PH4211 2013

Outline Answers

Question 1

a) $$Z = \sum_{n=0}^{\infty} e^{-\varepsilon_i/kT} \quad \text{where} \quad \varepsilon_i = \left(\tfrac{1}{2}+n\right)\hbar\omega$$

So $$Z = e^{-\frac{\hbar\omega}{2kT}} \underbrace{\sum_{n=0}^{\infty} \left[e^{-\hbar\omega/kT}\right]^n}_{\text{A GP}}$$

Sum of GP is $\dfrac{1}{1-e^{-\hbar\omega/kT}}$

$$\Rightarrow \quad Z = \frac{e^{-\hbar\omega/2kT}}{1-e^{-\hbar\omega/kT}}$$

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

$$Z = \frac{1}{2}\,\mathrm{cosech}\,\frac{\hbar\omega}{2kT}$$ [5]

b) $$Z = \sum e^{-\beta\varepsilon_i}$$

$$\frac{\partial Z}{\partial\beta} = -\sum \varepsilon_i e^{-\beta\varepsilon_i}$$

Now $E = \sum p_i \varepsilon_i$ and $p_i = \frac{1}{Z}e^{-\varepsilon_i/kT}$

$$= \frac{1}{Z}\sum \varepsilon_i e^{-\beta\varepsilon_i}$$

so $$E = -\frac{1}{Z}\frac{\partial Z}{\partial\beta}$$

$$E = -\frac{\partial \ln Z}{\partial\beta}$$ [5]

c)

$$E = -\frac{\partial}{\partial\beta} \ln\left(\frac{1}{2}\operatorname{cosech} \hbar\omega\beta/2\right)$$

$$= -\frac{\partial}{\partial\beta}\left[\ln\frac{1}{2} + \ln \operatorname{cosec} \hbar\omega\beta/2\right]$$

$$E = -\frac{\partial}{\partial\beta} \ln \operatorname{cosech} \hbar\omega\beta/2$$

use given integral

$$= \coth\frac{\hbar\omega\beta}{2} \times \frac{\hbar\omega}{2}.$$

$$= \frac{\hbar\omega}{2}\,\frac{\cosh \hbar\omega\beta/2}{\sinh \hbar\omega\beta/2}$$

$$= \frac{\hbar\omega}{2}\,\frac{e^{\hbar\omega\beta/2} + e^{-\hbar\omega\beta/2}}{e^{\hbar\omega\beta/2} - e^{-\hbar\omega\beta/2}}$$

Mult top & bottom by $e^{\hbar\omega\beta/2}$

$$E = \frac{\hbar\omega}{2}\,\frac{e^{\hbar\omega\beta}+1}{e^{\hbar\omega\beta}-1}$$

$$= \frac{\hbar\omega}{2}\,\frac{e^{\hbar\omega\beta}-1 + 2}{e^{\hbar\omega\beta}-1}$$

$$= \frac{\hbar\omega}{2}\left\{1 + \frac{2}{e^{\hbar\omega\beta}-1}\right\}$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/kT}-1}$$

[5]

d)

$$Z = \frac{1}{h}\iint e^{-\left(\frac{p^2}{2m}+\frac{kx^2}{2}\right)\beta}\,dp\,dx$$

$$= \frac{1}{h}\int e^{-\frac{p^2}{2m}\beta}\,dp\int e^{-\frac{kx^2}{2}\beta}\,dx$$

1st integral – put $\frac{p\sqrt{\beta}}{\sqrt{2m}} = z$ so $dp = \sqrt{\frac{2m}{\beta}}\,dz$.

2nd integral – put $\sqrt{\frac{k}{2}}\,x = z$ so $dx = \sqrt{\frac{2}{k\beta}}\,dz$

so $$Z = \frac{2}{h\beta}\sqrt{\frac{m}{k}}\underbrace{\left(\int e^{-z^2}dz\right)^2}_{\pi}$$

use given integral $\longrightarrow \pi$

$$Z = \frac{2\pi}{h\beta}\sqrt{\frac{m}{k}}$$

but $\underline{\omega = \sqrt{\frac{k}{m}}}$ ← frequency

so $$\underline{Z = \frac{kT}{\hbar\omega}}$$ [5]

e) $E = -\dfrac{\partial \ln Z}{\partial \beta}$

With $Z = \dfrac{1}{\hbar\omega\beta}$

$$E = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}$$

$$= +\cancel{\hbar\omega}\beta \frac{1}{\cancel{\hbar\omega}} \frac{1}{\beta^2}$$

$$= \frac{1}{\beta}$$

$$E = kT$$

[5]

f) Take $E = \dfrac{\hbar\omega}{2} + \dfrac{\hbar\omega}{e^{\hbar\omega/kT} - 1}$

expand the exponential:

$$E = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\frac{\hbar\omega}{kT} + \left(\frac{\hbar\omega}{kT}\right)^2\frac{1}{2} + \cdots}$$

$$= \frac{\hbar\omega}{2} + \frac{\hbar\omega}{\frac{\hbar\omega}{kT}\left(1 + \frac{\hbar\omega}{2kT} \cdots\right)}$$

