UNIVERSITETET I OSLO

Det matematisk-naturvitenskapelige fakultet

Eksamen i:	FYS2160
Eksamensdag:	1. desember 2017
Tid for eksamen:	1430–1830
Oppgavesettet er på:	3 sider
Vedlegg:	ingen
Tilatte hjelpemidler	Elektronisk kalkulator, godkjent for videregående skole Rottman: Matematisk formelsamling Øgrim og Lian: Fysiske størrelser og enheter To A4 ark med notater (det kan være skrift på begge sider av arket)

English version

You have to justify your answers

Oppgave 1

(a) The Gibbs free energy of two phases A and B of a pure substance are equal at the coexistence line in a phase diagram: $G_A = G_B$. Explain why the coexistence line is inclined.

$$\frac{dP}{dT} = \frac{S_A - S_B}{V_A - V_B} \tag{1}$$

where S_X is the entropy and V_x is the volume of the phase X.

Løsning:
Along the coexistence line $dG_A = dG_B$. Using the TDI:

$$-S_A dT + V_A dP = -S_B dT + V_B dP$$

and

$$\frac{dP}{dT} = \frac{S_B - S_A}{V_B - V_A}.$$

Unless there is no difference in the entropy between the two phases (or both entropies are zero) the coexistence line must be inclined (not vertical or horizontal).

(b) For "ordinary substances there are coexistence lines between gas-liquid, gas-solid, liquid-gas and between different crystalline solid phases. Why does only the coexistence line between gas and liquid end in a critical point? (All the other coexistence lines end in another coexistence line or in (TPV) equals zero or infinity:)

Løsning:
Fordi væske og gass er de eneste fasene som har samme symmetri. Siden de har samme symmetri kan man gå fra den ene fasen til den andre uten å krysse en fasegrense. Derfor må fasegrensen ende et sted. Det stedet er det kritiske punktet.

(c) Explain the principle of corresponding states.

Løsning:

(d) Do systems obeying the 1) ideal gas 2) van der Waals equation of state have a critical point?

Løsning:
Ideell gass har ikke flere faser og derfor ikke noe kritisk punkt. Den deriverte

$$dP/dV = -NkT/V^2 \tag{2}$$

kan aldri bli positiv slik som for vdW.

For ideal mixtures the density, $N_i/V_i = N/V$ is independent of the mixture composition, $x_i = N_i/N$, where N_i is the number of particles and V_i is the volume of component i and $N = \sum_i N_i$ is the total number of particles and $V = \sum_i V_i$ is the volume of the mixture. The entropy change of component i in an ideal mixture only depends on the volume available for i before and after mixing:

$$\Delta S_i = kN_i(\ln V - \ln V_i) \tag{3}$$

(e) Show that the chemical potential for component i in an ideal mixture is

$$\mu_i(x_i, T) = \mu_i^*(T) + kT \ln x_i \tag{4}$$

Løsning:
Denne løsningen skal jeg forenkle

$$\Delta S_i = kN_i \ln V/V_i \tag{5}$$

$N_i/V_i = N/V \Rightarrow V/V_i = N/N_i$

$$\begin{aligned} \Delta S_{tot} &= k\sum_i N_i \ln V/V_i & (6)\\ &= k\sum_i N_i \ln N/N_i & (7)\\ &= -kN\sum_i x_i \ln x_i & (8) \end{aligned}$$

$dx_i/dN_i = 1/N \Rightarrow dN_i = Ndx_i$

$$\mu_i = -T\left(\frac{\partial S}{\partial N_i}\right)_{E,V,N_{j\neq i}} = -\frac{T}{N}\left(\frac{\partial S}{\partial x_i}\right)_{E,V,x_{j\neq i}} = \mu_i^0 + \frac{T}{N}\left(\frac{\partial \Delta S}{\partial x_i}\right)_{E,V,x_{j\neq i}} \tag{9}$$

$\partial x_i \ln x_i/\partial x_i = \ln x_i + 1$

$$\mu_i = \mu_i^0 + kT + kT \ln x_i = \mu_i^* + kT \ln x_i \tag{10}$$

Oppgave 2

A rubber band of length $L(T) = l_0(T) + l(T)$ is stretched with a force f at each end. When $f = 0$ the length is $L = l_0$ and when $f > 0$ the dilatation is $l > 0$.

(a) Write an expression for the thermodynamic identity of the rubber band.

