Solution for statistical mechanics qual exam January 2005

1 Part A

A uniform system has \( N \) particles in a volume \( V \). The Helmholtz free energy \( F \) is given by \( F = E - TS \), where \( E \) is the internal energy, \( T \) is the absolute temperature, and \( S \) is the entropy. Use the first and second laws of thermodynamics to obtain the following results:

\[
S = -\left( \frac{\partial F}{\partial T} \right)_V, \quad p = -\left( \frac{\partial F}{\partial V} \right)_N, \quad \mu = \left( \frac{\partial F}{\partial N} \right)_T,
\]

where \( \mu \) is the chemical potential and \( p \) is the pressure.

The first law of thermodynamics states the conservation of energy. It is often written in differential form as

\[
dE = \delta W + \delta Q
\]

where \( \delta W \) is the work done on the system and \( \delta Q \) is the heat added to the system. Neither of these quantities is a perfect differential. In contrast, the important content of the first law is that the internal energy \( E \) is a function of the state of the system, so that \( dE \) is a perfect differential. For the system under consideration, the work done is \( \delta W = -pdV + \mu dN \), where \( p \) is the pressure and \( \mu \) is the chemical potential (the first term follows from elementary force considerations and the second can be considered a definition of \( \mu \)). The second law of thermodynamics can be written as \( \delta Q = TdS \), where the entropy \( S \) is also a function of the state of the system, so that \( dS \) is a perfect differential. Together, these relations give

\[
dE = TdS - pdV + \mu dN,
\]

implying that \( E \) is a natural function of the variables \( S, V, N \).

Direct calculation shows that the Helmholtz free energy \( F = E - TS \) has the corresponding differential

\[
dF = -SdT - pdV + \mu dN.
\]

Hence \( F \) is a natural function of the variables \( T, V, N \), and the desired relations follow by inspection as the appropriate partial derivatives.

2 Part B

An ideal gas consists of \( N \) indistinguishable ultrarelativistic classical particles (each has the dispersion relation \( \epsilon_p = cp \) where \( p = |\vec{p}| = \sqrt{p_x^2 + p_y^2 + p_z^2} \) and \( c \) is the speed of light in vacuum)

1. Calculate the partition function \( Z(T, V, N) \) for this gas.
The Hamiltonian for the \( N \)-body system is \( H = \sum_{j=1}^{N} \mathbf{p}_j \). For \( N \) classical indistinguishable particles, the partition function is an integral over all phase space

\[
Z = \frac{1}{N!h^{3N}} \int d^{3N} p \, d^{3N} q \, e^{-\beta H(p,q)},
\]

where \( \beta = (k_B T)^{-1} \), the factor \( N! \) arises from the permutations among the indistinguishable particles, and the factors of Planck’s constant \( h \) are needed to give the correct correspondence with quantum statistical mechanics.

It is easy to evaluate this integral to obtain the result

\[
Z = \frac{1}{N!} \left( \frac{V}{\lambda_R^3} \right)^N,
\]

where \( \lambda_R^3 = \pi^2 \hbar^2 c/(k_B T)^3 \) appears on doing the integrals. Note that the canonical partition function is indeed an explicit function of the variables \( T, V, N \), as anticipated.

2. Use Stirling’s approximation \( \ln N! \approx N \ln N - N \) to derive the following expression for the Helmholtz free energy

\[
F = -k_B TN \left[ \ln \left( \frac{V}{N \lambda_R^3} \right) + 1 \right],
\]

where \( \lambda_R = \pi^{2/3} \hbar^2 c/(k_B T) \) is the relativistic thermal wavelength. How does the classical limit constrain \( \lambda_R \) relative to the interparticle spacing \( \ell \equiv (V/N)^{1/3} \)?

The basic result of the canonical ensemble relates the Helmholtz free energy \( F \) to the canonical partition function \( Z \) according to \( F = -k_B T \ln Z \). Application to the result of part 1 and use of Stirling’s approximation readily give the result given in the problem. Note that \( F \) is indeed a function of the expected variables \( T, V, N \).

The thermal wavelength \( \lambda_R \) characterizes the ultrarelativistic de Broglie quantum waves at temperature \( T \). The classical limit (analogous to ray optics) requires that \( \lambda_R \) be much smaller than the interparticle spacing \( \ell \equiv (V/N)^{1/3} \), so that quantum diffraction is negligible. When \( \ell \sim \lambda_R \), quantum diffraction becomes important, along with the quantum statistics of identical particles; this happens at sufficiently low temperatures.

3. Use part A to find the equation of state and the chemical potential.

The partial derivative in Part A immediately gives the pressure \( p = Nk_B T/V \), which is simply the familiar equation of state for a classical ideal gas. Note that the ultrarelativistic dispersion relation plays no role here. Similarly, the chemical potential becomes

\[
\mu = -k_B T \ln \left( \frac{V}{N \lambda_R^3} \right).
\]

For an ideal classical gas, the quantity \( \mu/k_B T = \beta \mu \) is typically large and negative, because the classical occupation for each state contains a factor \( e^{\beta \mu} \), which must be small compared to 1 if quantum statistics are irrelevant.
4. Similarly, find the entropy and the heat capacity \( C_V \) at constant volume. How and why does \( C_V \) differ from that for an ideal nonrelativistic classical gas?

The partial derivative with respect to \( T \) from part A immediately gives the entropy

\[
S = Nk_B \left[ \ln \left( \frac{V}{N\lambda_R^3} \right) + 4 \right],
\]

where the additional contribution 3 comes from the derivative of the thermal wavelength. Note that \( S \) still depends on \( T \) through \( \lambda_R \).

The basic thermodynamic relation \( \delta Q = TdS \) leads to the desired heat capacity

\[
C_V = T \left( \frac{\partial S}{\partial T} \right)_{V,N} = 3Nk_B.
\]

It differs from the classical nonrelativistic result (which has a factor \( \frac{3}{2} \) instead of 3) because of the altered dispersion relation. Note that the usual equipartition theorem fails here, because each particle contributes a linear term to the energy, instead of the quadratic one familiar from nonrelativistic mechanics.

5. Find the heat capacity \( C_p \) at constant pressure. Find \( C_p - C_V \) and compare with the nonrelativistic result.

One easy way to obtain \( C_p \) is to re-express the entropy in terms of the pressure using the equation of state, giving

\[
S = Nk_B \left[ \ln \left( \frac{k_B T}{p\lambda_R^3} \right) + 4 \right].
\]

The extra factor of \( T \) means that \( C_p = T(\partial S/\partial T)_{p,N} = 4Nk_B \). The difference \( C_p - C_V = Nk_B \) now has the same value as for an ideal nonrelativistic gas (the difference follows from the equation of state, which is the same in both cases).