

Name and Surname:
Student ID:
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INSTRUCTIONS

Write all your steps with explanations of why you do those steps. The questions might contain extra information or too few information. If the question does not contain sufficient information, make necessary assumptions, stating why those assumptions are necessary.

YOU HAVE 4 HOURS WITH A POSSIBILITY OF EXTENSION

1. Comment on the following concepts (Just writing equations will not gain you any points): (3 points each, 18 points total)

- (a) Canonical Distribution

Solution:

If you consider a subsystem of a larger system such that the subsystem can exchange energy with the rest of the system, then the subsystem does not have a fixed energy. The probability that the system is in a state that has a given energy is given by the canonical distribution.

- (b) Grand canonical Distribution

Solution:

If the subsystem in the canonical distribution is also allowed to exchange particles with the rest of the system, so that the particle number of the subsystem is also not fixed, then the probability that the subsystem will be in a state that has a given energy and a given number of particles is given by the grand canonical distribution.

- (c) Chemical Potential

Solution:

It is the change in the energy of the system when one particle is added to the system keeping the temperature and the volume fixed. By adjusting the chemical potential of a system, one can fix the average number of particles in the system, just like by adjusting the temperature of a system, you fix the average energy of a system.

(d) Boltzmann Distribution

Solution:

In classical mechanics, all the particles are distinguishable. But the expression for entropy in this case does not turn out to be additive. Which is a paradox since the entropy by definition is an additive quantity. The resolution is to take into account the fact that if you exchange any two particles, the new state is the same state as the original state. This can be taken into account by introducing a factor $\frac{1}{N!}$ in the definition of the summation over state. This is correct only if in each state there is at most one particle.

(e) Fermi-Dirac and Bose-Einstein Distributions

Solution:

If the average number of particles in the states is not much less than one, then the prescription of including $\frac{1}{N!}$ is no longer valid. A more careful counting of the states has to be used. Quantum physics tells us that identical particles can be of two different statistics: fermions or bosons. More than 1 fermion can not exist in a given state. Any number of bosons can exist in the same state. The average number of fermions or bosons in a given state is given by the Fermi-Dirac or Bose-Einstein distributions respectively.

(f) Equipartition Theorem

Solution:

In classical statistical mechanics, if the energy can be expressed as the sum of only quadratic terms, then the contribution of each of the quadratic terms to the specific heat at constant volume is $\frac{1}{2}$. This is called equipartition theorem.

2. Consider the classical ideal gas which is made up of point like particles with no internal structures and whose energy momentum relation is given by $\epsilon = \alpha p^n$ where α is some constant and n is some integer. Assume that the system is confined to a volume V , is at a temperature T and has a chemical potential μ . Using the Grand Canonical Distribution (you will not get any points if you use canonical distribution, even if all the rest of your steps and your results are true.) (30 points)

(a) Calculate the partition function Z and obtain Ω (15 points)

Solution:

The partition function in the grand canonical ensemble is given

by

$$Z = \sum_{N,k} e^{-\beta(E_{Nk} - \mu N)} \quad (1)$$

where k labels the states and E_{Nk} is the energy of N particles if they are in the k^{th} state. If one separates the summation over N and the states of N particles,

$$Z = \sum_{N=0}^{\infty} e^{\beta\mu N} \sum_k e^{-\beta E_{Nk}} \quad (2)$$

where $E_{Nk} = \sum_{i=1}^N \alpha p_i^n$ is the energy of N particles. Note that the summation over the states just gives the partition function in the canonical ensemble of N particles. This partition function in turn can be expressed in terms of the partition function of a single particle as:

$$Z_N = \sum_k e^{-\beta E_{Nk}} = \frac{Z_1^N}{N!} \quad (3)$$

Hence the partition function in the canonical ensemble is:

$$Z = \sum_{N=0}^{\infty} \frac{1}{N!} \left(e^{\beta\mu} Z_1 \right)^N \quad (4)$$

but the summation over N is nothing but the Taylor expansion of the exponential. Hence

$$Z = \exp(e^{\beta\mu} Z_1) \quad (5)$$

Then Ω is obtained as:

$$\Omega = -T \ln Z = -T e^{\beta\mu} Z_1 \quad (6)$$

Thus to obtain the final expression of Ω , we need to calculate the partition function of a single particle in the canonical distribution:

$$\begin{aligned} Z_1 &= \int \frac{d^3 q d^3 p}{(2\pi\hbar)^3} e^{-\beta\alpha p^n} \\ &= \frac{V 4\pi}{(2\pi\hbar)^3} \int_0^{\infty} dp p^2 e^{-\beta\alpha p^n} \end{aligned} \quad (7)$$

