1. (35 %) Consider a system at equilibrium described by the grand canonical ensemble.

   a) Calculate the pressure for an ideal gas (non-interacting particles) and show that it is equivalent to \( pV = \langle N \rangle k_BT \).

   \[
   \beta pV = \ln Z_{GC} = \ln \sum_N \frac{e^{\beta \mu N}}{h^{3N} N!} \int \frac{d\Gamma e^{-\beta H}}{\lambda^{3N} N!} = \ln \sum_N \frac{V^N e^{\beta \mu N}}{\lambda^{3N} N!}
   \]

   \[= \frac{Ve^{\beta \mu}}{\lambda^3}, \quad \lambda = \sqrt{\frac{\hbar^2}{2m k_BT}}\]

   \[N = \frac{\partial}{\partial (\beta \mu)} \ln Z_{GC} = \frac{Ve^{\beta \mu}}{\lambda^3}\]

   \[\beta pV = N\]

   b) Show that the specific heat \( C = \frac{\partial E}{\partial T} |_{\alpha,V} \), where \( \alpha = -\beta \mu \), is proportional to the fluctuations in energy.

   \[E = -\frac{\partial}{\partial \beta} \ln Z_{GC} = \langle H \rangle\]

   \[
   \frac{\partial E}{\partial T} |_{\alpha,V} = \frac{\partial \beta}{\partial \beta} \frac{\partial E}{\partial \beta} |_{\alpha,V} = \frac{1}{T^2} \frac{\partial^2}{\partial \beta^2} \ln Z_{GC} = \frac{1}{T^2} \langle H (H - \langle H \rangle) \rangle
   \]

   \[= \frac{1}{T^2} \left( \langle H - \langle H \rangle \rangle^2 \right)\]

   c) Show that the specific heat above for a system with interacting particles is greater than that for non-interacting particles (i.e. \( H = K + V \) in the first case and \( H = K \) in the second case, where \( K \) is the kinetic energy).

   \[
   \left( \langle H - \langle H \rangle \rangle^2 \right) = \left( \langle (K - \langle K \rangle)^2 \rangle + \langle (V - \langle V \rangle)^2 \rangle - 2 \langle (K - \langle K \rangle) (V - \langle V \rangle) \rangle \right)
   \]

   \[= \left( \langle (K - \langle K \rangle)^2 \rangle + \langle (V - \langle V \rangle)^2 \rangle \right) \]

   \[\geq \left( \langle (K - \langle K \rangle)^2 \rangle \right)\]

   The second equality follows from the fact that \( \langle (K - \langle K \rangle) (V - \langle V \rangle) \rangle = 0 \) by performing the momentum integrations.
2. (35 %) Two of the equations of state for an ideal gas are

\[ F_E = \frac{1}{k_B T}, \quad F_V = \frac{p}{k_B T} = \frac{N}{V}. \]

a) Write the entropy \( S(E, V, N) \) in terms of the forces \( F \) and the extensive variables \( X \), and identify the chemical potential \( \mu \) in terms of the entropy.

\[
S = \frac{1}{T} E + \frac{p}{T} V - \frac{\mu}{T} N = k_B F_E E + k_B F_V V + k_B F_N N
\]

\[
\frac{\mu}{T} = -\frac{\partial S}{\partial N}|_{E,V}
\]

b) Determine the functional form of \( \mu = \mu(E, V, N) \).

\[
S = \frac{5}{2}Nk_B - \frac{\mu}{T}N
\]

\[
dS = d\left(\frac{5}{2}Nk_B - \frac{\mu}{T}N\right) = \frac{1}{T}dE + \frac{p}{T}dV - \frac{\mu}{T}dN = k_B \left(\frac{3N}{2E}dE + \frac{N}{V}dV - \frac{\mu}{k_BT}dN\right)
\]

or

\[
d\left(\frac{\mu}{T}\right) = -k_B \left(\frac{3}{2E}dE + \frac{1}{V}dV - \frac{5}{2N}dN\right) = k_B d\ln\left(\frac{E^{3/2}V}{N^{5/2}}\right)
\]

\[
\mu = -k_B T \ln\left(\frac{E^{3/2}V}{N^{5/2}}\right) = -\frac{2E}{3N} \ln\left(\frac{E^{3/2}V}{N^{5/2}}\right)
\]

3. (30 %) Suppose an initial state for an isolated system with fixed \( E, V, N \) is specified by a probability distribution function in gamma space \( \rho(\Gamma, 0) \).

a) How is the expectation value of an observable \( A \) defined at time \( t \)?

\[
\langle A \rangle = \int d\Gamma \rho(\Gamma, 0) A(\Gamma(t))
\]

b) What is a macrostate, and what is the special macrostate called the equilibrium state?

A macrostate is a specific set of values for a selected small set of observables, \( \{A_\alpha = a_\alpha\} \). Alternatively, it is the set of microstates (\( \Gamma \) points) corresponding to these values. The equilibrium macrostate is that one corresponding to the largest number of microstates.

c) What does it mean for a system to "approach equilibrium" from an arbitrary initial state?

The physical systems of interest are such that the equilibrium state is represented by most of the microstates of the energy surface. Hence for a given initial \( \Gamma \) point that may not be among the equilibrium set, its trajectory will wander across the energy surface and soon move among the equilibrium set. It is possible that it will move out of this set, but since the set is so large this will be a rare "fluctuation" away from equilibrium.