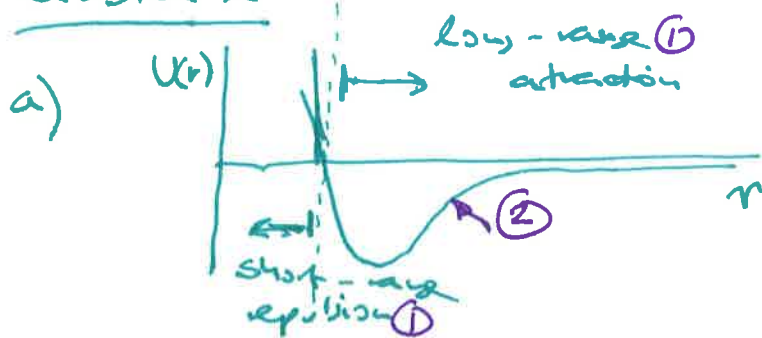


Question 1



[4]

Low-range attraction and short-range repulsion are treated separately.

Free-particle partition function is (1-particle).

$$z = \frac{V}{\Lambda^3}$$

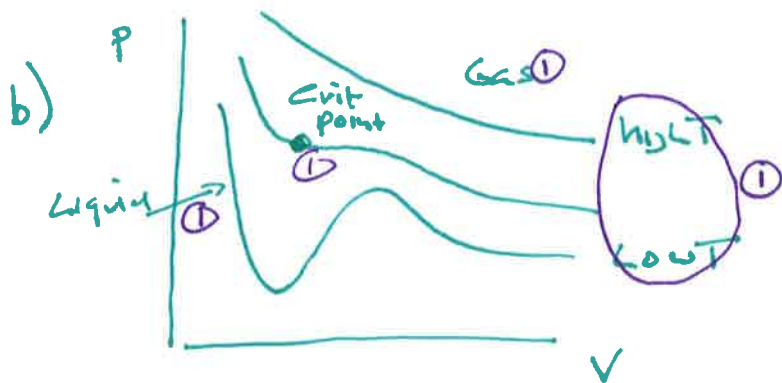
Account for low-range attraction by multiplying the P.F. by $e^{-\langle E \rangle / kT}$ where $\langle E \rangle$ is some average of the attractive potential.

Account for short-range repulsion by replacing V by $V - V_{ex}$ where V_{ex} follows from the 'hard core' of the repulsive potential.

So

$$z = \frac{(V - V_{ex}) e^{-\langle E \rangle / kT}}{\Lambda^3}$$

The vdW equation of state follows from the partition function.



At critical point the distinction between gas and liquid disappears.

[5]

Q1 Zettel.

c) At critical point

$$\left. \frac{\partial P}{\partial V} \right|_T = 0 \quad \text{and} \quad \left. \frac{\partial^2 P}{\partial V^2} \right|_T = 0 \quad (2)$$

So with VdU eqⁿ ⇒

$$P = \frac{NKT}{V - Nb} - a \frac{N^2}{V^2} \quad \# \quad (1)$$

and evaluate $\left. \frac{\partial P}{\partial V} \right|_T$, $\left. \frac{\partial^2 P}{\partial V^2} \right|_T$

set equal to zero & solve for T
Simultaneous equations for T, V_c . (1)

Subst the values of T, V into the VdU eqⁿ
to get P_c . (1) [5]

[Alternatively use the beautiful derivation of Stanley.]

d) Low density ($\frac{N}{V}$) permits like-order terms [4]
to be ignored.

e) With $\frac{NKT}{V - Nb} \approx \frac{\frac{N}{V}KT}{1 - \frac{Nb}{V}} = \frac{N}{V}KT \left[1 - \frac{Nb}{V} \right]^{-1}$

expⁿ using binomial expⁿ
 $= \frac{N}{V}KT \left[1 + \frac{Nb}{V} + \dots \right]$

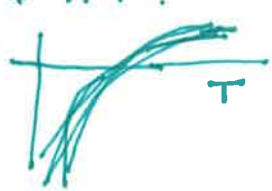
i.e. $\frac{NKT}{V - Nb} = KT \left[\frac{N}{V} + \left(\frac{N}{V}\right)^2 b + \dots \right]$

so using eq #

$$P = \frac{NKT}{V - Nb} - a \frac{N^2}{V^2} = KT \frac{N}{V} + KTb \frac{N^2}{V^2} - a \frac{N^2}{V^2} + \dots \quad [4]$$

$$\frac{P}{KT} = \frac{N}{V} + \left(\frac{N}{V}\right)^2 \left(b - \frac{a}{KT} \right) + \dots$$

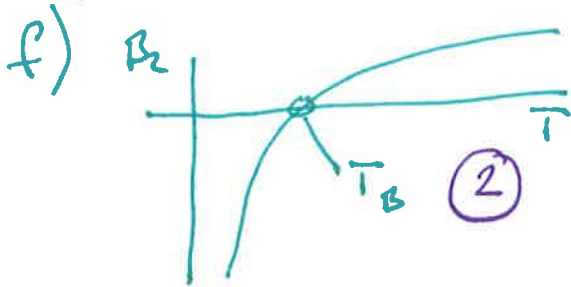
so $\beta_2(T) = b - \frac{a}{KT}$



[2]

Q, contd.

