# MARKSCHEME

1(a). *[BOOKWORK]*. The coefficient $B_2(T)$ is defined through the virial equation of state:

$$\frac{p}{k_{\mathrm{B}}T} = n + B_2(T)n^2 + \dots \ .$$

$B_2$ is related to the pairwise interaction potential $V(|r_i - r_j|)$:

$$B_2(T) = \frac{1}{2}\int \left[1 - e^{-\beta V(r)}\right]\mathrm{d}^3 r \ , \qquad \beta \equiv \frac{1}{k_{\mathrm{B}}T}\ .$$

For inert gases, something like a Lennard-Jones potential is applicable; long-range attraction, short-range repulsion.

At low $T$ (large $\beta$), the main contribution to the integral comes from large $r$ where $V(r)$ is negative, and gives $B_2(T) < 0$. At high $T$ (small $\beta$), the main contribution to the integral comes from small $r$ where $V(r)$ is large and positive, and gives $B_2(T) > 0$.

Data agrees well with Lennard-Jones expectation, except helium is a bit off due to quantum effects.

1(b). *[BOOKWORK]*. A single spin-half dipole of magnetic dipole $\mu$ in a magnetic field $B$ has energies $\epsilon_\pm = \pm\mu B$. The single particle partition function is

$$Z_1 = e^x + e^{-x} = 2\cosh x \ ; \qquad x \equiv \mu B/(k_{\mathrm{B}}T)\ .$$

The mean energy is

$$\langle U \rangle = p_+\epsilon_+ + p_-\epsilon_- = \frac{1}{Z_1}\left(e^{-x}\epsilon_+ + e^x\epsilon_-\right) = \mu B\frac{e^{-x} - e^x}{2\cosh x} = -\mu B\tanh x \ .$$

For $N$ dipoles, the magnetic entropy is

$$S = (U - F)/T = (U + Nk_{\mathrm{B}}T\ln Z_1)/T = Nk_{\mathrm{B}}\left[\ln(2\cosh x) - x\tanh x\right]\ .$$

Alternative form:
$$S = Nk_{\mathrm{B}}\left[\ln(1 + e^{-2x}) + 2x/(1 + e^{2x})\right]\ .$$

*[UNSEEN]*. The entropy depends only on the ratio $B/T$. Leads to adiabatic cooling: slowly reduce the magnetic field strength from $B_1$ to $B_2$ giving a final temperature $T_2 = (B_2/B_1)T_1$.

1(c). *[BOOKWORK].* Fermi-Dirac expression for average occupancy:

$$\langle n(\epsilon) \rangle = \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \ ; \qquad \mu = \mu(T) \ ; \qquad \beta = 1/(k_\mathrm{B} T) \ .$$

The occupancy is approximately a step function, with a rounded edge centred on the Fermi energy $\epsilon_F = \mu(T)$. For $\epsilon = \mu$ we have $\langle n \rangle = 1/2$, and for $\epsilon = \mu \pm k_\mathrm{B} T$ or $\mu \pm 2 k_\mathrm{B} T$ we have

$$\langle n(\mu \pm k_\mathrm{B} T) \rangle = \frac{1}{e^{\pm 1} + 1} = (0.27, \ 0.73) \ ; \qquad \langle n(\mu \pm 2 k_\mathrm{B} T) \rangle = \frac{1}{e^{\pm 2} + 1} = (0.12, \ 0.88) \ .$$

Hence the spreading of the Fermi edge is of order $\pm k_\mathrm{B} T$.

Heat capacity of a Fermi gas: only particles within $\pm k_\mathrm{B} T$ contribute. Treating these classically, they contribute an internal energy

$$U \sim \frac{3}{2} N k_\mathrm{B} T \sim \frac{3}{2} \times [g(\epsilon_\mathrm{F}) k_\mathrm{B} T] \times k_\mathrm{B} T \ .$$

Hence the heat capacity is

$$C \sim \frac{\partial U}{\partial T} \sim 3 g(\epsilon_\mathrm{F}) k_\mathrm{B}^2 T \ ,$$

which depends linearly on temperature $T$.

