

Candidate number:
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King's College London

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B.Sc. EXAMINATION

6CCP3212 Statistical Mechanics

Examiner: Dr Eugene Lim

**Examination Period 2
(Summer 2019)**

Time allowed: THREE hours

Candidates may answer as many parts as they wish from SECTION A, but the total mark for this section will be capped at 40.

Candidates should also answer TWO questions from SECTION B. No credit will be given for answering a further question from this section. The approximate mark for each part of a question is indicated in square brackets.

Calculators may be used. The following models are permitted: Casio fx83 and Casio fx85.

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Physical Constants

Permittivity of free space	$\epsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$
Permeability of free space	$\mu_0 = 4\pi \times 10^{-7} \text{ H m}^{-1}$
Speed of light in free space	$c = 2.998 \times 10^8 \text{ m s}^{-1}$
Gravitational constant	$G = 6.673 \times 10^{-11} \text{ N m}^2 \text{ kg}^{-2}$
Elementary charge	$e = 1.602 \times 10^{-19} \text{ C}$
Electron rest mass	$m_e = 9.109 \times 10^{-31} \text{ kg}$
Unified atomic mass unit	$m_u = 1.661 \times 10^{-27} \text{ kg} = 931.494 \text{ MeV } c^{-2}$
Proton rest mass	$m_p = 1.673 \times 10^{-27} \text{ kg}$
Neutron rest mass	$m_n = 1.675 \times 10^{-27} \text{ kg}$
Planck constant	$h = 6.626 \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1} = 8.617 \times 10^{-11} \text{ MeV K}^{-1}$
Stefan-Boltzmann constant	$\sigma = 5.670 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Gas constant	$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
Avogadro constant	$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
Molar volume of ideal gas at STP	$= 2.241 \times 10^{-2} \text{ m}^3$
One standard atmosphere	$P_0 = 1.013 \times 10^5 \text{ N m}^{-2}$

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Useful Information

Maxwell Relations

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

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P, \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S.$$

Fundamental Equation of Thermodynamics

$$dE = TdS - PdV + \mu dN$$

Thermodynamic Potentials

$$F = E - TS, \quad \Phi = E - TS + PV, \quad H = E + PV.$$

with differentials

$$dF = -SdT - PdV + \mu dN, \quad d\Phi = -SdT + VdP + \mu dN, \quad dH = TdS + VdP + \mu dN.$$

Heat Capacities

$$C_V = T \left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V, \quad C_P = T \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P.$$

Microcanonical Ensemble Entropy

$$S = k_b \ln \Omega$$

Canonical Partition Function and formulas

$$Z = \sum_r e^{-\beta E_r}, \quad P_r = \frac{1}{Z} e^{-\beta E_r}, \quad \langle X \rangle = \sum_r P_r X_r,$$

$$F = -k_b T \ln Z, \quad S = k_b \frac{\partial}{\partial T} (T \ln Z), \quad \text{Mean Energy } \langle E \rangle = -\left(\frac{\partial \ln Z}{\partial \beta}\right)$$

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Grand Canonical Ensemble Partition Function

$$\mathcal{Z} = \sum_r e^{-\beta(E_r - \mu N_r)} ,$$

Mean Energy $\langle E \rangle + \mu \langle N \rangle = - \left(\frac{\partial \ln \mathcal{Z}}{\partial \beta} \right)$, Mean Particle Number $\langle N \rangle = \frac{1}{\beta} \left(\frac{\partial \ln \mathcal{Z}}{\partial \mu} \right)$.

