

This is a closed-book/notes exam. You are allowed only blank sheets of paper and a writing implement. *Begin each problem on a separate page.* Before submitting your papers make certain that each sheet has your name on it.

Express your answers in terms of the given variables and standard constants. Credit for clear and complete solutions/answers only.

(check blackboard for possible amendments/additional information)

- (10 points) (a) Write the First law of thermodynamics and account for each term briefly. (b) Write the fundamental thermodynamic relation (differential form), including the term with number of particles. (c) Write the energy E as a function of its natural variables.
- (10 points) (a) Write the enthalpy in terms of E , P , and V . (b) What are the natural variables for the enthalpy? (c) Show that the enthalpy of a monatomic ideal gas depends only on temperature T .
- (10 points) Consider a system described by the van der Waals equation of state which expands at constant temperature from volume V_1 to volume V_2 . Assume that the density $\rho = N/V \ll 1$ over the range of volume of interest. (a) Calculate the work done on the gas to the lowest relevant order in ρ . (b) Calculate the work done on the gas under the same conditions assuming that the gas is ideal. (c) Find the difference $W_{\text{vdw}} - W_{\text{ideal}}$ and discuss the reason why this difference is positive or negative as a function of temperature.
- (10 points) Consider $N = 4$ noninteracting spins with magnetic moment μ that can point either parallel or antiparallel to the magnetic field B . If the total energy $E = -2\mu B$, (a) what are the accessible microstates and (b) the probability that a particular spin is up or down?
- (10 points) Consider $N = 9$ noninteracting spins with total energy $E = -\mu B$. (a) What is the number of up spins, (b) the number of accessible microstates, and (c) the probability that a particular spin is up or down?

Notes:

van der Waals equation of state:

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

binomial distribution:

$$P_N(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}$$

SAMPLEX MIDTERMS

- 1) a) First Law of Thermodynamics

$$E = Q + W$$

$$dE = dQ + dW$$

E is the internal energy, Q is the energy ^{transfer} from heating and W is the work done on the system

b) $dE = Tds - PdV + \mu dN - FTR$

- c) ~~if~~ since E is a state function
dE is an exact differential

$$dE = \frac{\partial E}{\partial s} ds + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial N} dN$$

$$E = E(s, V, N)$$

- 2) a) $H = E + PV$

$$dH = dE + PdV + VdP$$

from FTR

b) $dH = Tds - \cancel{PdV} + \mu dN + \cancel{PdV} + VdP$

$$dH = Tds + VdP + \mu dN$$

$$H = H(s, P, N)$$

- c) for a monoatomic gas

$$E = \frac{3}{2} NKT$$

$$PV = NKT$$

$$H = \frac{3}{2} NKT + NKT$$

$$H = \frac{5}{2} NKT$$

$$H = H(T)$$

- 3) van der Waals equation of state:

a) $\left(P + \frac{N^2}{V^2}a\right)(V - Nb) = NKT$

$$P = \frac{NKT}{V - Nb} - \frac{N^2}{V^2}a$$

$$P = \frac{N}{V}KT$$

$$P = \frac{\frac{N}{V}KT}{1 - \frac{Nb}{V}} - \frac{N^2}{V^2}a$$

$$P = \frac{\rho KT}{1 - \rho b} - \rho^2 a$$

$$\frac{1}{1 - \rho b} \approx 1 + \rho b$$

$$P = \rho KT(1 + \rho b) - \rho^2 a$$

$$P = \rho KT + \rho^2 bKT - \rho^2 a$$

$$P = \frac{N}{V}KT + \frac{N^2}{V^2}bKT - \frac{N^2}{V^2}a$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \left(\frac{N}{V}KT + \frac{N^2}{V^2}bKT - \frac{N^2}{V^2}a \right) dV$$

$$W = -NKT \ln V \Big|_{V_1}^{V_2} + \frac{N^2 b KT}{V} \Big|_{V_1}^{V_2} - \frac{N^2 a}{V} \Big|_{V_1}^{V_2}$$

$$W = -NKT \ln \left| \frac{V_2}{V_1} \right| + N^2 b KT \left(\frac{1}{V_2} - \frac{1}{V_1} \right) - N^2 a \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$$W = -NKT \ln \left| \frac{V_2}{V_1} \right| + N^2 (KTb - a) \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