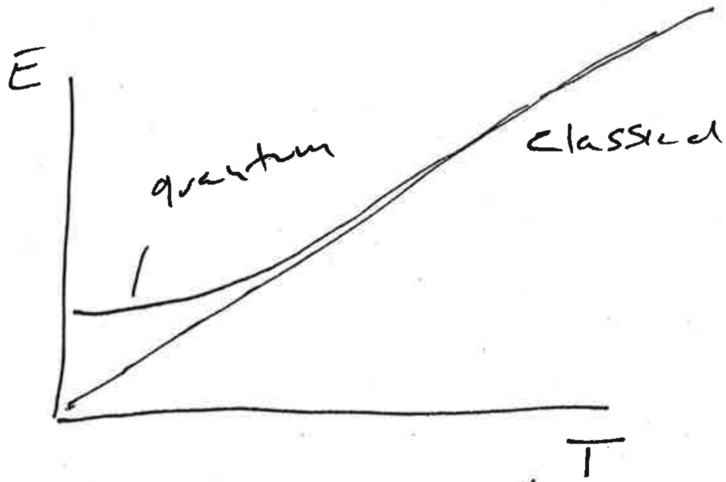
$$= \frac{\hbar\omega}{2} + kT\left[1 + \frac{\hbar\omega}{2kT} \cdots\right]^{-1}$$

$$= \frac{\hbar\omega}{2} + kT\left[1 - \frac{\hbar\omega}{2kT} + \cdots\right]$$

$$E = \cancel{\frac{\hbar\omega}{2}} + kT - \cancel{\frac{\hbar\omega}{2}} + \frac{\hbar^2\omega^2}{12kT} \cdots$$

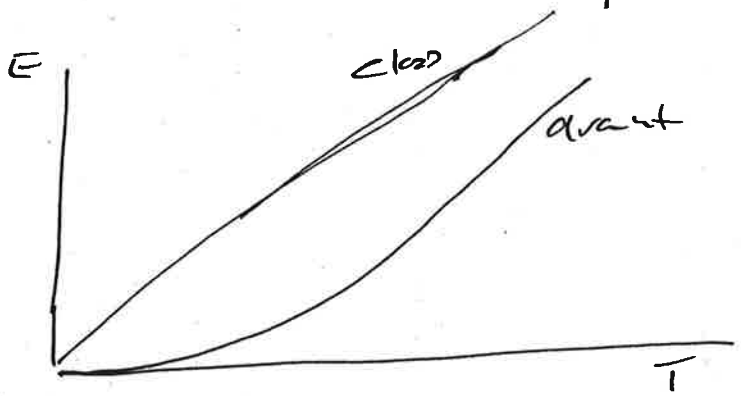
$$= kT + \frac{\hbar^2\omega}{12kT} + \cdots \qquad [5]$$

9) i



[4]

ii



[3]

iii If you ignore the zero point motion then the quantum & classical would not agree at high temp. [3]

— Correspondence principle !!

Total [40]

Question 2.

a) Order parameter: A measure of the order in the ordered phase. It will be zero in the disordered phase [4]

b) i) Ferromagnetic Case: Magnetization
ii) Ferroelectric Case Polarization [4]

c) Can only have scalar terms in the energy expansion, so must consider $\underset{\sim}{M} \cdot \underset{\sim}{M}$ or $\underset{\sim}{P} \cdot \underset{\sim}{P}$; Can't have $\underset{\sim}{M}$ or $\underset{\sim}{P}$ alone [4]

d) Must be terminated to exhibit the generic properties of the transition. Extra terms just give system-specific additions. [4]

Higher term's coefficient must be +ve to ensure system is stable / ϕ is bounded.

e) Ferromagnet:

$$F(\phi) = F_2\phi^2 + F_4\phi^4$$

$$\frac{\partial F}{\partial \phi} = 2F_2\phi + 4F_4\phi^3 = 0$$

So $\phi_0 = 0 \leftarrow$

or $F_2 + 2F_4\phi^2 = 0 \rightarrow \phi^2 = -\dfrac{F_2}{2F_4}$ [4]