Fermi-Dirac Distribution

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} + 1} .$$

Bose-Einstein Distribution

$$\langle N_{\mathbf{n}} \rangle = \frac{1}{e^{\beta(E_{\mathbf{n}} - \mu)} - 1} .$$

Thermal de Broglie wavelength

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

Stirling's Formula

$$\ln N! = N \ln N - N .$$

Polylog integrals

$$\int_0^\infty \frac{x^{n-1}}{e^x + 1} dx = (1 - 2^{1-n}) \Gamma(n) \zeta(n) , \quad (n > 0),$$

and

$$\int_0^\infty \frac{x^{n-1}}{e^x - 1} dx = \Gamma(n) \zeta(n) , \quad (n > 1),$$

with Riemann Zeta function

$$\zeta(p) \equiv \sum_{n=1}^{\infty} \frac{1}{n^p} ,$$

and the Gamma function

$$\Gamma(n) \equiv \int_0^\infty x^{n-1} e^{-x} dx .$$

The Gamma function for $n > 0$ integers is

$$\Gamma(n) = (n - 1)! , \quad n \in \mathcal{N} - \{0\} .$$

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Common values for half-integer Gamma functions

$$\Gamma(1/2) = \sqrt{\pi} , \Gamma(3/2) = \frac{\sqrt{\pi}}{2} , \Gamma(5/2) = \frac{3\sqrt{\pi}}{4} , \Gamma(7/2) = \frac{15\sqrt{\pi}}{8} .$$

and Zeta functions

$$\zeta(3/2) = 2.612 , \zeta(2) = \frac{\pi^2}{6} , \zeta(5/2) = 1.341 , \zeta(3) = 1.202 , \zeta(7/2) = 1.127 .$$

Gaussian Integral

$$I = \int_{-\infty}^{\infty} e^{-ax^2} dx = \sqrt{\frac{\pi}{a}} .$$

Geometric Sum

$$\sum_{n=0}^{n=\infty} x^n = \frac{1}{1-x} , |x| < 1 .$$

A derivative identity between x , y and z with a single constraint $x(y, z)$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Differential transform from $f(x, y) \rightarrow f(x, z)$ for a function $f(x, y)$ with a constraint $x = x(y, z)$

$$\left(\frac{\partial f}{\partial x}\right)_z = \left(\frac{\partial f}{\partial x}\right)_y + \left(\frac{\partial f}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z .$$

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SECTION A

Answer SECTION A in an answer book.

Answer as many parts of this section as you wish. Your total mark for this section will be capped at 40.

1.1 State what is meant by a *statistical ensemble* of a system S . Define clearly each term used in your description.

[3 marks]B

1.2 State the *equipartition theorem* in any of its forms.

[3 marks]B

1.3 State which of the following are exact differentials. Integrate the equation if it is exact.

(i) $dG(x, y) = 2x(y + 1)dx + x^2dy$.

(ii) $dG(x, y, z) = (2xe^{2y} + z)dx + 2e^{2y}x^2dy + xdz$.

(iii) $dG(x, y) = (x + 2y)dx + \frac{x^3}{3}dy$.

[9 marks]P

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1.4 A gas is described by the Van der Waals equation of state given by

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

For fixed N , $a > 0$, $b > 0$ and by arguing that a gas has to be stable under *isothermal* compression, show that

$$T > \frac{2aN(bN - V)^2}{k_bV^3} .$$

(*Hint*: Consider the change in pressure with respect to changes in volume.)

[8 marks]U

1.5 Recall that the entropy of a system can be written in the Shannon form as

$$S = -k_b \sum_i P_i \ln P_i$$

where P_i is the probability of the i -th microstate occurring. Calculate the entropy of a 6-sided die. Generalize the result to an n -sided die.

[6 marks]U

1.6 Consider a thermodynamic system with state variables P , T and V , related by some equation of state $P(V, T)$. By performing a coordinate transform from $S(P, T) \rightarrow S(T, V)$, show that

$$\left(\frac{\partial S}{\partial T} \right)_V = \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial S}{\partial T} \right)_P .$$

You may use any formula provided.

[6 marks]B

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1.7 The Maxwell-Boltzmann distribution of a gas at temperature T is given by

$$f(v)e^{-mv^2/2k_bT} = \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} v^2 e^{-mv^2/2k_bT} ,$$

where the absolute velocity is

$$v = \sqrt{v_x^2 + v_y^2 + v_z^2} ,$$

Calculate the mean inverse velocity $\langle v^{-1} \rangle$.