To calculate the integral, make the change of variable $y = \beta\alpha p^n$ or $p = 1/(\alpha\beta)^{\frac{1}{n}} y^{\frac{1}{n}}$. Then

$$Z_1 = \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \int_0^\infty dy y^{\frac{3}{n}-1} e^{-y} \quad (8)$$

From the table at the end, the integral can be obtained as $\left(\frac{3}{n} - 1\right)!$. Hence

$$Z_1 = \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \quad (9)$$

Thus the free energy is obtained as:

$$\Omega = -T e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \quad (10)$$

(b) Calculate F , S , E and W . (5 points)

Solution:

F and Ω are related through $F = \Omega + \mu N$ where N is the average number of particles, given by:

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{V,T} = e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \quad (11)$$

and hence

$$\begin{aligned} F &= -T e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! + \mu e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \\ &= e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! (-T + \mu) \end{aligned} \quad (12)$$

It is also possible to eliminate the chemical potential in favor of the average number of particles:

$$\mu = -T \ln \left[\frac{V}{2nN\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \right] \quad (13)$$

Substituting in the expression for the free energy F , we obtain:

$$F = -NT \ln \left[\frac{eV}{2nN\pi^2\hbar^3} \left(\frac{T}{\alpha}\right)^{\frac{3}{n}} \left(\frac{3}{n} - 1\right)! \right] \quad (14)$$

The entropy can be obtained either from Ω through

$$S = - \left(\frac{\partial \Omega}{\partial T} \right)_{V, \mu} \quad (15)$$

or from F through

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V, N} \quad (16)$$

(Note that even though the two derivatives are with respect to T , that parameters that are kept constant are different and hence the two derivatives are different.) Using the derivative of F ,

$$S = N \ln \left[\frac{eV}{2nN\pi^2\hbar^3} \left(\frac{T}{\alpha} \right)^{\frac{3}{n}} \left(\frac{3}{n} - 1 \right)! \right] + \frac{3N}{n} = -\frac{F}{T} + \frac{3N}{n} \quad (17)$$

The energy is then obtained as

$$E = F + TS = F + T \left(-\frac{F}{T} + \frac{3N}{n} \right) = \frac{3}{n}NT \quad (18)$$

W is defined as $W = E + PV$. To simplify the calculations note that $\Omega = -PV$ and hence $W = E - \Omega$. Substituting

$$W = \frac{3}{n}NT + T e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha} \right)^{\frac{3}{n}} \left(\frac{3}{n} - 1 \right)! \quad (19)$$

We can not leave it in this form as N and μ are related. Eliminating μ in favor of N , one obtains:

$$W = \frac{3}{n}NT - NT \quad (20)$$

- (c) Calculate the equation of state of the system. (5 points)

Solution:

The equation of state can be obtained from

$$PV = -\Omega = T e^{\beta\mu} \frac{V}{2n\pi^2\hbar^3} \left(\frac{T}{\alpha} \right)^{\frac{3}{n}} \left(\frac{3}{n} - 1 \right)! = NT \quad (21)$$

- (d) Calculate C_V and show that for $n = 2$, the results that you have obtained reduces to the result of the classical equipartition theorem results. (5 points)