So put $\phi_+ = +\sqrt{-F_2/2F_4} \leftarrow$

$\phi_- = -\sqrt{-F_2/2F_4} \leftarrow$

f) $F_2 = a(T - T_c)$ $\quad F_4 = b$

$$\frac{\partial^2 F}{\partial \phi^2} = 2F_2 + 12F_4\phi^2$$

$$= 2a(T-T_c) + 12b\phi^2$$

at roots $\pm$ $\quad \dfrac{\partial^2 F}{\partial \phi^2} = 2a(T-T_c) - \dfrac{\cancel{12}^{6}\cancel{b}\, a(T-T_c)}{\cancel{2b}}$

$$= -4a(T-T_c).$$

at root 0 $\quad \dfrac{\partial^2 F}{\partial \phi^2} = +2a(T-T_c)$

i $T < T_c$

$$\frac{\partial^2 F}{\partial \phi^2} > 0 \quad \text{at} \quad \phi_+ \text{ \& } \phi_- \qquad (4)$$

ii $T < T_c$

$$\frac{d^2 F}{d\phi^2} < 0 \quad \text{at} \quad \phi_0 \qquad (4)$$

iii $T > T_c$ ϕ_+ & ϕ_- are imaginary ∴ don't exist

ϕ_0 is real – this is the only real one. (4)

iv $T > T_c$

$$\frac{d^2 F}{d\phi^2} > 0 \quad \text{at } \phi_0 \qquad (4)$$

Explanation:

$T < T_c$ ϕ_+ & ϕ_- are the stable roots

ϕ_0 is unstable

$T > T_c$ only ϕ_0 exists (4)

and this is stable.

[20]

Total [40]

Question 3

a) $$Z = \frac{1}{N!} \iint e^{-\mathcal{H}/kT} d^{3N}p \, d^{3N}q$$

$$\mathcal{H} = \sum \frac{p^2}{2m} + U(q)$$

So $$\mathcal{H} = T + V$$

$$Z = \frac{1}{N!} \int e^{-T(p)/kT} d^{3N}p \int e^{-U(q)/kT} d^{3N}q$$

$$Z_{id} = \frac{V^N}{N!} \int e^{-T(p)/kT} d^{3N}p$$

appears from integral over q

So $$Q = \frac{1}{V^N} \int e^{-U(q)/kT} d^{3N}q$$ [8]

b) $$F = -kT \ln Z = -kT \{ \ln Z + \ln Q \}$$

$$P = -\frac{\partial F}{\partial V}\Big|_{T,N}$$

$$= kT \left(\frac{\partial \ln Z_{id}}{\partial V}\Big|_{T,N} + \frac{\partial \ln Q_N}{\partial V}\Big|_{T,N} \right)$$

$$= kT \left(\frac{N}{V} + \frac{\partial \ln Q_N}{\partial V}\Big|_{T,N} \right)$$ [8]

ideal gas bit

c) In the ratio $\frac{U}{kT}$ since U is either 0 or ∞ it cannot depend on T

So $e^{-U/kT}$ does not depend on T

Then Q does not depend on T

$\frac{\partial \ln Q}{\partial V}$ does not depend on T

— will depend on N, V

but must be intensive, so can only depend on N/V

So Virial coefficients cannot depend on T [8]

d) $$\frac{PV}{NkT} = 1 + \frac{V}{N} \left.\frac{\partial \ln Q_N}{\partial V}\right|_{T,N}$$

but σ^3 is the only value in the system.

So $\frac{V}{N} \left.\frac{\partial \ln Q_N}{\partial V}\right|_{T,N}$ must be a function of $\frac{V}{\sigma N}$ or $\frac{N\sigma}{V}$

~~D~~ Derive eqn of state from expanding Q_N in a cluster expansion.

This gives a virial expansion.

Virial coeffs B_n up to B_{10} have been determined.

Can get good eqn of state:

Carnahan + Starling or Padé. [8]

[e] Must be transition to solid at high enough ~~temperature~~ pressure — since you can't increase β here.

— Maybe amorphous solid or maybe a lattice.

There is no liquid transition — since you need an attractive force to have a self-bound system.

Molecular dynamics simulations support this.

[8]

Qustn 4

"The Arrow of Time"

* 2nd Law → entropy increase. This is an observed fact.

* Liouville's theorem says density in phase space is constant.

* But 2nd law says (essentially) that the density in phase space appears to decrease.