[8 marks]B

1.8 Consider a gas of non-relativistic quantum particles trapped in a 2 dimensional square with lengths a and area $A = a^2$. For these quantum particles, the energy is given by

$$E_{\mathbf{n}} = \frac{\hbar^2 k^2}{2m} = \frac{4\pi^2 \hbar^2}{2ma^2} (n_x^2 + n_y^2) , \quad k = \sqrt{k_x^2 + k_y^2} ,$$

where $n_x, n_y = 0, 1, 2, 3, \dots$ label the possible quantum numbers, and $n_i = ak_i/(2\pi)$. By converting the sum into an integral

$$\sum_{\mathbf{n}} \rightarrow \int dn_x dn_y ,$$

show that the density of states $g(E)$ is given by

$$g(E) = \tilde{g} \frac{2\pi mA}{(2\pi\hbar)^2} .$$

(*Hint*: You might find the following relationship

$$\int dk^2 \rightarrow \int_0^{2\pi} d\theta \int_0^k k dk .$$

useful.)

[8 marks]B

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1.9 Consider the following Landau Functional

$$F(T) = F_0(T) + \alpha(T - T_c)m^2 + bm^4 ,$$

where T_c is the critical temperature, and $\alpha > 0$, $b > 0$ are constants. Find the equilibrium points of this functional. Plot $F(T)$ for the two cases where $T < T_c$ and $T > T_c$. What is the order of the phase transition that this functional models? Justify your assertion.

[9 marks]B

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Solutions

1.1 An ensemble is the space of all possible microstates consistent with some constraints. A microstate is a point in the system's dynamical phase space.

1.2 Either mean energy per d.o.f. per particle is $3/2k_bT$ or

$$\left\langle x_k \frac{\partial H}{\partial x_k} \right\rangle = \frac{1}{\beta} = k_bT \quad (1)$$

are fine.

1.3 (i) Exact. $G(x, y) = x^2(y + 1)$ (ii) Exact. $G(x, y, z) = e^{2y}x^2 + xz$. (iii) Inexact.

1.4 Rewrite

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

and then stability of gas (from bookwork) implies that $(\frac{\partial P}{\partial V})_T < 0$, which gives the required condition.

1.5 The probability of each microstate in a n -th sided die is $P_i = 1/n$, so $S = -k_b \sum_i P_i \ln P_i = k_b n \times (1/n) \ln n = k_b \ln n$. For 6 sided die this is $S = k_b \ln 6$.

1.6 This is straight out of a homework problem. First write

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP + \left(\frac{\partial S}{\partial T} \right)_P dT .$$

And then consider $S(P, T) \rightarrow S(T, V)$, and the identity (given in list of formulae)

$$\left(\frac{\partial f}{\partial x} \right)_z = \left(\frac{\partial f}{\partial x} \right)_y + \left(\frac{\partial f}{\partial y} \right)_x \left(\frac{\partial y}{\partial x} \right)_z , \quad (3)$$

this becomes

$$dS = \left(\frac{\partial S}{\partial V} \right)_T dV + \left[\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial S}{\partial P} \right)_T + \left(\frac{\partial S}{\partial T} \right)_P \right] dT \quad (4)$$

and comparing the coefficient of dT gets the final answer.

1.7 Straightforward integral

$$\begin{aligned}
\langle v^{-1} \rangle &= \int_0^\infty v^{-1} f(v) e^{-mv^2/2k_bT} \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} \int_0^\infty v e^{-mv^2/2k_bT} dv \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{3/2} \left[-\frac{k_bT e^{-av^2}}{m} \right]_0^\infty \\
&= \sqrt{\frac{2}{\pi}} \left(\frac{m}{k_bT} \right)^{1/2} .
\end{aligned} \tag{5}$$