## 2(a). *[BOOKWORK]*. **Thermodynamic ensembles**

Microcanonical ensemble: system is isolated with fixed energy. A given macrostate corresponds to a multiplicity of microstates, each of which is assumed equally likely to occur (PEEP). The equlibrium state is the one with the biggest number of microstates. Gibbs entropy: $S = -k_B \sum_i p_i \ln(p_i)$.

Canonical ensemble: consider a (small) system in contact with a reservoir. System can exchange energy with the reservoir, so its energy fluctuates, but its temperature is well defined. Find $p(E_i) \propto e^{-E_i/k_B T}$, leading to partition function $Z = \sum_i e^{-E_i/k_B T}$, from which can determine thermodynamic potentials, $F = -k_B T \ln Z$ etc.

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.

## 2(b). *[BOOKWORK]*. **Brownian motion**

Small grain moves irregularly in response to fluctuating force from a heat bath (liquid at temperature $T$). Described by *Langevin equation* $m\ddot{x} = -\gamma\dot{x} + \xi(t)$, which is dissipative friction $\gamma$ plus random stochastic forces $\xi(t)$, normally taken to be Gaussian white noise. For random, uncorrelated case, $\langle\xi(t)\rangle = 0$ and $\langle\xi(t_1)\xi(t_2)\rangle = \Gamma\delta(t_1 - t_2)$, find average kinetic energy $(m/2)\langle u^2 \rangle = \Gamma/4\gamma$. Then, from equipartition, friction and stochastic are related: $\Gamma = 2\gamma k_B T$.

For Brownian motion of a free particle, taking the long time limit $t \gg m/\gamma$, $\langle\ddot{x}\rangle = 0$, obtain Einstein's diffusion law $\langle x^2 \rangle = 2Dt$ (or $\langle \boldsymbol{r}^2 \rangle = 6Dt$ in 3D), with $D = k_B T/\gamma$. The rms displacement increases as $\sqrt{t}$.

For Brownian motion of a confined particle (harmonic potential $V(x) = (1/2)\alpha x^2$) (e.g. particle on a lattice site), Langevin equation becomes $m\ddot{x} = -\alpha x - \gamma\dot{x} + \xi(t)$. Find $\langle x^2 \rangle = k_B T/\alpha$, as expected from equipartition: $(1/2)\alpha\langle x^2 \rangle = (1/2)k_B T$. Relevant to diffuse thermal scattering of particles from a solid (Debye-Waller scattering).

2(c). *[BOOKWORK].* **The Landau theory of phase transitions**

Applies to systems where phases are distinguished by an *order parameter*, e.g. magnetisation $M$, a position-independent 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 $F$ 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. At given temperature $T$, minimise $F$ as a function of the order parameter to find the equilibrium state.

Aimed mainly at continuous transitions but can also be applied to first order transitions (with a latent heat).

e.g. magnetisation: at high $T$ the free energy $F$ has a minimum at the disordered state $M = 0$. As $T$ falls below *critical temperature* $T_c$ the minimum moves to an ordered state $M \neq 0$. An applied field $B$ breaks the symmetry, leads to hysteresis.

3. *[BOOKWORK]*. Chemical potential for identical bosons: always negative, negligibly small at low temperature $T < T_0$, then rapidly grows more negative at high $T$. Bose-Einstein condensate: ground state occupancy grows below $T_0$. Occurs (for a gas) when thermal de Broglie wavelength comparable to interatomic spacing, $n\lambda^3 \sim 2.6$. Experimental observation in rubidium: peak around zero velocity at (very) low temperature.