Løsning:
Vanligvis er $W = -PdV$, her er $W = fdl$, dvs. at f tilsvarer $-P$ og l tilsvarer V. 1. lov: $dU = Q + W$, TDI: $dU = TdS - PdV$ blir nå $dU = TdS + fdl$

(b) Show that the thermodynamic identity for the Helmholtz free energy, F, can be written

$$dF = fdl - SdT \tag{11}$$

Løsning:
$F = U - TS$

$$\begin{aligned} dF &= dU - TdS - SdT && (12)\\ &= TdS + fdl - TdS - SdT && (13)\\ &= fdl - SdT && (14) \end{aligned}$$

(c) Show that the force f for a given dilatation l can be written as a derivative of Helmholtz free energy:

$$f = \left(\frac{\partial F}{\partial l}\right)_T \tag{15}$$

and by the entropy:

$$f = -T\left(\frac{\partial S}{\partial l}\right)_E . \tag{16}$$

Løsning:
N holdes konstant fordi massen til strikken ikke endres.

$$\begin{aligned} dF &= fdl - SdT && (17)\\ &= \left(\frac{\partial F}{\partial l}\right)_{T,N} dl - \left(\frac{\partial F}{\partial T}\right)_{l,N} dT && (18)\\ \Rightarrow\ f &= \left(\frac{\partial F}{\partial l}\right)_{T,N} && (19) \end{aligned}$$

$$\begin{aligned} dU &= TdS - fdl \qquad \Rightarrow && (20)\\ dS &= dU/T - fdl/T && (21)\\ &= \left(\frac{\partial S}{\partial E}\right)_{l,N} dE - \left(\frac{\partial S}{\partial l}\right)_{T,N} dl && (22)\\ \Rightarrow\ f &= -T\left(\frac{\partial S}{\partial l}\right)_{E,N} && (23) \end{aligned}$$

We will now use a microscopic model of the rubber band made of a polymer. Assume the polymer being stretched consistes of N monomers of length δ The monomers are attached to each other andcan extend either to the right or to the left. That is, each monomer has two possible states

$$s_i = \begin{cases} +1 & \text{høyre} \\ \text{-1} & \text{venstre} \end{cases} \tag{24}$$

that are equally probable. When the rubber band is stretched some of the turns (change of direction between neighbours) are straightened out. The dilatation of the rubber band is then $l = \delta \sum_i s_i$.

(d) If N_h is the number of monomers directed to the right show that the multiplicity of the rubber band is

$$\Omega(N_h, N) = \binom{N}{N_h} \tag{25}$$

and use Stirling's approxmation $\ln(N!) \approx N \ln N - N$ to find the entropy.

(26)

Løsning:
Hvis vi setter $s_i' = (s_i + 1)/2 = 1$ for høyre og 0 for venstre så er det tydelig et binært problem med N plasser der N_h "partikler" kan plasseres på $\binom{N}{N_h}$ måter. (Eller N plasser der N_h skal velges.) Derfor er

$$\begin{aligned}
\Omega(N_h, N) &= \binom{N}{N_h} = \frac{N!}{N_!(N - N_h)!} && (27)\\
S &= k \ln \Omega && (28)\\
&= k \ln(N!) - \ln(N_h!) - \ln((N - N_h)!) && (29)\\
&= k(N \ln N - N_h \ln N_h - (N - N_h) \ln(N - N_h)) && (30)
\end{aligned}$$

(e) show that the force is given by

$$f = \frac{kT}{2\delta} \ln \frac{N\delta + l}{N\delta - l} \tag{31}$$

Løsning:

$$f = -T \left(\frac{\partial S}{\partial l} \right)_{E,N} \tag{32}$$

$l/\delta = \sum_i s_i = N_h - N_v$, $N = N_h + N_v$, $N + l/\delta = 2N_h$, $\Rightarrow N_h = (N + l/\delta)/2$

$$\left(\frac{\partial S}{\partial l} \right)_{E,N} = \left(\frac{\partial S}{\partial N_h} \right)_{E,N} \left(\frac{\partial N_h}{\partial l} \right)_{E,N} = \frac{1}{2\delta} \left(\frac{\partial S}{\partial N_h} \right)_{E,N} \tag{33}$$

$$\begin{aligned}
\frac{\partial S}{\partial N_h} &= k(-\ln N_h - 1 + \ln(N - N_h) + 1) && (34)\\
&= k(\ln(N - N_h) - \ln N_h) && (35)\\
&= k \ln(\frac{N}{N_h} - 1) && (36)\\
\Rightarrow \quad f &= -\frac{kT}{2\delta} \ln \frac{N - N_h}{N_h} = f = \frac{kT}{2\delta} \ln \frac{N\delta + l}{N\delta - l} && (37)
\end{aligned}$$

(f) Show that when the polymers are curled up ($l << N\delta$) the rubber band follows Hooke's law, that is, the dilatation is proportional to the force. Find the spring constant.