1.8 This is a problem from the homework. In two dimensions, the sum over all microstates is a sum over all possible n_x and n_y , which we can convert into an integral

$$\sum_{\mathbf{n}} \rightarrow \int dn_x dn_y . \tag{6}$$

And now using $dE = \hbar^2 k / m dk$, and $dn = a / (2\pi) dk$ we have

$$\begin{aligned}
\int dn_x dn_y &= \tilde{g} \frac{A}{(2\pi)^2} \int d^2k \\
&= \tilde{g} \frac{A}{(2\pi)^2} \int 2\pi k dk \\
&= \tilde{g} \frac{A}{(2\pi)^2} \int 2\pi \frac{m}{\hbar^2} dE \\
&= \tilde{g} \frac{A}{(2\pi\hbar)^2} \int 2\pi m dE
\end{aligned} \tag{7}$$

where in the 2nd line we have used the fact that $\int dk^2 \rightarrow \int_0^{2\pi} d\theta \int_0^k k dk$, and hence

$$g(E) = \tilde{g} \frac{2\pi mA}{(2\pi\hbar)^2} \tag{8}$$

1.9 Finding the minima by $\partial F / \partial m = 0$, gets us the equilibrium solutions $m = 0$, $m = \pm \sqrt{-a/2m}$ where $a = \alpha(T - T_c)$. For the system to model a 2nd order phase transition, $\partial^2 F / \partial T^2$ must be discontinuous at $T = T_c$, and this is true since

$$\lim_{T \rightarrow T_c^-} \frac{\partial^2 F}{\partial T^2} - \lim_{T \rightarrow T_c^+} \frac{\partial^2 F}{\partial T^2} = \frac{\alpha^2}{b} , \tag{9}$$

and the system is discontinuous at 2nd order.

SECTION B - Answer TWO questions
Answer SECTION B in an answer book

- 2) Consider a thermodynamic system with a fixed number of particles described by the following equation of state

$$P = AVT^4 ,$$

where $A > 0$ is a positive definite constant.

- (a) State what is meant by a *function of state*.

[2 marks] B

- (b) By considering the fundamental equation of thermodynamics for fixed number of particles, show that

$$\left(\frac{\partial S}{\partial E}\right)_V = \frac{1}{T} , \quad \left(\frac{\partial S}{\partial V}\right)_E = \frac{P}{T} .$$

[6 marks] U

- (c) The energy E of the system is a function of state given by

$$E = \frac{3}{2}PV .$$

Express $1/T$ and P/T as functions of E and V , and hence using the result of (b), show that the entropy of the system is given by

$$S = \frac{4}{3} \left(\frac{3A}{2}\right)^{1/4} V^{1/2} E^{3/4} + \text{const} .$$

[10 marks] U

- (d) Calculate the Helmholtz Free energy F of this system as a function of V and T .

[4 marks] U,P

QUESTION CONTINUES ON NEXT PAGE
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(e) Suppose a different system possesses an equation of state of the following form

$$P = AVT^n ,$$

where $n > 0$ is some positive definite constant, with the energy given by $E = (3/2)PV$ as above and $A > 0$. Can this system be a valid thermodynamic system if $n \neq 4$? Justify your assertions. (*Hint*: Recall that S is a function of state.)

[8 marks] U

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Solution 2

(a) A function of state is a thermodynamic quantity that is an exact function of its state variables.

(b) From $dE = TdS - PdV$, we have $dS = (1/T)dE + (P/T)dV$, and expressing $S(E, V)$ we obtain the required relationships.