- b. For ideal gas

$$P = NKT, \quad P = \frac{NKT}{V}$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \frac{NKT}{V} dV$$

$$W = -NKT \ln \left| \frac{V_2}{V_1} \right|$$

$$W_{vdw} - W_{ideal} = N^2 (kT_b - a) \left(\frac{1}{V_2} - \frac{1}{V_1} \right)$$

$W_{vdw} \gg W_{ideal}$ in order to overcome intermolecular forces of attraction

4) $N=4$ $E_{tot} = -2\mu_B$

Given this macrostate, a particle w/ spin up has energy $E = -\mu_B$, thus for the system to obtain/satisfy energy $E = -2\mu_B$, ^{at least} 3 spins must be up and 1 down, thus total # of accessible microstates would be

$$\Omega = \binom{4}{3} = \frac{4!}{3!(4-3)!} = \frac{4 \cdot 3 \cdot 2 \cdot 1}{3 \cdot 2 \cdot 1 \cdot 1}$$

$$\Omega = 4$$

$\uparrow \uparrow \uparrow \downarrow$

$\uparrow \downarrow \uparrow \uparrow$

$\uparrow \uparrow \downarrow \uparrow$

$\downarrow \uparrow \uparrow \uparrow$

b) $P(\uparrow) = \frac{3}{4}$ $P(\downarrow) = \frac{1}{4}$

5) for $N=9$ w/ $E = -\mu_B$

a) To satisfy macrostate, there must be at least 5 spins up and 4 spins down

$$\Omega = \binom{9}{5} = \frac{9!}{5!(9-5)!} = \frac{9 \cdot 8 \cdot 7 \cdot 6 \cdot 5!}{5! \cdot 4 \cdot 3 \cdot 2 \cdot 1}$$

$$\Omega = 126$$

$$P(\uparrow) = \frac{5}{9} \quad P(\downarrow) = \frac{4}{9}$$

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1. (10 points) Determine the natural variables of the following thermodynamics potentials by direct differentiation, and the thermodynamic variables obtained directly from them:
 - (a) $H = E + PV$,
 - (b) $F = E - TS$,
 - (c) $G = F + PV$.
2. (10 points) (a) Which thermodynamic potentials are equal at $T = 0$?
 - (b) Explain each item of equality that you enumerated in part (a).
 - (c) What can you say about the heat capacity at $T = 0$? The (internal) energy, E ?
3. (10 points) (a) Find an expression that will enable you to calculate $(\partial E / \partial V)_T$ for a gas, given its (pressure) equation of state. (b) Evaluate for an ideal gas.
4. (10 points) (a) If the Legendre transform of $f(x)$ is $g(m)$, write the expression for $g(m)$.
 - (b) Obtain the Helmholtz free energy from the enthalpy by application of Legendre transformations (all potentials expressed in terms of their natural variables).
 - (c) Are there other ways of obtaining the Helmholtz free energy, F , from the enthalpy, H ? Calculate/explain.
5. (10 points) (a) Consider $N = 4$ noninteracting spins with magnetic moment μ that can point either parallel or antiparallel to the magnetic field B . If the total energy $E = -2\mu B$, (a.1) what are the accessible microstates and (a.2) the probability that a particular spin is up or down?
 - (b) Consider $N = 9$ noninteracting spins with total energy $E = -\mu B$. (b.1) What is the number of up spins, (b.2) the number of accessible microstates, and (b.3) the probability that a particular spin is up or down?