Løsning:

$$f = \frac{kT}{2\delta}\ln\frac{1+\epsilon}{1-\epsilon}, \qquad \epsilon = \frac{l}{N\delta} \tag{38}$$

$$= \frac{kT}{2\delta}(2\epsilon + 2\epsilon^3/3 + \ldots) \tag{39}$$

$$= \frac{kT\epsilon}{\delta} = \frac{kT}{N\delta^2}l = cl \tag{40}$$

fjærkonstant $$c = \frac{kT}{N\delta^2} \tag{41}$$

(g) If we suspend a weight in the rubber band and heat the rubber band, will the weight not move, move up or move down? Justify your answer.

Løsning:
Fjærkonstanten øker med temperaturen. Det fører til at når strikken varmes opp vil strikken trekke seg sammen og loddet bevege seg oppover.

We wish to understand the relation between the entropy and the dilatation of the rubber band to analyse the heat flow in/out of the rubber band. We still assume that ($l << N\delta$).

(h) Use a Maxwell relation to show that

$$\left(\frac{\partial S}{\partial f}\right)_T = -\frac{l}{T} \tag{42}$$

Løsning:

(i) When the rubber band is stretched slowly, will there be heat flowing into the band, out of the band or will there be no heat flow? Justify your answer.

Løsning:

(j) Draw a cyclic process in a $f - L$-diagram where the force $f = 0$ in state 1) and 3) and $f > 0$ in state 2). Along the path 1)→2) the rubber band is stretched slowly. Along the path 2)→3) the force is quickly reduced. Along the path 3)→1) the force on the rubber band is not changed. Indicate the heat flow, the type of process of each path and justify the shape of the path (straight, curved...)

Løsning:

The analysis of the rubber band model shows that the force is related to the entropy, that is, how ordered the polymer is. In order to test if the internal energy matters we wil make a model where each monomer has the energy $\delta\epsilon$ independent of s_i. This signifies that the (total internal) energy of the polymer in state i is $\epsilon_i = N\delta\epsilon$. We may now write the partition function as

$$Z = \sum_i e^{-\epsilon_i/kT} = \Omega(N_h, N)e^{-N\delta\epsilon/kT}. \tag{43}$$

(k) Use the partition function to find an expression for the force and compare to the expression we found for the microcanonical ensemble. Comment the result.

Løsning:

(44)

Dette betyr at denne fjærkraften er rent entropisk og har ikke noe energibidrag.

Oppgave 3

In this problem we will study a one dimensional electron gas. The energy states of an electron (a Fermion) in a one dimensional box of length L is given by

$$\epsilon_n = an^2 \ , \ n = 1, 2, \dots \ , \tag{45}$$

where

$$a = \frac{\hbar^2}{2m}\left(\frac{\pi}{L}\right)^2 \ . \tag{46}$$

(a) Find the density of states $g(\epsilon)$ of the system.

Løsning:
Vi finner tilstandstettheten ved å ta utgangspunkt i at i n-rommet er tilstandstettheten 2: For hver n-verdi har vi to tilstander svarende til de to spinntilstandene til et Fermion, slik at $g(n) = 2$. Vi finner tilstandstettheten i energirommet ved

$$g(\epsilon)d\epsilon = g(n)dn \ , \tag{47}$$

$$g(\epsilon) = g(n)\frac{1}{d\epsilon/dn} = \frac{2}{2an} \ , \tag{48}$$

hvor $n = \sqrt{\epsilon/a}$ gir

$$g(\epsilon) = \frac{g(n)}{d\epsilon/dn} = \frac{2\sqrt{a}}{2a\sqrt{\epsilon}} = \frac{1}{\sqrt{a\epsilon}} \ . \tag{49}$$

(b) Find the Fermi-energy of the system.

Løsning:
Fermi-energien ϵ_F er det kjemiske potensialet ved $T = 0$. Ved $T = 0$ er alle tilstander opp til og med ϵ_F besatt, slik at

$$\begin{aligned} N &= \int_0^\infty g(\epsilon) f(\epsilon, \mu, T) d\epsilon \\ &= \int_0^{\epsilon_F} g(\epsilon) d\epsilon \\ &= \int_0^{\epsilon_F} (a\epsilon)^{-1/2} \, d\epsilon \\ &= a^{-1/2} 2\epsilon_F^{1/2} \ . \end{aligned} \tag{50}$$

Dette gir

$$\epsilon_F = \frac{1}{4}N^2 a \ , \tag{51}$$

We will now study the system at low temperatures. At low temperatures we may assume that $\mu \simeq \epsilon_F$ and that $kT \ll \epsilon_F$. We may approximate the heat capacity of the gas by

$$C_V \simeq g(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{\partial f}{\partial T} d\epsilon \,, \tag{52}$$

where f is the Fermi-Dirac distribution function.

