1: Numerical values you may need.

Problem 1: Short Questions

(a) (7 points) Explain thoroughly in words and mathematical relations, starting from fundamental principles of thermodynamics, how the melting temperature of ice changes with pressure. Explain also the signs (positive or negative) of the properties in your explanation.

Solution:
Answering this question amounts to deriving the Clausius-Clapeyron relation.

- 1 point: The solid-liquid coexistence curve in a T-P phase diagram defines how the **equilibrium** between the two phases depends on T and P.
- 1 point: Moving along the coexistence line the change in Gibbs free energy must be the same for both phases: $dG_l = dG_s$.
- 1 point: The thermodynamic identity for Gibbs free energy is $G = -SdT + VdP$
- 1 point: The slope of the coexistence line is $\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{S_l - S_s}{V_l - V_s}$
- 1 point: $\Delta S = S_l - S_s > 0$ because there is more disorder when going from a crystalline to a disordered, liquid state. (Entropies are always positive.)
- 1 point: $\Delta V = V_l - V_s < 0$ because ice floats on water (peculiarity of H_2O). (Volumes are always positive.)
- 1 point: Therefore $\frac{dP}{dT} < 0$, and $\frac{dT}{dP} < 0$ that is, the melting temperature decreases when the pressure increases.

(b) (7 points) What is the change of entropy in 1 kg of H_2O at atmospheric pressure when the temperature is reduced from 10C to -10C?

Solution:

- 1 point: Infinitesimally, the entropy change is related to heat as,

$$dS = \frac{\delta Q}{T}$$

- 1 point: For heating/cooling with no phase transition $\delta Q = CdT$
- 1 point: Thus, the entropy change is

$$dS = C \int_{T_i}^{T_f} \frac{dT}{T} \rightarrow \Delta S = C \ln\left(\frac{T_f}{T_i}\right)$$

- 1 point: For phase change $dS = L/T_m$, where L is the latent heat.
- 1 point: Correct numbers for water from 10C to 0C as in: $\Delta S = C \ln\left(\frac{T_f}{T_i}\right)$
- 1 points Correct numbers for ice from 0C to -10C as in: $\Delta S_{1,2} = C \ln\left(\frac{T_f}{T_i}\right)$
- 1 point: Correct numbers in $\Delta S = L/T$ and correct summation

(c) (3 points) The emissivity, ϵ of glass is about 0.9. You have a sheet with one black side, $\epsilon \approx 1$, and one shiny side $\epsilon \approx 0.1$ that is made to cover the windshield of your car. On warm, sunny days you can use the sheet to avoid heating your car when parked. On cold, clear winter nights you can use the sheet to slow down cooling of your car and windshield. Explain which side of the blanket should face outwards in each case and why.

Solution:
The shiny side should always face out!

- 1 point: The emissivity of a surface equals it's absorptivity.
- 1 point: Thus the shiny side will absorb only 10% of heat radiated towards it and should face out in sun radiation in summer.
- 1 point: The shiny side only radiates 10% of heat compared to a black body radiator and will therefore loose heat to the clear, cold winter sky much slower than the dark side or the glass itself.

(d) (4 points) An diatomic ideal gas in a 3D box undergoes a quasitatic isothermal compression in which its volume is reduced by 25% . Compute the work done on the system.

Solution:

- 1 point: Compression work is $dW = PdV$
- 1 point:
$$W = -\int_V^{0.75V} P(V)dV$$
- 1 point: the pressure is determined by the equation of state of the ideal gas
$$P = \frac{NkT}{V}$$
- 1 point: Thus,
$$W = -NkT\int_V^{0.75V} \frac{dV}{V} = NkT\ln(\frac{4}{3})$$

(e) (4 points) Using the same gas compression as above, compute the internal energy in the initial and final state. Discuss each step in your calculation. What is the change in the internal energy during the isothermal compression?

Solution:

- 1 point: The internal energy of the ideal gas depends only on its kinetic energy.
- 1 point: Through the equipartition of energy, the kinetic energy is given in units $kT/2$ thermal energy per degree of freedom.
- 1 point: For a diatomic gas, there are 3 translational degrees of freedom plus 2 rotational degrees of freedom per particle. Thus, $f = 5$.

- 1 point: Since the temperature is the same in the initial and final states, the internal energy is also the same

$$U_1 = \frac{f}{2}NkT = \frac{5}{2}NkT = U_2$$

Thus,

$$\Delta U = 0$$

(f) (3 points) How much heat is exchanged during the isothermal compression discussed in the previous 2 questions? Discuss the heat exchange and entropy change during this process.

Solution:

- 1 point: From the first law of thermodynamics

$$Q = \Delta U - W = -W$$

- 1 point:

$$Q = -W = -NkT\ln(\frac{4}{3}) < 0$$

This means that the energy received in the form of work done on the system is released to a thermal reservoir as heat because the process is isothermal.

- 1 point: For a quasistatic process the heat is also related to change in entropy, thus

$$Q = T\Delta S = -NkT\ln(\frac{4}{3}) < 0$$

so entropy is lower in the compressed final state.