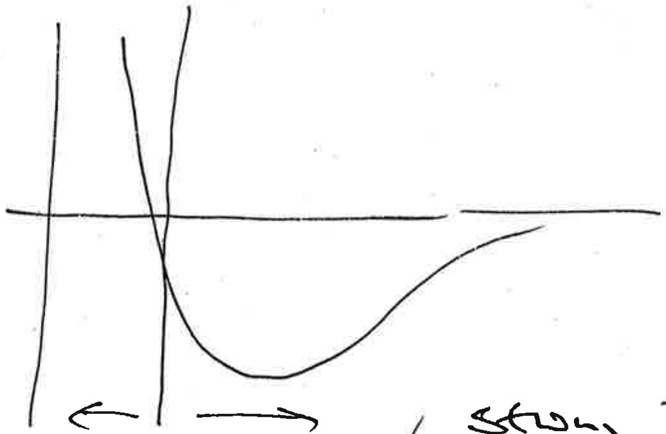
* Resolution in terms of coarse graining.

* Different explanations of coarse graining:
  1. nature of flow in phase space
  2. Possibly "fractal" – dendritic.
  3. Measure ~~seems~~ independent of the scale of the graining.
  4. Possibly use the Uncertainty Principle — but Ian Ford doesn't like this.

* Is time-reversal invariance true at the fundamental level — Beta decay or expansion of the Universe.

Question 5.

a)



separate (strong repulsion) from (weak attraction)

Repulsion → ~~excluded~~ excluded volume

Attract → add $e^{-\varepsilon/kT}$

$$\rightarrow \qquad z = \frac{V - V_{ex}}{\Lambda^3} e^{-\varepsilon/kT}$$

b) $$F = -kT \ln Z$$

but $$Z = \frac{1}{N!} z^N$$

so $$\ln Z = N \ln z - \ln N!$$

$$= N \ln z - N \ln N + N(\ln e)$$

$$= N \ln \frac{z}{Ne}$$

so $$F = -NkT \ln \frac{z}{Ne}$$

$$P = -\left.\frac{\partial F}{\partial V}\right|_{T,N}$$

$$F = -NkT\left\{\ln\left[V - V_{ex}\right] - \ln\Lambda + \frac{\varepsilon(V)}{kT}\right\}$$

$$P = \cancel{\ln}\, NkT\left\{\frac{1}{V - V_{ex}}\right\} - N\frac{\partial\varepsilon}{\partial V}$$

$$\rightarrow \left(P + N\frac{\partial\varepsilon}{\partial V}\right)\left(V - V_{ex}\right) = NkT$$

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

if $a = \frac{V^2}{N}\frac{\partial\varepsilon}{\partial V}$ & $b = \frac{V_{ex}}{N}$

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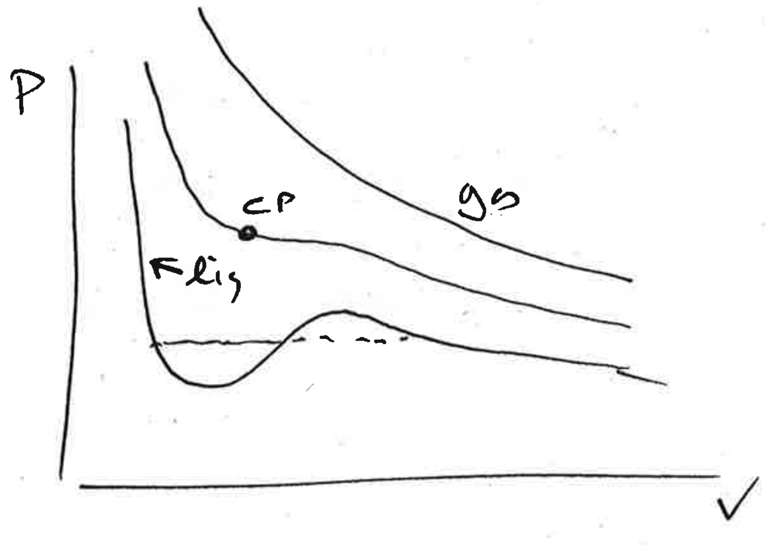
c)



d) At critical point

$$\frac{\partial p}{\partial v} = 0 \quad \underline{\text{and}} \quad \frac{\partial^2 p}{\partial v^2} = 0$$

– point of inflection.

Either grind through the differentiating and solve the equation

or use the stanley approach.

e) Deviations from ideal gas behaviour (at high-ish temp) gives the a and b parameters.

From this you can get T_c which predicts the temp <u>below which</u> you must go to get liquefaction.