

# MARKSCHEME

- 1(a). *[UNSEEN but familiar from similar questions on the Examples Sheet]*  
Given the partition function

$$Z = \frac{1}{N!} \left( \frac{mk_{\text{B}}T}{2\pi\hbar^2} \right)^{3N/2} (V - Nb)^N e^{aN^2/k_{\text{B}}TV} .$$

Helmholtz free energy :

$$F = -k_{\text{B}}T \ln Z = -k_{\text{B}}T \left[ -\ln(N!) + \frac{3N}{2} \ln \left( \frac{mk_{\text{B}}T}{2\pi\hbar^2} \right) + N \ln(V - Nb) + \frac{aN^2}{k_{\text{B}}TV} \right] .$$

Pressure :

$$p = - \left( \frac{\partial F}{\partial V} \right)_T = k_{\text{B}}T \left[ \frac{N}{V - Nb} - \frac{aN^2}{k_{\text{B}}TV^2} \right] = \frac{Nk_{\text{B}}T}{V - Nb} - \frac{aN^2}{V^2} ,$$

which is the equation of state for a van der Waals gas.

- 1(b). *[BOOKWORK]*. Given

$$U = TS - pV + \mu N .$$

Hence

$$dU = TdS + SdT - pdV - Vdp + \mu dN + Nd\mu .$$

First Law:

$$dU = TdS - pdV + \mu dN .$$

Equate the above :

$$0 = SdT - Vdp + Nd\mu .$$

Dividing by  $N$  then gives Gibbs-Duhem equation ( $s \equiv S/N$ ,  $v \equiv V/N$ ):

$$\boxed{0 = s dT - v dp + d\mu} .$$

1(c). [UNSEEN, but based on a calculation worked through in lectures]. Given

$$\left(\frac{\partial^2 F}{\partial U^2}\right)_V = \frac{1}{TC_V}.$$

Expanding  $F(U)$  about its minimum at equilibrium gives

$$F = F_0 + \frac{1}{2} \left(\frac{\partial^2 F}{\partial U^2}\right)_V (\Delta U)^2 + \dots \approx F_0 + \frac{(\Delta U)^2}{2TC_V}.$$

The probability distribution  $P(U) \propto e^{-F/k_B T}$  then corresponds to Gaussian fluctuations in internal energy with variance

$$\langle (\Delta U)^2 \rangle = k_B T^2 C_V.$$

For an ideal monatomic gas, we have  $U = C_V T = (3/2)Nk_B T$ . Hence

$$\frac{\sqrt{\langle \Delta U^2 \rangle}}{U} = \frac{\sqrt{k_B T^2 C_V}}{C_V T} = \sqrt{\frac{k_B}{C_V}} = \sqrt{\frac{2}{3N}} = \sqrt{\frac{2k_B T}{3pV}}.$$

For  $1 \text{ cm}^3$  of ideal monatomic gas at room temperature and pressure:

$$\frac{\sqrt{\langle \Delta U^2 \rangle}}{U} = \sqrt{\frac{2 \times (1.38 \times 10^{-23}) \times 300}{3 \times 10^5 \times (10^{-6})}} = \boxed{1.7 \times 10^{-10}}.$$

Comment: tiny, because  $N$  huge.

2(a). [BOOKWORK]. Non-ideal gases and the virial expansion.

Describe particle interactions by a potential  $\phi(r)$  such as the Lennard-Jones 6-12 potential. Averages involving the interaction energy can be handled using the two-particle distribution function  $P_2(\mathbf{r}_1, \mathbf{r}_2)$  which is the probability density of finding a particle at  $\mathbf{r}_1$  and another at  $\mathbf{r}_2$ . For a gas,  $P_2$  depends only on  $r_{12}$ , and can then define a radial distribution function  $g(r_{12})$ .

Using the virial theorem, can obtain the equation of state in terms of an integral over  $g(r)$ . Expanding  $g(r)$  in powers of  $n = N/V$  leads to the virial expansion

$$p/(k_B T) = n + B_2(T)n^2 + B_3(T)n^3 + \dots,$$

where the  $m$ 'th virial coefficient  $B_m(T)$  reflects  $m$ -body correlations in the equation of state.

For imperfect gases at low temperatures, where only 2-body interactions are relevant, can approximate  $g(r) = e^{-\beta\phi(r)}$  to obtain  $B_2(T)$ . Using L-J 6-12 for example gives good agreement with data (except helium, due to quantum effects). At high  $T$ ,  $B_2(T)$  is dominated by hard core repulsion and is positive and constant. At low  $T$ ,  $B_2(T)$  is dominated by van der Waals attraction and is negative and goes as  $1/T$ .

The Boyle temperature is defined by  $B_2(T) = 0$  (so closest to ideal gas).

2(b). [BOOKWORK]. Bose-Einstein condensation.