MIDTERM EXAM SOLUTION

1) a) $H = E + PV$
 $dH = dE + PdV + VdP$
 from FTR, replace dE
 $dH = (Tds - PdV + \mu dN) + PdV + VdP$
 $dH = Tds + VdP + \mu dN$
 $H = H(S, P, N)$
 since H is a state function, it follows:

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,N} dS + \left(\frac{\partial H}{\partial P}\right)_{S,N} dP + \left(\frac{\partial H}{\partial N}\right)_{S,P} dN$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N}, \quad V = \left(\frac{\partial H}{\partial P}\right)_{S,N}, \quad \mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}$$

b) $F = E - TS$
 $dF = dE - Tds - SdT$
 from FTR, replace dE
 $dF = (Tds - PdV + \mu dN) - Tds - SdT$
 $dF = -SdT - PdV + \mu dN \quad F = F(T, V, N)$

F is a state function so that:

$$dF = \left(\frac{\partial F}{\partial T}\right)_{V,N} dT + \left(\frac{\partial F}{\partial V}\right)_{T,N} dV + \left(\frac{\partial F}{\partial N}\right)_{T,V} dN$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}$$

c) $G = F + PV$
 $dG = dF + PdV + VdP$
 $dG = dE - Tds - SdT + PdV + VdP$
 replace dE via FTR
 $dG = Tds - PdV + \mu dN - Tds - SdT + PdV + VdP$
 $dG = -SdT + VdP + \mu dN$
 $G = G(T, P, N)$

G is a state function so:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,N} dT + \left(\frac{\partial G}{\partial P}\right)_{T,N} dP + \left(\frac{\partial G}{\partial N}\right)_{T,P} dN$$

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

2) a) From the relations of thermodynamic potentials

$$H = E + PV$$

$$F = E - TS$$

$$G = F + PV$$

at $T=0$, automatically, we see that $F = E$ and replacing this in $H = E + PV$
 $H = F + PV = G$
 $H = G$

$$E = TS - PV; E = -PV$$

$$H = -PV + PV = 0 = G$$

b) The Helmholtz free energy is equal to the internal energy of the system at $T=0$. since for this state, E is only a function of the work done on the system we find that Gibbs free energy and Enthalpy approaches 0 at $T=0$.

c) At $T=0$, we find that $\lim_{T \rightarrow 0} S = 0$ as per the third law of thermodynamics and from the relation

$$ds = \frac{dq}{T} = \frac{cdT}{T} \quad (\text{where } c \text{ is heat capacity})$$

Then c must also approach 0. The change in internal energy of the system ($dE = Tds - PdV$) would only be a function of the work done on the system.

3) using thermodynamic relation

$$F = E - TS$$

$$dF = dE - Tds - SdT$$

$$dF = -SdT - PdV + \mu dN$$

$$F = F(T, V, N)$$

$$\left(\frac{\partial F}{\partial V}\right)_T = -S\left(\frac{\partial T}{\partial P}\right)_V - P$$

$$\frac{\partial}{\partial V} (E - TS) = -S\left(\frac{\partial T}{\partial P}\right)_V - P$$

$$\left(\frac{\partial E}{\partial V}\right)_T = -S\left(\frac{\partial T}{\partial P}\right)_V - P$$

from $E = E(T, P)$
 $dE = \left(\frac{\partial E}{\partial T}\right) dT + \left(\frac{\partial E}{\partial P}\right) dP$
 $\frac{\partial E}{\partial T} = T$ $\frac{\partial E}{\partial P} = V$

b) For an ideal gas

$$PV = NkT$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{\partial}{\partial T} \left(\frac{NkT}{V}\right)\right) - \frac{NkT}{V}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = T \left(\frac{Nk}{V}\right) - \frac{NkT}{V}$$

$$\left(\frac{\partial E}{\partial V}\right)_T = 0$$

a) $g(m) = f(x) - xm$
 where $m = f'(x)$

b) since $H = H(S, P, N)$ and $F = F(T, V, N)$ we first apply Legendre transform to H to change dependence of $S \rightarrow T$, obtaining $G = G(T, P, N)$ and apply another Legendre transform to G to change dependence transform to G to change dependence $P \rightarrow V$