	ϵ_1	ϵ_2	ϵ_3	$\sum_i \epsilon_i$	E	E'
1	$+\epsilon$	$+\epsilon$	$+\epsilon$	$+3\epsilon$	$-9a_1 + 81a_2$	$-9a_1 + 81a_2 + 3\alpha\epsilon$
2	$+\epsilon$	$+\epsilon$	$-\epsilon$	$+\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 + \alpha\epsilon$
3	$+\epsilon$	$-\epsilon$	$+\epsilon$	$+\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 + \alpha\epsilon$
4	$+\epsilon$	$-\epsilon$	$-\epsilon$	$-\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 - \alpha\epsilon$
5	$-\epsilon$	$+\epsilon$	$+\epsilon$	$+\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 + \alpha\epsilon$
6	$-\epsilon$	$+\epsilon$	$-\epsilon$	$-\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 - \alpha\epsilon$
7	$-\epsilon$	$-\epsilon$	$+\epsilon$	$-\epsilon$	$-a_1 + a_2$	$-a_1 + a_2 - \alpha\epsilon$
8	$-\epsilon$	$-\epsilon$	$-\epsilon$	-3ϵ	$-9a_1 + 81a_2$	$-9a_1 + 81a_2 - 3\alpha\epsilon$

Table 1:

Solution:

We had already obtained E in the previous part.

$$E = \frac{3}{n}NT \quad (22)$$

The C_V is the derivative of E with respect to T at constant volume V and N :

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N} = \frac{3}{n}N \quad (23)$$

For $n = 2$, $C_V = \frac{3N}{2}$ which is the result of the equipartition theorem.

3. Consider 3 dipoles that can have the energies $+\epsilon$ or $-\epsilon$ only. Let ϵ_i denote the energy of the i^{th} dipole. Assume that the energy of the system can be written in the form

$$E = -m^2 \left(\sum_i \epsilon_i \right)^2 + \lambda^2 \left(\sum_i \epsilon_i \right)^4 \quad (24)$$

where m and λ are some positive constants. (42 points)

- (a) Fill Table 1 with the possible states of the system. In total, the system can be in 8 different states. (for the time being leave the last column empty) (5 points)

Solution:

Check the table. In the table, $a_1 = m^2\epsilon^2$ and $a_2 = \lambda^2\epsilon^4$

E	Degeneracy
$-a_1 + a_2$	6
$-9a_1 + 81a_2$	2

Table 2:

- (b) In Table 2, write the possible values of energy that the system can have and also their degeneracy. (2 points)

Solution:

There are only two possible energy values. Their values and the degeneracies are written in Table 2.

- (c) If the system has temperature T , calculate its partition function (3 points), its energy E (2 points) and $\langle \sum_i \epsilon_i \rangle$ (5 points)

Solution:

The partition function of the system is:

$$Z = 6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)} \quad (25)$$

From the partition function, the free energy F of the system can be obtained as:

$$F = -T \ln \left(6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)} \right) \quad (26)$$

Differentiating with respect to T , the entropy of the system is obtained as:

$$\begin{aligned} S &= -\frac{\partial F}{\partial T} = \ln \left(6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)} \right) \\ &+ T \frac{6(-a_1 + a_2) \frac{1}{T^2} e^{-\beta(-a_1+a_2)} + 2(-9a_1 + 81a_2) \frac{1}{T^2} e^{-\beta(-9a_1+81a_2)}}{6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)}} \\ &= -\frac{F}{T} + \frac{1}{T} \frac{6(-a_1 + a_2) e^{-\beta(-a_1+a_2)} + 2(-9a_1 + 81a_2) e^{-\beta(-9a_1+81a_2)}}{6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)}} \end{aligned} \quad (27)$$

Hence the energy of the system is given by:

$$E = F + TS$$

$$= \frac{6(-a_1 + a_2)e^{-\beta(-a_1+a_2)} + 2(-9a_1 + 81a_2)e^{-\beta(-9a_1+81a_2)}}{6e^{-\beta(-a_1+a_2)} + 2e^{-\beta(-9a_1+81a_2)}} \quad (28)$$