*[BOOKWORK]*. Hard-wall boundary conditions: $\psi = 0$ for $x, y, z = 0$ and $x, y, z = a$:

$$k_x = \frac{n_x \pi}{a}, \quad k_y = \frac{n_y \pi}{a}, \quad k_z = \frac{n_z \pi}{a}; \qquad n_x, n_y, n_z \geq 1.$$

Corresponds to one state in a volume

$$\mathrm{d}^3\boldsymbol{k} = \mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z = \left(\frac{\pi}{a}\right)^3 = \frac{\pi^3}{V}; \qquad g(\boldsymbol{k})\,\mathrm{d}^3\boldsymbol{k} = \frac{V}{\pi^3}\,\mathrm{d}^3\boldsymbol{k}.$$

Number of states in $\mathrm{d}k$ (positive octant only):

$$g(k)\,\mathrm{d}k = \frac{V}{\pi^3}\frac{4\pi k^2\,\mathrm{d}k}{8} = \frac{Vk^2}{2\pi^2}\,\mathrm{d}k. \tag{1}$$

where $\epsilon = p^2/(2m) = \hbar^2 k^2/(2m)$.

*[UNSEEN]*. In an isotropic confining potential $U(r)$, for a particle with total energy $\epsilon$, the momentum $p = \hbar k$ depends on radius:

$$\epsilon = \frac{p(r)^2}{2m} + U(r); \qquad p(r) = \hbar k(r) = \sqrt{2m(\epsilon - U(r))}.$$

Applying Equation (1) to a shell of thickness $\mathrm{d}r$ gives

$$g(r, k)\,\mathrm{d}r\,\mathrm{d}k = \frac{k^2}{2\pi^2}\left(4\pi r^2\,\mathrm{d}r\right)\mathrm{d}k = \frac{2k^2 r^2}{\pi}\,\mathrm{d}r\,\mathrm{d}k.$$

Convert to energy $\epsilon$:

$$g(r, \epsilon) = g(r, k)\frac{\mathrm{d}k}{\mathrm{d}\epsilon} = \frac{2k^2 r^2}{\pi}\frac{m}{\hbar^2 k} = \frac{2mr^2}{\pi\hbar^2}k(r).$$

A particle of energy $\epsilon$ is confined to the region $0 < r < r_\epsilon$ where $\epsilon = U(r_\epsilon)$:

$$g(\epsilon) = \frac{2m}{\pi\hbar^3}\int_0^{r_\epsilon} r^2 p(r)\,\mathrm{d}r = \frac{(2m)^{3/2}}{\pi\hbar^3}\int_0^{r_\epsilon} r^2\sqrt{\epsilon - U(r)}\,\mathrm{d}r.$$

*[UNSEEN]*. For a harmonic potential $U(r) = (1/2)m\omega^2 r^2$:

$$g(\epsilon) = \frac{(2m)^{3/2}}{\pi\hbar^3}\int_0^{r_\epsilon} r^2\sqrt{\epsilon - (m\omega^2/2)r^2}\,\mathrm{d}r; \qquad \epsilon = \frac{1}{2}m\omega^2 r_\epsilon^2.$$

Using the trigonometric substitution

$$\frac{m\omega^2}{2\epsilon}r^2 = \sin^2\theta; \qquad \frac{\mathrm{d}r}{\mathrm{d}\theta} = \sqrt{\frac{2\epsilon}{m\omega^2}}\cos\theta$$

gives

$$g(\epsilon) = \frac{8\epsilon^2}{\pi(\hbar\omega)^3} \int_0^{\pi/2} \sin^2\theta \cos^2\theta \, d\theta \ .$$

Using standard trig identities, this is

$$g(\epsilon) = \frac{2\epsilon^2}{\pi(\hbar\omega)^3} \int_0^{\pi/2} \sin^2 2\theta \, d\theta = \frac{\epsilon^2}{\pi(\hbar\omega)^3} \int_0^{\pi/2} (1 - \cos 4\theta) \, d\theta = \boxed{\frac{\epsilon^2}{2(\hbar\omega)^3}} \ .$$