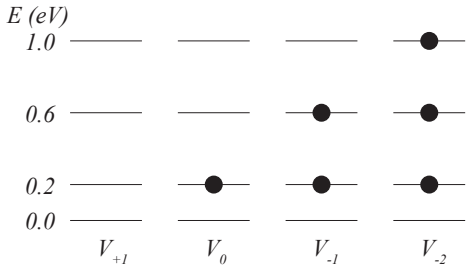


Figure 1: Illustration of how the occupation of various energy levels gives various charges for a vacancy.

Problem 2: Charged vacancies

Consider a crystalline lattice where the empty lattice sites are called vacancies. These vacancies can be occupied by electrons independently of each other. We assume that the vacancy can have four possible charge configurations with net charge $+1, 0, -1, -2$ when different levels are occupied by electrons. The energy levels are sketched in Figure 1.Let us introduce $\epsilon = 0.2$ eV, such that the energy levels are then 0, ϵ, 3ϵ , 5ϵ. Thus, each vacancy has four charge-states labelled as V_1, V_0, V_{-1}, V_{-2}.

Assume that the energy for the unoccupied vacancy is zero. Ignore the spin of the electron.

(a) (4 points) Compute the Gibbs sum $Z_G(\epsilon, T, \mu)$ of one vacancy as the Gibbs sum depending on energy level ϵ, temperature T and chemical potential μ. Show that it reduces to

$$Z_G = 1 + e^{\frac{\mu-\epsilon}{kT}} + e^{\frac{2(\mu-2\epsilon)}{kT}} + e^{\frac{3(\mu-3\epsilon)}{kT}} \ .$$

Solution:
The system is a vacancy in thermal and diffusive equilibrium with all the electrons in the crystal.

- 2 points: We can therefore form Gibbs sum for one vacancy, where the number of particles is the number of electrons bound to the vacancy.

State	s	V_{+1}	V_0	V_{-1}	V_{-2}
Electrons	N	0	1	2	3
Energy	$\sum_{s(N)} \varepsilon(s)$	0	ϵ	$(1+3)\epsilon = 4\epsilon$	$(1+3+5)\epsilon = 9\epsilon$

- 1 point: The general expression for the Gibbs sum is

$$Z_G = \sum_N \sum_{s(N)} \exp((N\mu - \varepsilon(s(N)))/kT) \tag{1}$$

- 1 point: The Gibbs sum is therefore (show calculation)

$$Z_G = 1 + e^{\frac{\mu-\epsilon}{kT}} + e^{\frac{2(\mu-2\epsilon)}{kT}} + e^{\frac{3(\mu-3\epsilon)}{kT}} \ . \tag{2}$$

(b) (6 points) Compute the average occupation $\langle N \rangle$ of the charge state of the vacancy. Show that when the chemical potential for electrons, $\mu = 0.2$ eV and at room temperature, the average occupation reduces to

$$\langle N \rangle \simeq \frac{1}{2} \ . \tag{3}$$

Solution:

- 1 point: We find the average number, $\langle N \rangle$ from $\langle N \rangle = \sum_N NP(N)$
- 1 point: $P(N) = \frac{\exp((N\mu - \epsilon(s(N)))/kT)}{Z_G}$
- 1 point:

$$\langle N \rangle = \sum_N \sum_{s(N)} \frac{1}{Z_G} N \exp((N\mu - \epsilon(s(N)))/kT) = \frac{0 \cdot 1 + 1 \cdot e^{\frac{\mu-\epsilon}{kT}} + 2 \cdot e^{\frac{2(\mu-2\epsilon)}{kT}} + 3 \cdot e^{\frac{3(\mu-3\epsilon)}{kT}}}{e^{\frac{\mu-\epsilon}{kT}} + e^{\frac{2(\mu-2\epsilon)}{kT}} + e^{\frac{3(\mu-3\epsilon)}{kT}}} . \tag{4}$$

- 1 point: We insert $\mu = 0.2eV = \epsilon$ and get

$$\langle N \rangle = \frac{1 + 2e^{\frac{-2\epsilon}{kT}} + 3e^{\frac{-6\epsilon}{kT}}}{1 + 1 + e^{\frac{-2\epsilon}{kT}} + e^{-\frac{6\epsilon}{kT}}} . \tag{5}$$

- 1 point: At room temperature $kT = 0.026$ eV $\ll \epsilon$, which means that the exponential terms are approximately 0.
- 1 point: This means that

$$\langle N \rangle \simeq \frac{1}{1+1} = \frac{1}{2} . \tag{6}$$

The average charge state of the vacancy therefore corresponds to having 1/2 electron on average bound to the vacancy, the charge is therefore +1/2

(c) (3 points) What is the average charge state of the vacancy when the chemical potential is instead 0.6 eV?

Solution:

- 1 point: In this case, $\mu = 0.6$ eV $= 3\epsilon$. This gives

$$\langle N \rangle = \frac{1e^{\frac{2\epsilon}{kT}} + 2e^{\frac{2\epsilon}{kT}} + 3}{1 + e^{\frac{2\epsilon}{kT}} + e^{\frac{2\epsilon}{kT}} + 1} \tag{7}$$

- 1 point:

$$\langle N \rangle = \frac{3}{2} \frac{1 + e^{\frac{2\epsilon}{kT}}}{1 + e^{\frac{2\epsilon}{kT}}} = \frac{3}{2} . \tag{8}$$

- 1 point: The charge state of the vacancy corresponds to having 3/2 electrons bound to the vacancy, and the charge of the vacancy is $-1/2$.