From Table 1, it is seen that there is 1 state that has $\sum_i \epsilon_i = 3\epsilon$ and this state has energy $-9a_1 + 81a_2$ thus $p(\sum_i \epsilon_i = 3\epsilon) = Z^{-1}e^{-\beta(-9a_1+81a_2)}$; 3 states that have $\sum_i \epsilon_i = \epsilon$ and these states all have energies $-a_1 + a_2$, hence $p(\sum_i \epsilon_i = \epsilon) = 3Z^{-1}e^{-\beta(-a_1+a_2)}$; 3 states that have $\sum_i \epsilon_i = -\epsilon$ and these states all have energies $-a_1 + a_2$, hence $p(\sum_i \epsilon_i = -\epsilon) = 3Z^{-1}e^{-\beta(-a_1+a_2)}$; and 1 state that has $\sum_i \epsilon_i = -3\epsilon$ and this state has energy $-9a_1 + 81a_2$ thus $p(\sum_i \epsilon_i = -3\epsilon) = Z^{-1}e^{-\beta(-9a_1+81a_2)}$. Thus the average is given by:

$$\begin{aligned} \langle \sum_i \epsilon_i \rangle &= 3\epsilon p(\sum_i \epsilon_i = 3\epsilon) + \epsilon p(\sum_i \epsilon_i = \epsilon) \\ &+ (-\epsilon)p(\sum_i \epsilon_i = -\epsilon) + (-3\epsilon)p(\sum_i \epsilon_i = -3\epsilon) + \\ &= 3\epsilon Z^{-1}e^{-\beta(-9a_1+81a_2)} + \epsilon 3Z^{-1}e^{-\beta(-a_1+a_2)} \\ &+ (-\epsilon)3Z^{-1}e^{-\beta(-a_1+a_2)} + (-3\epsilon)Z^{-1}e^{-\beta(-9a_1+81a_2)} \\ &= 0 \end{aligned} \quad (29)$$

Hence the average is zero independent of the temperature.

(d) What is

$$\lim_{T \rightarrow 0} \langle \sum_i \epsilon_i \rangle \quad (30)$$

(5 points)

Solution:

In the previous section, the average is shown to be zero for all values of T and hence:

$$\lim_{T \rightarrow 0} \langle \sum_i \epsilon_i \rangle = 0 \quad (31)$$

(e) Now assume that you add the term $\alpha \sum_i \epsilon_i$ to the energy of the system for some positive constant α . Fill the last column of Table 1 with the new energy values of the system. (5 points)

Solution:

Check Table 1.

- (f) For the new system, calculate $\langle \sum_i \epsilon_i \rangle$ as a function of α (10 points)

Solution:

The partition function of the system can be written as:

$$\begin{aligned} Z &= \sum_{k=1}^8 e^{-\beta(E_k - \alpha \sum_i \epsilon_i)} \\ &= e^{-\beta(-8a_1 + 81a_2 + 3\alpha\epsilon)} + 3e^{-\beta(-a_1 + a_2 + \alpha\epsilon)} \\ &\quad + 3e^{-\beta(-a_1 + a_2 - \alpha\epsilon)} + e^{-\beta(-8a_1 + 81a_2 - 3\alpha\epsilon)} \end{aligned} \quad (32)$$

where $k = 1, \dots, 8$ denote the 8 states of the system. Note that the average $\langle \sum_i \epsilon_i \rangle$ can be written as:

$$\begin{aligned} \langle \sum_i \epsilon_i \rangle &= Z^{-1} \sum_{k=1}^8 e^{-\beta(E_k + \alpha \sum_i \epsilon_i)} \left(\sum_i \epsilon_i \right) \\ &= -T Z^{-1} \sum_{k=1}^8 \frac{\partial}{\partial \alpha} e^{-\beta(E_k + \alpha \sum_i \epsilon_i)} = -T \frac{\partial \ln Z}{\partial \alpha} \\ &= 3\epsilon \frac{e^{-\beta(-8a_1 + 81a_2 + 3\alpha\epsilon)} + e^{-\beta(-a_1 + a_2 + \alpha\epsilon)} - e^{-\beta(-a_1 + a_2 - \alpha\epsilon)} - e^{-\beta(-8a_1 + 81a_2 - 3\alpha\epsilon)}}{e^{-\beta(-8a_1 + 81a_2 + 3\alpha\epsilon)} + 3e^{-\beta(-a_1 + a_2 + \alpha\epsilon)} + 3e^{-\beta(-a_1 + a_2 - \alpha\epsilon)} + e^{-\beta(-8a_1 + 81a_2 - 3\alpha\epsilon)}} \end{aligned} \quad (33)$$