*[UNSEEN, but paralleling the treatment of unconfined bosons in lectures].*
Total number of particles for identical bosons:

$$N = \int_0^\infty n(\epsilon)g(\epsilon) \, d\epsilon = \int_0^\infty \frac{g(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1} \, d\epsilon \ .$$

The ground state $\epsilon = 0$ needs to be treated separately, because $g(0) = 0$:

$$N = N_0 + \frac{1}{2(\hbar\omega)^3} \int_0^\infty \frac{\epsilon^2}{e^{\beta(\epsilon-\mu)} - 1} \, d\epsilon \ .$$

At low temperature can effectively set $\mu = 0$. Changing also to $x = \beta\epsilon$ then gives

$$N = N_0 + \frac{1}{2(\hbar\omega)^3} \frac{1}{\beta^3} \int_0^\infty \frac{x^2}{e^x - 1} \, dx \approx N_0 + \frac{(2.404)(k_\mathrm{B}T)^3}{2(\hbar\omega)^3} \ .$$

This can be written as

$$N = N_0 + N(T/T_0)^3 \ ,$$

where the Bose condensation temperature $T_0$ is

$$\boxed{T_0 = \left(\frac{2}{2.404}\right)^{1/3} \frac{\hbar\omega}{k_\mathrm{B}} N^{1/3}} \ .$$

Sketch of ground state occupancy $N_0$ versus $T$: Starts with $N_0 = N$ at $T = 0$, falls monotonically and increasingly steeply until hits $N_0 = 0$ at $T = T_0$, then stays at $N_0 = 0$ for all $T > T_0$.

4. *[BOOKWORK]*. In a classical gas, the particles are regarded as independent thermodynamic entities, and the single particle partition functions can be multiplied together. Must also divide by $N!$ since the particles are indistinguishable:

$$Z_N = \frac{1}{N!}(Z_1)^N \ .$$

Using Stirling's approximation, the Helmholtz free energy is

$$F = -k_{\mathrm{B}}T \ln Z = -k_{\mathrm{B}}T \left[ N \ln Z_1 - N \ln N + N \right] \ .$$

Using $\mathrm{d}F = -S\,\mathrm{d}T - p\,\mathrm{d}V + \mu\,\mathrm{d}N$, the chemical potential is

$$\boxed{\mu = \left( \frac{\partial F}{\partial N} \right)_{T,V} = -k_{\mathrm{B}}T \left[ \ln Z_1 - \ln N \right]} \ . \tag{2}$$

*[BOOKWORK]*. Consider a closed system consisting of the open system of interest plus a reservoir:

$$\mathrm{d}S_{\mathrm{tot}} = \mathrm{d}S + \mathrm{d}S_R \geq 0 \ .$$

The First and Second Laws applied to the reservoir give

$$\mathrm{d}U_R = T_R\,\mathrm{d}S_R - p_R\,\mathrm{d}V_R + \mu_R\,\mathrm{d}N_R \ .$$

Hence

$$\mathrm{d}S_{\mathrm{tot}} = \mathrm{d}S + \frac{\mathrm{d}U_R + p_R\,\mathrm{d}V_R - \mu_R\,\mathrm{d}N_R}{T_R} \geq 0 \ .$$

Using $\mathrm{d}U_R = -\mathrm{d}U$, $\mathrm{d}V_R = -\mathrm{d}V$, $\mathrm{d}N_R = -\mathrm{d}N$ then gives

$$T_R\,\mathrm{d}S_{\mathrm{tot}} = T_R\,\mathrm{d}S - \mathrm{d}U - p_R\,\mathrm{d}V + \mu_R\,\mathrm{d}N \geq 0 \ .$$

At constant temperature, pressure and particle number, we have $p_R = p$, $T_R = T$, $\mathrm{d}N = 0$:

$$T\,\mathrm{d}S_{\mathrm{tot}} = T\,\mathrm{d}S - \mathrm{d}U - p\,\mathrm{d}V \geq 0 \ .$$