For a gas of a fixed number  $N$  of bosonic particles, integrating the Bose-Einstein distribution gives the dependence of the chemical potential  $\mu$  on  $T$ . At high  $T$ ,  $\mu$  is large and negative. Becomes less negative as  $T$  is reduced, but cannot become zero or positive. Below some temperature, must get a pile-up of particles in the ground state. Occupation number of the ground state is proportional to the size of the system.

For  $T \approx 0$ , find  $\mu \approx -k_B T/N$ . For  $T = 1$  K for example, find  $\mu \sim 10^{-46}$  J, which is much lower than the first excited state of the system. Calculate the number of particles in the excited states by setting  $\mu = 0$ ; by subtraction the number in the ground state is  $N_0 = N[1 - (T/T_0)^{3/2}]$ , where  $T_0$  is the *Bose condensation temperature*. Find  $U \propto T^{5/2}$  and  $C(T) \propto T^{3/2}$ .

Early evidence for BEC in superfluid  $^4\text{He}$ ,  $\lambda$ -transition. Discovered unambiguously in 1995 in dilute supersaturated vapour of rubidium-87 atoms, at a temperature below 100 nK. Above about 100 nK find Maxwell-Boltzmann distribution, while below 100 nK find sharp peak in momentum distribution centred on  $k = 0$ .

2(c). [BOOKWORK]. Fermi gases and specific heat of metals at low temperature.

Fermi-Dirac distribution:  $\langle n \rangle = 1/[e^{\beta(\epsilon - \mu)} + 1]$ . At  $T = 0$  becomes a step function up to the chemical potential  $\mu(0) = \epsilon_F$ , the Fermi energy. Integration to get  $N$  gives  $\mu(0) \propto (N/V)^{2/3}$ . At  $T = 0$ , also find  $U(0) \propto \epsilon_F^{5/2}$ .

As  $T$  increases, the step in the Fermi-Dirac distribution becomes symmetrically more rounded and  $\mu(T)$  slowly decreases. Can express equation of state via an integral over  $\epsilon^{3/2}n(\epsilon)$ . Expanding the integrand, at low  $T$  find  $S = C_V = (\pi^2/3)g(\epsilon_F)k_B^2T$ , i.e.  $C_V = \gamma T$ .

In a metal, the Fermi temperature  $T_F = \epsilon_F/k_B$  is very large, typically 50,000 K, so low temperature theory of ideal Fermi gas is a good approximation. The electrons give a contribution  $C(T) \propto T$ , while the phonons give a contribution  $C(T) \propto T^3$ . Phonons dominate at room temperature, but electrons significant at low temperature.

Plot  $C/T$  versus  $T^2$  allows electron and phonon contributions to be extracted from intercept and slope.

3. *[BOOKWORK]*. Grand canonical ensemble: an infinite number of subsystems each coupled to an identical reservoir with which can exchange particles as well as energy. Probability of a given partition of  $U$ ,  $N$ , between system and reservoir is proportional to the number of microstates of the reservoir. Grand partition function  $\Xi$  is evaluated by summing over all particle numbers and all energy levels, equals the product of the grand partition functions  $\Xi_i$  for each energy level. Treat the energy levels as thermodynamic systems; then easy to incorporate indistinguishability (Fermi and Bose statistics).

All thermodynamic information can be obtained from  $\Xi$ , which is usually simpler to evaluate than the partition function.

Examples: classical and quantum ideal gases; Maxwell-Boltzmann, Fermi-Dirac, Bose-Einstein distributions.

*[BOOKWORK]*. Grand partition function for energy level  $\epsilon_k$ :

$$\Xi_k = \sum_n e^{-\beta(\epsilon_k - \mu)n} = \sum_n (e^{-\beta(\epsilon_k - \mu)})^n ,$$

where  $\beta \equiv 1/k_B T$ . For a classical ideal gas, the chemical potential  $\mu$  is large and negative, so  $\beta(\epsilon_k - \mu) \gg 1$  for all  $\epsilon_k$ . Hence

$$\boxed{\Xi_k \approx 1 + e^{-\beta(\epsilon_k - \mu)}} .$$

Grand potential for each energy level:

$$\Phi_k = -k_B T \ln \Xi_k \approx -k_B T \ln(1 + e^{-\beta(\epsilon_k - \mu)}) \approx -k_B T e^{-\beta(\epsilon_k - \mu)} .$$

Sum over all states to get the grand potential:

$$\Phi = \sum_k \Phi_k = -k_B T \int_0^\infty g(\epsilon) e^{-\beta(\epsilon - \mu)} d\epsilon .$$

Given  $g(\epsilon) = (V m^{3/2} / \sqrt{2\pi^2 \hbar^3}) \epsilon^{1/2}$ , this is

$$\Phi = -k_B T \frac{V}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} e^{\beta\mu} \int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon .$$