(c) Justify the expression for C_V. Use the expression to show that the heat capacity at low temperatures has the form $C = \alpha T^m$, and determine the constants α and m.

Løsning:
For å begrunne uttrykket er det tilstrekkelig å se på to aspekter av uttrykket.

Vi finner varmekapasisteten fra energien U:

$$C_V = \frac{d}{dT} \int_0^\infty \epsilon g(\epsilon) f(\epsilon, \mu, T) d\epsilon = \int_0^\infty \epsilon g(\epsilon) \frac{df(\epsilon, \mu, T)}{dT} d\epsilon \,. \tag{53}$$

Når T er liten er den deriverte av step-funksjonen f ikke-null i kun et lite område rundt ϵ_F. Vi kan derfor anta at $g(\epsilon)$ er konstant og lik $g(\epsilon_F)$ i dette området. Vi kan derfor sette $g(\epsilon_F)$ utenfor integralet.

Den andre delen av uttrykket finner vi fra N:

$$N = \int_0^\infty g(\epsilon) f(\epsilon, \mu, T) d\epsilon \,, \tag{54}$$

mens $dN/dT = 0$, slik at $\epsilon_F dN/dT = 0$ og vi kan derfor legge dette inn i likningen for C_V uten å endre den. Dermed har vi begrunnet uttrykket.

Så skal vi bruke uttrykket til å finne C_V i dette tilfellet. For å gjøre det trenger vi å finne df/dT når vi antar at $\mu = \epsilon_F$ slik at all T-avhengighet er i det eksplisitte T-leddet i $f(\epsilon, \epsilon_F, T)$. Vi finner

$$C_V = g(\epsilon_F) \int_0^\infty \frac{(\epsilon - \epsilon_F)^2}{kT^2} \frac{e^{(\epsilon - \epsilon_F)/kT}}{\left(e^{(\epsilon - \epsilon_F)/kT} + 1\right)^2} d\epsilon \,. \tag{55}$$

Vi endrer variabel til $x = (\epsilon - \epsilon_F)/kT$ og får:

$$C_V = g(\epsilon_F) \int_{-\epsilon_F/kT}^\infty \frac{x^2 (kT)^3}{kT^2} \frac{e^x}{(e^x + 1)^2} dx \,. \tag{56}$$

Siden $\epsilon_F \gg kT$ kan vi sette den nedre grensen i integralet til null:

$$C_V = g(\epsilon_F) k^2 T \int_0^\infty \frac{x^2\, e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3} g(\epsilon_F) k^2 T \,. \tag{57}$$

Vi kan nå sette inn for $g(\epsilon_F) = N^2 a/4$ som gir

$$C_V = \frac{\pi^2}{3} (\epsilon_F a)^{-1/2} k^2 T = \alpha T \,. \tag{58}$$

Vi ser at C_V er lineær i T slik at $m = 1$ og at konstanten α er

$$\alpha = \frac{\pi^2}{3} (\epsilon_F a)^{-1/2} k^2 \,. \tag{59}$$

If we stretch the one dimensional electron gas a distance ΔL with a force K we perform the work $W = K \Delta L$ on the gas.

(d) Find the thermodynamic identity of the system

Løsning:
Vi vet at den termodynamiske identiteten generelt er

$$TdS = dU + dW - \mu dN \ , \tag{60}$$

hvor dW er arbeidet utført på systemet. I dette tilfellet er $dW = KdL$ slik at vi får

$$TdS = dU + KdL - \mu dN \ . \tag{61}$$

(e) Find an expression for the entropy S of the system.

Løsning:
Vi finner entropien ved å integere opp varmekapasiteten:

$$S(T) - S(0) = \int_0^T \frac{C_V}{T} dT = \alpha T \ , \tag{62}$$

hvor vi merker oss at α avhenger av både N og L og at $S(0) = 0$ fra termodynamikkens tredje hovedsetning, slik at

$$S = \alpha(L, N)T \ . \tag{63}$$

(f) Find an expression for the energy U of the system.

Løsning:

$$U = \frac{2}{3\sqrt{a}} \epsilon_F^{3/2} + \alpha T^2/2. \tag{64}$$

(g) Find the equation of state of the system.

(h) *(This problem counts twice)* Sketch a Carnot cycle with this system as the medium in a $K - L$ diagram. Explain all the sub processesand find the efficiency of the machine.