(c) Simple algebra gets us

$$\frac{1}{T} = \left(\frac{3A}{2}\right)^{1/4} V^{1/2} E^{-1/4}, \quad (10)$$

and

$$\frac{P}{T} = \frac{2}{3} \left(\frac{3A}{2}\right)^{1/4} V^{-1/2} E^{3/4}. \quad (11)$$

Using (c), it is easy to see by direct integration

$$S = \frac{4}{3} \left(\frac{3A}{2}\right)^{1/4} V^{1/2} E^{3/4} + \text{const}. \quad (12)$$

(d) Using $F = E - TS$, it is easy to show via algebra that

$$F = \frac{3A}{2} V^2 T^4 - T \left[\frac{4}{3} \left(\frac{3A}{2}\right)^{1/4} V^{1/2} T^3 + \text{const} \right]. \quad (13)$$

(e) S is a function of state and hence must be exact, and thus using the relationship for exactness (one can also directly integrate but this is easier)

$$\left(\frac{\partial(1/T)}{\partial V}\right)_E = \left(\frac{\partial(P/T)}{\partial E}\right)_V \quad (14)$$

we get

$$\left(\frac{3A}{2}\right)^{1/n} \frac{2}{n} V^{-1+2/n} E^{-1/n} = \frac{2}{3} \left(\frac{3A}{2}\right)^{1/n} V^{-1+2/n} E^{-1/n} \left(1 - \frac{1}{n}\right) \quad (15)$$

which for consistency $n = 4$, thus the system is not valid if $n \neq 4$.

3) Consider a system with two *distinguishable particles*. Each particle can be in one of the two single particle energy states $\epsilon_0 = 0$ and $\epsilon_1 = \Delta$. The system is in thermal equilibrium with a heat bath of temperature T .

(a) How many microstates are there in this system? List them, and then derive the partition function for this ensemble.

[6 marks] P

(b) Calculate the mean energy of the system, and show that it is given by

$$\langle E \rangle = \frac{2\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}} .$$

[4 marks] P

(c) Calculate the Helmholtz Free energy F and the entropy of the system S . What is S in the *low* temperature limit $\beta\Delta \gg 1$? State which microstate the system would be in at this limit.

[8 marks] U

(d) Suppose the particles are *indistinguishable*. State how many microstates are there for the system if the particles are (i) bosons and (ii) fermions.

[4 marks] U

(e) Suppose each of the two distinguishable particles can be now in $N + 1$ single particle energy states (instead of 2), with energies $\epsilon_0 = 0$, $\epsilon_i = \Delta$ for $i = 1, 2, \dots, N$. Derive the partition function for this system, and calculate its entropy S . Show that the limit when the particles are in the lowest energy state $(0, 0)$ occurs when $\beta\Delta \gg 1 + \ln N$.

[8 marks] U

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Solution 3

(a) There are four microstates $(0, 0)$, $(0, \Delta)$, $(\Delta, 0)$ and (Δ, Δ) . The partition function is

$$Z = (1 + e^{-\beta\Delta})^2 \quad (16)$$

using $Z = Z_1^2$ where the single particle partition function $Z_1 = 1 + e^{-\beta\Delta}$.

(b) Straightforward algebra using

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta}. \quad (17)$$

(c) The Helmholtz free energy $F = -k_b T \ln Z = -2k_b T \ln(1 + e^{-\beta\Delta})$. And the entropy is

$$\begin{aligned} S &= -\left(\frac{\partial F}{\partial T}\right)_V \\ &= 2k_b \left[\ln(1 + e^{-\beta\Delta}) + \frac{\beta\Delta e^{-\beta\Delta}}{1 + e^{\beta\Delta}} \right]. \end{aligned} \quad (18)$$

In the low temperature limit, $e^{-\beta\Delta} \rightarrow 0$, so $S \rightarrow 0$. The entropy vanishes and the system is in the ground state $(0, 0)$ with zero energy.

(d) (i) For Bosons, the microstates $(0, \Delta)$ and $(\Delta, 0)$ are indistinguishable, so the total number of microstates is 3. (ii) For fermions, the only microstate possible is $(0, \Delta)$.