$$G = H(S, P, N) - S \frac{\partial H}{\partial S}$$

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P, N} dS + \left(\frac{\partial H}{\partial P}\right)_{S, N} dP + \left(\frac{\partial H}{\partial N}\right)_{S, P} dN$$

noting

$$dH = dE + PdV + VdP$$

$$dH = Tds - PdV + \mu dN + PdV + VdP$$

$$dH = Tds + VdP + \mu dN$$

$$\frac{\partial H}{\partial S} = T$$

$$G = H - ST$$

$$dG = dH - SdT - Tds$$

$$dG = Tds + VdP + \mu dN - SdT - Tds$$

$$dG = -SdT + VdP + \mu dN$$

$$G = G(T, P, N)$$

$$F = G(T, P, N) - P \frac{\partial G}{\partial P}$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, N} dT + \left(\frac{\partial G}{\partial P}\right)_{T, N} dP + \left(\frac{\partial G}{\partial N}\right)_{T, P} dN$$

$$\frac{\partial G}{\partial P} = V$$

$$F = G(T, P, N) - PV$$

$$dF = dG - PdV - VdP$$

$$dF = -SdT + \mu dN - PdV$$

$$dF = -SdT + \mu dN - PdV$$

$$F = F(T, V, N)$$

c) yes, using Legendre transform changing dependence $H(S, P, N) \rightarrow F(T, V, N)$

$P \rightarrow V$ then $S \rightarrow T$

or noting $H = E + PV$

$$G = F + PV$$

$$H = E + G - F$$

$$F = E + G - H$$

$$dF = dE + dG - dH$$

$$dF = Tds - PdV + \mu dN + (-SdT - VdP + \mu dN) - (Tds - PdV + \mu dN)$$

$$dF = -SdT - PdV + \mu dN$$

$$F = F(T, V, N)$$

5) a) spin up $E = -\mu_B$

spin down $E = \mu_B$ given $E_{\text{tot}} = 2\mu_B$

at least 3 spin up and 1 down to satisfy macrostate $N=4$,

$$\binom{N}{n} = \frac{N!}{n!(N-n)!}$$

$$\binom{4}{3} = \frac{4!}{3!(4-3)!} = 4$$

$$P(\uparrow) = 3/4 \quad P(\downarrow) = 1 - P(\uparrow) = 1/4$$

b) macrostate: $N=9$, $E_{\text{tot}} = -\mu_B$

5 spin up, 4 spin down

$$\binom{9}{5} = \frac{9!}{5!(9-5)!} = \frac{9 \cdot 8 \cdot 7 \cdot 6 \cdot 5!}{5! \cdot 4!} = 126$$

$$P(\uparrow) = 5/9 \quad P(\downarrow) = 4/9$$

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Problems

- (10 points) (a) How is the uncertainty function related to the thermodynamic entropy? (b) To the statistical entropy? (c) What is the relationship of the thermodynamic entropy to the "arrow of time" (direction of time)? Explain each part briefly.
- (10 points) (a) Show that $F = -kT \ln Z$ is equivalent to $F = E - TS$. (b) What are the natural variables for F ? Show by using the fundamental thermodynamic relation. (c) What is the appropriate ensemble? Explain briefly.
- (10 points) (a) Show that for one harmonic oscillator: $f = \frac{1}{2} \hbar \omega + kT \ln(1 - e^{-\beta \hbar \omega})$. (b) Calculate the corresponding entropy. (c) What is the corresponding mean energy? What is the mean energy if there are N harmonic oscillators in equilibrium with a heat bath at temperature T ?
- (10 points) Consider an Ising chain of N spins with interaction constant J and free boundary conditions. (a) If all the spins are parallel, what is the energy of the system? (b) What is the energy change if an inner spin is flipped? (c) Is there a relationship between domain size and the energy of the chain? Explain briefly.
- (10 points) Find the form of the density of states in k -space for standing waves in (a) a two-dimensional box, and (b) in a one-dimensional box. (c) How do they compare with the three-dimensional case? Explain briefly.