(3)



$$B_2 = 0 = b - \frac{a}{kT_B}$$

$$\text{So } kT_B = \frac{a}{b}$$

$$\text{Since } kT_c = \frac{8a}{27b}$$

$$\text{It follows that } T_c = \frac{8}{27} T_B \quad (3) \quad [5]$$

g) $T_B = 413\text{K}$ so T_c is predicted to be $\frac{8}{27} \times 413\text{K} = 122\text{K}$. (2)

Real value of T_c is 151K .

So predicted value is 19% too low. (1)

Order of magnitude it is not too bad.

Result relies on the VdW eqn of state.

So we conclude that the VdW eqn of state is not so good in the vicinity of the critical point. (1) [7]

Question 2

a) Brownian motion is the motion of a 'macroscopic' particle under the random bombardment of the atoms/molecules of the fluid in which it is immersed. (3)

While the effect of a single impact is not discernible, the slight imbalance of the result of many impacts is discernible as a random motion. The 'statistics' of this random motion permits one to infer the effect of a single impact.

The effect of 'single impacts' \Rightarrow $\frac{1}{2}mv^2$ of atoms/molecules. (4) [7]

b) Brownian particle stationary in a fluid appears no mean force. (3)

A moving Brownian particle appears more energetic impact from the front or less energetic impact from the rear.



So there is a net force against the direction of the motion. (3) [6]

c) The L.E. is an inhomogeneous 1st order ODE. The first term of the solution is the complementary function (transient response) & the second term is the Particular Integral (steady state response). (3)

At long times only the P.I. remains & the velocity depends fundamentally on the fluctuating force $F(t)$ (4) [7]

Q2 cont.

(5)

d) An overdamped oscillator of $f(t)$ gives the behavior of the average velocity of a fluctuation of f towards its mean value. (3)

Many ways it is an average of $f(t)$ weighted by its value at $t=0$. So positive fluctuations are multiplied by a positive $f(0)$ & negative fluctuations by a negative $f(0)$. So the overall average is non-zero. (4) [7]

e) Equipartition states that the average kinetic energy of a Brownian particle. And this is a classical/macroscopic object. The purpose of the fluid is simply to establish equilibrium at temperature T . [6]

f)
$$\langle v^2 \rangle = \frac{1}{M} \int_0^{\infty} \langle f(t) f(t) \rangle dt = \frac{kT}{M}$$

So
$$\frac{1}{M} = \frac{1}{kT} \int_0^{\infty} \langle f(t) f(t) \rangle dt$$
 (4)

LHS is dissipation (fluid)

RHS is fluctuation ($f(t)$)

So expression relates fluctuations to dissipation — via response plan in input-output.

The point is this is a very general result transcending the particular model here.

This is the dissipation theorem. (3) [7]

Q.3

6

a) Order parameter is a measure of the order in a system. In the ordered phase the O.P. will be non-zero. In the disordered phase the O.P. will be zero. [4]

b) Landau expansion - must be performed in order to derive the general form of the transition (in the vicinity of the critical point). However at high order terms only introduce model-dependent specific features. (3)

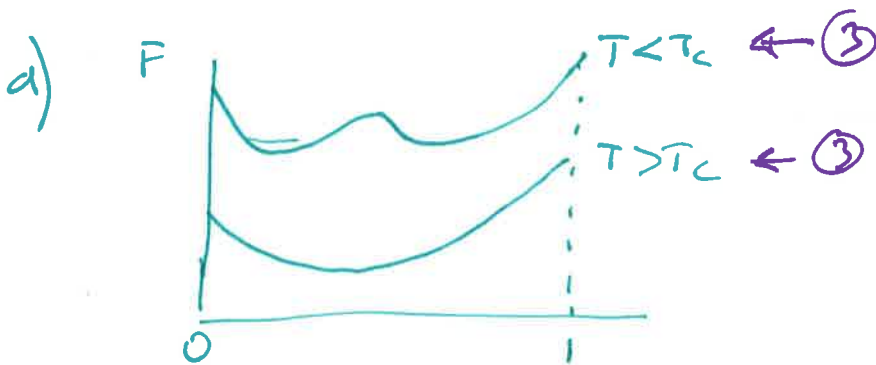
Need terms at least up to 4th order. Higher order terms must be even order with positive coefficient for stability. So if 4th order term is not positive then must go to 6th order. And so on... (3) [6]

c) Coupled O.P. - one value of the O.P. one to system is fixed - e.g. density of a fluid. (2)

Non Cou. O.P. - No interaction or one value of the O.P. e.g. - ferromagnet. (2)

Cou. O.P. - Define equlib by double tangent method.