(e) In this system, the partition function for a single particle is $Z_1 = 1 + Ne^{-\beta\Delta}$. The astute will notice that the calculation is then exactly the same as the 2 energy level systems, with the replacement $e^{-\beta\Delta} \rightarrow Ne^{-\beta\Delta}$, so the entropy is

$$S = 2k_b \left[\ln(1 + Ne^{-\beta\Delta}) + \frac{\beta\Delta Ne^{-\beta\Delta}}{1 + Ne^{\beta\Delta}} \right]. \quad (19)$$

The limit for the particles to be in the ground state $(0, 0)$ is when $S \rightarrow 0$, and this occurs when $Ne^{-\beta\Delta} \rightarrow 0$, or $\beta\Delta - \ln N \gg 1$.

4) The energy spectrum for a simple quantum harmonic oscillator in 1D is given by

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

where ω is the natural frequency of the oscillator.

(a) Show that the partition function for this system is

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

[6 marks] B

(b) Consider a 3D lattice of N *non-interacting* atoms. Each atom can vibrate in 3 different directions, and each vibrational mode can be modeled as a single 1D simple quantum harmonic oscillator. Derive the partition function for this system.

[2 marks] P

(c) Show that the Helmholtz Free energy for this lattice crystal of atoms is

$$F = \frac{3}{2} N \hbar\omega + 3 N k_b T \ln (1 - e^{-\beta\hbar\omega}) .$$

[4 marks] P

(d) Calculate the mean energy $\langle E \rangle$.

[6 marks] P

(e) Calculate the heat capacity at constant volume C_V of this system. Find the behaviour of C_V at low and high temperatures of this system and hence plot C_V as a function of T . Show that it obeys the Dulong-Petit law at high temperatures. Compare this result to that of the (more accurately predictive) Debye model where $C_V \propto T^3$ at low temperatures. What is the primary assumption of this model that does not accurately describe the physics of a lattice of atoms?

[12 marks] U,P

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Solution 4

(a) The partition function is

$$\begin{aligned}
 Z &= \sum_n e^{-\beta E_n} \\
 &= e^{-\beta\hbar\omega/2} \sum_n e^{-N\beta\hbar\omega} \\
 &= e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}} \\
 &= \frac{1}{e^{\beta\hbar\omega/2} - e^{-\beta\hbar\omega/2}} \tag{20}
 \end{aligned}$$

(b) Each atom has 3 degrees of freedom, and there are N such atoms. Since the atoms are non-interacting the partition function is then a product of $3N$ degrees of freedom $Z = Z_1^{3N}$.

(c) This is simple application of the formula $F = -k_b T \ln Z$, i.e.

$$\begin{aligned}
 F &= -k_b T \ln Z \\
 &= -3Nk_b T \ln \left(e^{-\beta\hbar\omega/2} \frac{1}{1 - e^{-\beta\hbar\omega}} \right) \\
 &= \frac{3}{2} N\hbar\omega + 3Nk_b T \ln (1 - e^{-\beta\hbar\omega}) . \tag{21}
 \end{aligned}$$

(d)

$$\begin{aligned}
 \langle E \rangle &= - \left(\frac{\partial \ln Z}{\partial \beta} \right) \\
 &= 3N\hbar\omega \left[\frac{1}{e^{\beta\hbar\omega} - 1} + \frac{1}{2} \right] \tag{22}
 \end{aligned}$$

(e) The heat capacity is

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3Nk_b (\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} . \tag{23}$$

At low temperatures $\beta\hbar\omega \rightarrow \infty$, so $e^{\beta\hbar\omega} \gg 1$, thus $C_V \approx 3Nk_b (\beta\hbar\omega)^2 e^{-\beta\hbar\omega} \rightarrow 0$. On the other hand, at high temperatures $\beta\hbar\omega \rightarrow 0$, so $e^{\beta\hbar\omega} \approx 1 + \beta\hbar\omega$ and $C_V \rightarrow 3Nk_b$ which is the Dulong-Petit law. The problem with this model is that the atoms in reality cannot oscillate independently of each other as they interact strongly (in order to form a lattice). In the limit of low temperatures, $C_V \propto T^{-2} e^{-\hbar\omega/k_b T}$, so is exponential in T instead of T^3 . This is not observed in experiments.