Problem 3: Classical ideal gas particle in 2D

Consider a classical particle of mass m moving freely with a velocity $\vec{v}$ in a finite domain in the $x-y$ plane of area $A = L^2$. The particle is at thermal equilibrium with a thermal bath at temperature T.

(a) (6 points) Compute its partition function over all possible microstates determined by varying the velocity $\vec{v}$ and position $\vec{r}$ using this formula

$$Z_1 = \frac{m^2}{h^2} \int_A d\vec{r} \int d\vec{v} e^{-E/(kT)}$$

where h is the Planck's constant and E is the energy of the particle in a given microstate at temperature T.

(*Hint: Use the Gaussian integral* $\int_{-\infty}^{+\infty} dx\, e^{-ax^2} = \sqrt{\pi/a}, \qquad a > 0$)

Solution:

- 1 point: The kinetic energy of the particle is $E = m(v_x + v_y)^2/2$.
- 1 point: Thus, the Boltzmann factor for a microstate with velocity $\vec{v}$ is

$$e^{-\beta m(v_x^2+v_y^2)/2}$$

depends only on the velocity.

- 1 point: This means that all positions are equally probable, thus the integral over space reduces to the area, $\int_A d\vec{r} = A$
- 1 point: Since the microstates are defined by $\vec{v}$ and $\vec{r}$, which are continuous variables, the partition function is an integral over the velocity space and position space, thus

$$Z_1(T) = \frac{Am^2}{h^2} \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y e^{-\beta m(v_x^2+v_y^2)/2}$$

- 1 point: The integrand function has separable variables, thus the integrals factorise into a product of identical integrals.

$$Z_1(T) = \frac{Am^2}{h^2} \left(\int_{-\infty}^{+\infty} dv_x e^{-\beta m v_x^2/2} \right)^2$$

- 1 point: Using the Gaussian integral, this reduces to

$$Z_1(T) = \frac{2\pi mkT}{h^2} A$$

(b) (3 points) Show that the partition function Z_1 computed above is determined by the thermal wavelength $\Lambda(T) = \sqrt{h^2/(2\pi mkT)}$, and reduces to the simple expression

$$Z_1(T) = \left(\frac{L}{\Lambda(T)} \right)^2$$

Considering that the partition function is the weighted sum of states, what does this expression imply?

Solution:

- 1 point: $A = L^2$, $\Lambda(T)^2 = h^2/(2\pi mkT)$, thus $Z_1(T) = \left(\frac{L}{\Lambda(T)}\right)^2$
- 2 points: The one-particle partition function is analogous to the multiplicity function for isolated system and presents the number of possible configurations of placing a particle with a thermal wavelength Λ in a square domain of linear size L. The available area is divided into unit cells of area Λ^2, thus the total number of unit cells is L^2/Λ^2.

(c) (2 points) Compute the Helmholtz free energy of the particle at temperature T.

Solution:
The free energy is

- 1 point $F_1(T) = -kT \ln Z_1$
- 1 point $F_1(T) = -2kT \ln\left(\frac{L}{\Lambda(T)}\right)$

(d) (2 points) Compute the entropy of the particle.

Solution:
There are at least two ways in which we can derive entropy. One is from its thermodynamic definition from the Helmholtz free energy:

$$S(A,T) = -\left(\frac{\partial F_1}{\partial T}\right)_A = k \ln\left(\frac{2\pi mkT}{h^2}A\right) + k = k \ln\left(\frac{A}{\Lambda^2}\right) + k$$

Alternatively, we can also use the transformation between thermodyanmic potentials:

$$F = U - ST \rightarrow S = \frac{U - F}{T} = k \ln\left(\frac{A}{\Lambda^2}\right) + k$$

where the internal energy is given by the equipartition of energy $U = 2kT/2 = kT$ (2 translational degrees of freedom in 2d).

(e) (5 points) Consider now an ideal gas of N particles treated above. Compute the total Helmholtz free energy $F_N(T)$ and the pressure $P(T)$ of the ideal gas and comment the result.

Solution:

- 1 point: The 1 particle partition function must be exponentiated by N and divided by $N!$ for gases (not distinguishable particles), thus $F_N = -kT \ln\left(\frac{Z_1^N}{N!}\right)$
- 1 point: We use Stirling's approximation of $\ln N! \approx N \ln N - N$
- 1 point: Thus, $F_N = -NkT\left[\ln\left(\frac{Z_1}{N}\right) + 1\right] = -NkT\left[\ln\left(\frac{A}{N\Lambda^2(T)}\right) + 1\right]$
- 1 point: $P = -\frac{\partial F}{\partial A} = \frac{\partial NkT \ln A}{\partial A} = \frac{NkT}{A}$
- 1 point: This is the 2-dimensional version of the ideal gas law.