Non Cou. O.P. - Define equlib by minimizing free energy. (2) [6]



[6]

e) First term is the energy - dep. on $x(1-x)$, αT . (3)

2nd term is the entropy - standard form for a 2-state system ($\sum P_i \ln P_i$) (3) [6]

Q3 contd.

7

f) Ternary after to 4th term, since $\frac{2}{3}T_c$'s positive. (3)

At the critical point $x_c = \frac{1}{2}$. So we need to use the O.P. to the denominator from the value at the crit. point. i.e. use $x = \frac{1}{2}$ (3) [6]

g) ~~$F_m - F_0 = f = (T - T_c) \phi^2 + \frac{2}{3} T_c \phi^2$~~

Use $f = \frac{F_m - F_0}{2NK}$ or $\phi = x - \frac{1}{2}$

equil. defined by $\frac{\partial f}{\partial \phi} = 0 = 2(T - T_c)\phi + \frac{4}{3}T_c\phi^2$

so $\phi = 0$ or $\phi^2 = \frac{2(T - T_c)}{\frac{4}{3}T_c} = \frac{3}{4} \left(\frac{T}{T_c} - 1 \right)$.

$\phi = \sqrt{\frac{3}{4} \left[\frac{T}{T_c} - 1 \right]}^{\frac{1}{2}}$ — critical exponent β . (4)

Empirically β is close to $\frac{1}{3}$.

This is because of fluctuations: Landau's mean field theory (2) shows effect of fluctuations. [6]

Quest- 4.

8

Negative Temperatures:

- * From Boltzmann factor $P \propto e^{-E/kT}$
- higher occupation of higher energy
transfers to negative temperatures. (8)
- * If higher energy states have higher occupation
then the system is an upper bound to the energy
states. (8)
- * From a state of positive energy, can
insert particles to get equivalent
negative energy. (8)
- * As well as spin systems (with an upper-bound
energy) a partially-filled band can
also exhibit negative temperatures. (8)
- * Negative temperature state has unoccupied low
energy states, so is potentially unstable/
metastable. In radiators can cause
stimulated emission. This is how a
Laser works. (8)

Q. 5

a) $S = k \ln \Omega$

S is entropy

k is Boltzmann's constant

Ω is no of microstates in macrostate. (4)

Since possible A occurrence of a macrostate is proportional to Ω , as since a system is "most likely to be found in its most probable state" it follows that the observed state will have maximal probability or is maximum. (4)

In other words a system will go to the state of maximum entropy consistent with the constraints imposed upon it. (2)

[10]



$\Omega = \Omega_1(E_1) \Omega_2(E_2)$
 $= \Omega_1(E) \Omega_2(E_T - E)$

but $E_1 + E_2 = E_T$

Maximize:

$\frac{d\Omega}{dE} = \frac{d\Omega_1}{dE} \Omega_2 - \frac{d\Omega_2}{dE} \Omega_1 = 0$

$\frac{1}{\Omega_1} \frac{d\Omega_1}{dE} = \frac{1}{\Omega_2} \frac{d\Omega_2}{dE}$
Property of System 1 Property of System 2

Q5 contd.

part 4 contd.

So in equilib

$$\frac{1}{r_1} \frac{dL_1}{dE} \text{ of system 1 is equal to}$$

$$\frac{1}{r_2} \frac{dL_2}{dE} \text{ of system 2}$$

$$\text{or } \frac{dL_1}{dE} = \frac{dL_2}{dE}$$

Obviously $\frac{dL_1}{dE}$ is related to $\frac{dL_2}{dE}$.

Since they flow from system with low $\frac{dL}{dE}$ to high $\frac{dL}{dE}$ it must be an inverse relation.

$$\text{Since } S = kL, \text{ then } \frac{dL}{dE} = \frac{1}{k} \frac{dS}{dE}$$

$$\text{we identify } \underline{\underline{\frac{1}{k} = \frac{dS}{dE}}} \quad (8)$$

Equilibrium here is identical with the most possible macrostate. (4)

[10]

Q3 Total.

(10)

c) $\frac{dS}{dE}$ gives an extremum

~~$\frac{d^2S}{dE^2}$ gives a minimum~~

$\frac{d^2S}{dE^2} < 0$ gives a maximum. (3)

$$\frac{d^2S}{dE^2} = \frac{d}{dE} \frac{1}{T} = -\frac{1}{T^2} \frac{dT}{dE}$$

so we have $\frac{1}{T^2} \frac{dT}{dE} > 0$

$$\text{or } T^2 \frac{dE}{dT} > 0 \quad (4)$$

but $\frac{dE}{dT} = C$ heat capacity.

so since $T^2 > 0$ it follows

that C must be > 0 (3)

[10]

d) If the ground state of a system is non-degenerate, then $\Omega_0 = 1$. (1)

so for the lowest energy state

$$S = k \ln \Omega_0 = 0 \quad (2)$$

Even if the ground state is not degenerate, in the thermodynamic limit, what we require is $S/N \rightarrow 0 \Rightarrow T \rightarrow 0$. (1)

You need to have discrete states - that's why Quantum Mechanics is needed. (3)

[10]

40