The integral is

$$\int_0^\infty \epsilon^{1/2} e^{-\beta\epsilon} d\epsilon = \frac{2}{\beta^{3/2}} \int_0^\infty x^2 e^{-x^2} dx = \frac{2}{\beta^{3/2}} \frac{\sqrt{\pi}}{4} = \frac{\sqrt{\pi}}{2\beta^{3/2}} .$$

$$\boxed{\Phi = -k_B T \frac{V}{\lambda^3} \exp\left(\frac{\mu}{k_B T}\right)} ,$$

where

$$\lambda = \sqrt{\frac{2\pi\hbar^2}{mk_B T}} .$$

Obtain  $N$  from

$$N = - \left( \frac{\partial \Phi}{\partial \mu} \right)_{T,V} = \frac{V}{\lambda^3} \exp \left( \frac{\mu}{k_B T} \right) .$$

Rearrange to find the chemical potential:

$$\boxed{\mu = k_B T \ln \left( \frac{N \lambda^3}{V} \right)} .$$

[BOOKWORK, though not directly covered on the Examples Sheet; the closest is a question where molecules adsorbed on a surface are treated as an ideal 2D gas].

Vapour in thermal equilibrium with surface: each surface site is either empty ( $N_0 = 0$ ,  $E_0 = 0$ ) or full ( $N_1 = 1$ ,  $E_1 = -\epsilon$ ). The grand partition function for a single site is therefore

$$\Xi = \sum_i e^{-\beta(E_i - \mu_s N_i)} = 1 + z_s e^{\beta(\epsilon + \mu_s)} ,$$

where  $z_s$  takes vibrational motion into account. The corresponding grand potential is

$$\Phi = -k_B T \ln \Xi = -k_B T \ln [1 + z_s e^{\beta(\epsilon + \mu_s)}] .$$

The average occupation of the site is

$$\theta = \frac{N}{N_s} = - \left( \frac{\partial \Phi}{\partial \mu_s} \right)_{T,V} = \frac{z_s e^{\beta(\epsilon + \mu_s)}}{1 + z_s e^{\beta(\epsilon + \mu_s)}} .$$

Rearranging gives

$$\boxed{\mu_s = -\epsilon + k_B T \ln \left[ \frac{\theta}{(1 - \theta) z_s} \right]} .$$

Equating the chemical potentials,  $\mu = \mu_s$ , gives

$$k_B T \ln \left( \frac{N \lambda^3}{V} \right) = -\epsilon + k_B T \ln \left[ \frac{\theta}{(1 - \theta) z_s} \right] ,$$

and hence

$$\ln \left[ \frac{N \lambda^3}{V} \frac{(1 - \theta) z_s}{\theta} \right] = -\frac{\epsilon}{k_B T} .$$

Using  $pV = Nk_B T$ , this rearranges as

$$\boxed{\theta = \frac{p}{p + \alpha(T)} , \quad \alpha(T) \equiv \frac{k_B T}{\lambda^3 z_s} e^{-\beta \epsilon}} .$$

Sketch  $\theta$  as a function of  $p$  at fixed  $T$ :  $\theta$  rises monotonically from zero at  $p = 0$  and asymptotically approaches  $\theta = 1$  from below.

4. [BOOKWORK]. Landau theory of phase transitions: Phases are distinguished by an *order parameter*, e.g. magnetisation  $M$ , a macroscopic quantity which can change abruptly at a phase transition. The *mean field approximation* assumes that interactions with other constituents can be represented by their average effect. In Landau theory, expand the free energy near the phase transition as a power series in the order parameter. For a symmetric system (e.g. a magnetic system with no applied field) only have even powers. Minimise  $F$  to find the equilibrium state. Aimed mainly at continuous transitions but can also be applied to first order transitions.

[UNSEEN, though similar forms for  $F(\phi, T)$  are treated in the lectures and on the Examples Sheet]. Free energy:

$$F(\phi, T) = \frac{1}{2}c(T^2 - T_0^2)\phi^2 - \frac{aT}{12\pi}\phi^3 + \frac{\lambda}{4}\phi^4.$$

First and second derivatives wrt  $\phi$ :

$$\begin{aligned} F'(\phi, T) &= c(T^2 - T_0^2)\phi - \frac{aT}{4\pi}\phi^2 + \lambda\phi^3 \\ F''(\phi, T) &= c(T^2 - T_0^2) - \frac{aT}{2\pi}\phi + 3\lambda\phi^2 \end{aligned}$$

At  $\phi = 0$ :

$$F(0, T) = F'(0, T) = 0, \quad F''(0, T) = c(T^2 - T_0^2).$$

Since  $c > 0$ ,  $F(\phi)$  has a minimum at  $\phi = 0$  if  $T > T_0$  and a maximum at  $\phi = 0$  if  $T < T_0$ .