- (g) In your new expression of $\langle \sum_i \epsilon_i \rangle$ for the modified system, first take the limit $T \rightarrow 0$ and then the limit $B \rightarrow 0$ and show that the value that you obtain is different from the value you have obtained in part (d). If you take the limits in the other order, you would have obtained the result of part (d). Hence the limits do not commute. (10 points)

Solution:

In the limit $T \rightarrow 0$, $\beta \rightarrow \infty$ and hence in the partition function only the contribution of exponents that are the most positive are important, the other ones go to zero much faster.

To determine which term in the partition function remains, we need to know which energy $E_1 = -a_1 + a_2$ or $E_2 = -9a_1 + 81a_2$ is lower than the other, that is what is the ground state of our system. (Note that we are also assuming that the $\alpha \sum_i \epsilon_i$ term is sufficiently small so that it does not effect the ordering of the states. $E_1 > E_2$ if $a_1 > 10a_2$ and $E_1 < E_2$ if $a_1 < 10a_2$. Let's consider the first case: Since $E_1 > E_2$, it is only the exponents which contain E_2 that survive in the limit $T \rightarrow 0$: Hence, in this

limit

$$\lim_{T \rightarrow 0} \langle \sum_i \epsilon_i \rangle = 3\epsilon \frac{-e^{-\beta(-9a_1+81a_2-3\alpha\epsilon)}}{e^{-\beta(-9a_1+81a_2-3\alpha\epsilon)}} = -3\epsilon \quad (34)$$

Note that, the additional term lifts the degeneracy between the 1st and the 8th state and after the addition of the term, the 8th state is the ground state. This state has $\sum_i \epsilon_i = -3\epsilon$.

In the other case, i.e. $E_1 < E_2$, only the term that contains the exponent of E_1 survives and hence in this limit:

$$\lim_{T \rightarrow 0} \langle \sum_i \epsilon_i \rangle = 3\epsilon \frac{-e^{-\beta(-a_1+a_2-\alpha\epsilon)}}{3e^{-\beta(-a_1+a_2-\alpha\epsilon)}} = -\epsilon \quad (35)$$

Note that in this limit also, although the degeneracy between the state that have $\sum_i \epsilon_i = \epsilon$ and $\sum_i \epsilon_i = -\epsilon$ is not completely lifted, due to the extra term, the states that have $\sum_i \epsilon_i = -\epsilon$ has a slightly lower energy. And hence in the limit $T \rightarrow 0$ the system settles in its ground state also in this case.

In both the cases, the limit is independent of α , hence taking the limit $\alpha \rightarrow 0$ does not change the result.

- (h) Note that in the original system, without the additional term, the energy does not change if you replace every ϵ_i with $-\epsilon_i$. It is said that the system has a symmetry. Under this symmetry $\sum_i \epsilon_i$ changes sign. $\langle \sum_i \epsilon_i \rangle$ is invariant under this symmetry only if $\langle \sum_i \epsilon_i \rangle = 0$ as you should have found in part (d). If you add the additional term, this symmetry is no longer respected, and hence $\langle \sum_i \epsilon_i \rangle$ acquires a non-zero value. And this is reflected in the value of $\langle \sum_i \epsilon_i \rangle$ in the limit $T \rightarrow 0$ at some non-zero value of α . If you take the limit $\alpha \rightarrow 0$ after the limit $T \rightarrow 0$, although the energy acquires the symmetry, $\langle \sum_i \epsilon_i \rangle$ still remains non-zero violating the symmetry. It is said that the symmetry of the system is broken.