FINALS (AMPLEX)

2) a) $F = -kT \ln Z$

$F = E - TS$

We can rewrite $\beta F = -\ln Z$

$$d(\beta F) = \underbrace{-\frac{1}{Z} \frac{dZ}{d\beta}}_{\bar{E}} d\beta - \underbrace{\frac{1}{Z} \frac{dZ}{dV}}_{-\beta \bar{P}} dV$$

$$d(\beta F) = \bar{E} d\beta + (-\beta \bar{P}) dV$$

$$d(\beta F) = \bar{E} d\beta + \beta d\bar{E} - \beta d\bar{P} - \beta \bar{P} dV$$

$$d(\beta F) = d(\beta E) - \beta(d\bar{E} + \bar{P} dV)$$

$$d(\beta F - \beta E) = -\beta(d\bar{E} + \bar{P} dV)$$

$$dE = T ds - P dV$$

$$d(\beta F - \beta E) = -\beta T ds$$

$$d(\beta F - \beta E) = -ds/k$$

$$\beta(F - E) = -S/k$$

$$F - E = -ST$$

$$\boxed{F = E - TS}$$

b) $dF = dE - T ds - S dT$

$$dF = T ds - P dV + \mu dN - T ds - S dT$$

$$dF = -S dT - P dV + \mu dN$$

$$F = F(T, V, N)$$

c) canonical ensemble because the macrostates specified for a canonical ensemble are T, V and N etc are the natural variables of F

1) The thermodynamic entropy is a non-exact differential defined as $ds = \frac{dQ}{T}$ and the uncertainty function

$$S(x) = A \ln x$$

$$S(\Omega) = \ln \Omega$$

note: max S (entropy) when system is at equilibrium

Arrow of time: irreversibility
presence of the quantity S
allows for a direction to be identified

3) a) For one harmonic oscillator

$$f = \frac{1}{2} \hbar \omega + kT \ln(1 - e^{-\beta \hbar \omega})$$

a harmonic oscillator:

$$E_n = (n + \frac{1}{2}) \hbar \omega, n = 0, 1, 2, 3, \dots$$

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta(n + \frac{1}{2}) \hbar \omega}$$

$$Z_1 = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega \frac{n}{2}} e^{-\beta \hbar \omega \frac{1}{2}}$$

$$\text{Let } x = e^{-\beta \hbar \omega}$$

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

$$Z_1 = e^{-\beta \hbar \omega \frac{1}{2}} \sum_{n=0}^{\infty} (e^{-\beta \hbar \omega})^n$$

$$Z_1 = \frac{e^{-\beta \hbar \omega / 2}}{1 - e^{-\beta \hbar \omega}}$$

$$f = -kT \ln Z_1$$

$$f = -kT \left[-\frac{\beta \hbar \omega}{2} + \ln(1 - e^{-\beta \hbar \omega}) \right]$$

$$\boxed{f = \frac{\hbar \omega}{2} - kT \ln(1 - e^{-\beta \hbar \omega})}$$

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

$$S = \frac{\partial}{\partial T} \left[\frac{\hbar \omega}{2} - kT \ln(1 - e^{-\hbar \omega / kT}) \right]$$

$$S = -k \ln(1 - e^{-\hbar \omega / kT}) + (kT) \frac{\hbar \omega}{kT^2} \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}$$

$$\boxed{S = -k \ln(1 - e^{-\beta \hbar \omega}) + \frac{\hbar \omega}{T} \frac{e^{-\beta \hbar \omega}}{1 - e^{-\beta \hbar \omega}}}$$

c) $\bar{E} = \frac{\partial}{\partial \beta} \ln Z_1$

$$\bar{E} = \frac{\partial}{\partial \beta} \left[-\frac{\beta \hbar \omega}{2} + \ln(1 - e^{-\beta \hbar \omega}) \right]$$

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