Using $\mathrm{d}p = 0$, $\mathrm{d}T = 0$ gives $\mathrm{d}(pV) = p\,\mathrm{d}V$ and $\mathrm{d}(TS) = T\,\mathrm{d}S$, and hence

$$T\,\mathrm{d}S_{\mathrm{tot}} = \mathrm{d}(TS) - \mathrm{d}U - \mathrm{d}(pV) = -\mathrm{d}(U - TS + pV) = -\mathrm{d}G \geq 0 \ .$$

Hence $\mathrm{d}G \leq 0$, and in equilibrium the Gibbs free energy is a minimum:

$$\boxed{\mathrm{d}G = 0} \ .$$

*[BOOKWORK]*. Differentiating $G = U - TS + pV$ gives

$$\mathrm{d}G = \mathrm{d}U - T\,\mathrm{d}S - S\,\mathrm{d}T + p\,\mathrm{d}V + V\,\mathrm{d}p$$

Using $\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \mu\,\mathrm{d}N$ then gives

$$\boxed{\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}p + \mu\,\mathrm{d}N} \ .$$

Combining $G = U - TS + pV$ with $U = TS - pV + \mu N$ also gives

$$\boxed{G = \mu N} \ .$$

*[UNSEEN, though chemical reactions are discussed in lectures].* For the two-component system, $G = \mu_A N_A + \mu_B N_B$, which differentiates to give

$$\mathrm{d}G = \sum_i \mu_i \,\mathrm{d}N_i + \sum_i N_i \,\mathrm{d}\mu_i \ .$$

Differentiating $U = TS - pV + \sum_i \mu_i N_i$ gives

$$\mathrm{d}U = T \,\mathrm{d}S + S \,\mathrm{d}T - p \,\mathrm{d}V - V \,\mathrm{d}p + \sum_i \mu_i \,\mathrm{d}N_i + \sum_i N_i \,\mathrm{d}\mu_i \ .$$

Hence (Gibbs-Duhem) :

$$S \,\mathrm{d}T - V \,\mathrm{d}p + \sum_i N_i \,\mathrm{d}\mu_i = 0 \ .$$

At constant temperature and pressure, this becomes

$$\sum_i N_i \,\mathrm{d}\mu_i = 0 \ .$$

Hence, in equilibrium,

$$\mathrm{d}G = \sum_i \mu_i \,\mathrm{d}N_i = 0 \ . \tag{3}$$

For components A and B interacting through $A \rightleftharpoons 2B$, and if there is no particle exchange with the surroundings, changes in particle numbers are related via

$$-2 \,\mathrm{d}N_A = \mathrm{d}N_B \ .$$

Hence Equation (3) becomes

$$\boxed{\mu_A = 2\mu_B} \ . \tag{4}$$

Combining Equation (4) with Equation (2) gives

$$-k_{\mathrm{B}}T \left[\ln Z_1^{(A)} - \ln N_A\right] = -2k_{\mathrm{B}}T \left[\ln Z_1^{(B)} - \ln N_B\right] \ .$$

Given $Z_1^{(A)} = C_A V T^{3/2}$ and $Z_1^{(B)} = C_B V T^{3/2}$, this rearranges as

$$K_N \equiv \frac{N_B^2}{N_A} = \frac{(Z_1^{(B)})^2}{Z_1^{(A)}} = \frac{C_B^2}{C_A} V T^{3/2} \ ,$$

which is a function of $V$ and $T$ only.

If the density is increased at fixed $V$ and $T$, then both $N_A$ and $N_B$ increase. To keep $N_B^2/N_A$ constant, $N_A$ must increase by a bigger factor than $N_B$. Hence there is less dissociation at higher pressure.

*[BOOKWORK].* The probability of dissociation depends only on temperature, while the probability of recombination depends also on the probability of two products running into each other; recombination becomes much less likely at low pressure.