4. In the class, we had shown that the free energy F of a classical ideal gas made up of particles with internal degrees of freedom can be written as:

$$F = -NT \ln \left[\frac{eV}{N} \left(\frac{mT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \sum_k e^{-\beta\epsilon_k} \right] \quad (36)$$

where k specifies the internal state of the system and ϵ_k is the internal energy. Without knowing the structure of the molecule, it is not possible to calculate the sum. But note that the sum depends only on the temperature T of the system. Hence the free energy of the system can be written as

$$F = -NT \ln \frac{eV}{N} + Nf(T) \quad (37)$$

for some unknown function $f(T)$. Let the specific heat of the system be written as $C_V = Nc_V$ where c_V is the specific heat per particle. Assume that c_V is constant. (20 points)

- (a) Show that

$$f(T) = -c_V T \ln T - \chi T + \epsilon_0 \quad (38)$$

where χ and ϵ_0 are some constants. (10 points)

Solution:

In terms of F , the entropy of the system can be written as:

$$S = - \left(\frac{\partial F}{\partial T} \right)_{V,N} = N \ln \frac{eV}{N} - Nf'(T) \quad (39)$$

and hence the energy is:

$$\begin{aligned} E &= F + TS = -NT \ln \frac{eV}{N} + Nf(T) + NT \ln \frac{eV}{N} - NTf'(T) \\ &= N(f(T) - Tf'(T)) \end{aligned} \quad (40)$$

By differentiating E with respect to T , one obtains for the specific heat at constant volume:

$$Nc_V = C_V = N \frac{d}{dT} (f(T) - Tf'(T)) \quad (41)$$

or

$$c_V = \frac{d}{dT} (f(T) - Tf'(T)) \quad (42)$$

Integrating both sides with respect to T ,

$$f(T) - Tf'(T) = c_V T + k_1 \quad (43)$$

where k_1 is some constant. Deviding both sides by T^2 , one can write this differential equation in the form:

$$\frac{c_V}{T} + \frac{k_1}{T^2} = \frac{f(T)}{T^2} - \frac{f'(T)}{T^2} = -\frac{d}{dT} \frac{f(T)}{T} \quad (44)$$

Integrating both sides again with respect to T , we find:

$$\frac{f(T)}{T} = -c_V \ln T + \frac{k_1}{T} + k_2 \quad (45)$$

where k_2 is an integration constant. This can be written as:

$$f(T) = -c_V T \ln T + k_2 T + k_1 \quad (46)$$

Identifying $k_2 = -\chi$ and $k_1 = \epsilon_0$, we find:

$$f(T) = -c_V T \ln T - \chi T + \epsilon_0 \quad (47)$$

(b) Calculate S , E , Ω , μ for this. (10 points)

Solution:

With the result of the previous part, the free energy is:

$$F = -NT \ln \frac{eV}{N} - NTc_V \ln T - \chi NT + N\epsilon_0 \quad (48)$$

Then the entropy of the system is:

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V} = N \ln \frac{eV}{N} + Nc_V \ln T + Nc_V + \chi N \quad (49)$$

The energy is:

$$\begin{aligned} E &= F + TS = -NT \ln \frac{eV}{N} - NTc_V \ln T - \chi NT + N\epsilon_0 \\ &+ NT \ln \frac{eV}{N} + NTc_V \ln T + NTc_V + \chi NT \\ &= N\epsilon_0 + NTc_V \end{aligned} \quad (50)$$

The chemical potential μ can be obtained from F by differentiating with respect to N :

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = -T \ln \frac{eV}{N} + T - Tc_V \ln T - \chi T + \epsilon_0 = \frac{F}{N} + T \quad (51)$$

And then the free energy Ω is related to F through:

$$\Omega = F - \mu N = F - N \left(\frac{F}{N} + T \right) = -NT \quad (52)$$

You can use the following formulas/definitions without deriving them:

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

$$dF = -SdT - PdV + \mu dN$$

$$dW = TdS + VdP + \mu dN$$

$$d\Phi = -SdT + VdP + \mu dN$$

$$d\Omega = -SdT - PdV - Nd\mu$$

$$F = E - ST ; W = E + PV ; \Phi = E - ST + PV ; \Omega = F - \mu N$$

$$S = \ln \Delta\Gamma(E) ; \Delta\Gamma(E) = \Delta E \frac{\partial}{\partial E} \Gamma(E)$$

$$\ln N! \simeq N \ln N - N$$

$$\int_0^\infty x^n e^{-x} = n!$$

$$\beta = \frac{1}{T}, \quad k = 1$$

For anything else, you need to derive it.