Since  $\lambda > 0$ , we always have  $F \rightarrow +\infty$  as  $\phi \rightarrow +\infty$ .

Look for zeros  $F(\phi, T) = 0$  with  $\phi > 0$ :

$$0 = \frac{1}{2}c(T^2 - T_0^2) - \frac{aT}{12\pi}\phi + \frac{\lambda}{4}\phi^2.$$

Thus

$$\phi = \frac{1}{2\lambda} \left[ \frac{aT}{3\pi} \pm \sqrt{\left(\frac{aT}{3\pi}\right)^2 - 8\lambda c(T^2 - T_0^2)} \right].$$

Can write this as

$$\phi = \frac{aT}{6\pi\lambda} \left[ 1 \pm \sqrt{1 - \frac{(T^2 - T_0^2)}{\gamma T^2}} \right], \quad \gamma \equiv \frac{a^2}{72\pi^2\lambda c}.$$

If  $T < T_0$  (for any  $\gamma$ ): there is a single zero with  $\phi > 0$ . Since  $F(\phi)$  has a maximum with  $F = 0$  at  $\phi = 0$ , and  $F \rightarrow +\infty$  as  $\phi \rightarrow +\infty$ , there must be an overall minimum with  $F(\phi) < 0$  at  $\phi > 0$  (for any  $\gamma$ ).

If  $T > T_0$  and  $(T^2 - T_0^2) > \gamma T^2$ : there are no zeros with  $\phi > 0$ , and the overall minimum of  $F(\phi)$  must be at  $\phi = 0$ . The conditions correspond to  $\gamma < 1$  and  $T > T^* > T_0$  where

$$T^* \equiv \frac{1}{\sqrt{1 - \gamma}} T_0.$$

If  $T > T_0$  and  $(T^2 - T_0^2) < \gamma T^2$ : there are two zeros with  $\phi > 0$ , and hence an overall minimum with  $F(\phi) < 0$  between these two zeros. The conditions are satisfied either if  $\gamma > 1$  (for any  $T > T_0$ ) or if  $\gamma < 1$  and  $T_0 < T < T^*$ .

If  $T > T_0$  and  $(T^2 - T_0^2) = \gamma T^2$ : we have  $T = T^*$ , and there is a minimum with  $F(\phi^*) = 0$  at

$$\phi^* = \frac{aT^*}{6\pi\lambda} .$$

[UNSEEN]. For  $\gamma < 1$ , the system must start out (at high temperature) in the phase  $\phi = 0$ , since this is the only minimum of  $F(\phi)$ . As the system cools through  $T = T^*$ , the overall minimum jumps to  $\phi = \phi^*$ , but there is a potential barrier to overcome, keeping the system in  $\phi = 0$ . With further cooling, to  $T = T_0$ ,  $F(\phi)$  becomes a maximum at  $\phi = 0$ , and there is no longer a potential barrier. At this point, the system undergoes a first order transition from  $\phi = 0$  to the overall minimum with  $\phi > 0$ .

For  $\gamma > 1$ , a phase transition can be similarly obtained, also at  $T = T_0$ , but now  $\phi = 0$  is only a *local* minimum. If the system is initially in the *overall* minimum of  $F(\phi)$ , with  $\phi > 0$ , it just stays there and there is no transition.

[UNSEEN]. For the Universe to undergo a first order transition from a phase corresponding to the overall minimum of  $F(\phi)$  requires  $\phi = 0$  initially and  $\gamma < 1$ . The condition  $\phi^* > T^*$  for viable models then gives also

$$\frac{a}{6\pi\lambda} > 1 .$$

The constraints  $\gamma < 1$  and  $\phi^* > T^*$  give, respectively,

$$\frac{\lambda c}{a^2} > \frac{1}{72\pi^2} , \quad \frac{\lambda}{a} < \frac{1}{6\pi} .$$

With  $\lambda/a = m_H^2/m_0^2$  and  $c/a = A + m_H^2/m_0^2$ , these constraints are

$$\frac{m_H^2}{m_0^2} \left( A + \frac{m_H^2}{m_0^2} \right) > \frac{1}{72\pi^2} = 0.00141 , \quad \frac{m_H^2}{m_0^2} < \frac{1}{6\pi} = 0.053 .$$

The first of these (from  $\gamma < 1$ ) gives a lower bound on  $m_H$ , while the second (from  $\phi^* > T^*$ ) gives an upper bound.

For  $m_0 = 223.9$  u,  $A = 0.95$  and  $m_H = 134$  u, the left-hand sides of the above constraints are 0.47 and 0.36 respectively, i.e. the first inequality is satisfied but the second fails, i.e. the model is not viable given the measured Higgs mass.