1. (35 %) The energy in the canonical ensemble is not constant.
   a) Define a measure of the fluctuation of the energy in the canonical ensemble.

   $\Delta = \sqrt{\frac{\langle H^2 \rangle - \langle H \rangle^2}{\langle H \rangle^2}}$

   b) Show that the energy fluctuations are related to the specific heat and that they are small.

   $\langle H \rangle = -\partial_\beta \ln Z_c, \quad Z_c = \frac{1}{h^{3N} N!} \int d\Gamma e^{-\beta H}$

   $\langle H^2 \rangle - \langle H \rangle^2 = \partial_\beta^2 \ln Z_c = -\partial_\beta E = \frac{1}{k_B T} C_V$

   so

   $\Delta = \sqrt{\frac{C_V}{k_B T E^2}} \sim \frac{1}{\sqrt{N}}$

   c) Determine the probability density $P(\epsilon)$ to find a value for the energy $\epsilon$ in the canonical ensemble.

   $P(\epsilon) = \langle \delta(\epsilon - H) \rangle = \frac{1}{h^{3N} N!} e^{\beta F} \int d\Gamma \delta(E - H) e^{-\beta H}$

   $= e^{\beta (F - \epsilon)} \frac{1}{h^{3N} N!} \int d\Gamma \delta(E - H) = e^{\beta (F - \epsilon + TS(\epsilon))}$

   The entropy has a maximum at $\epsilon = E$ so

   $F - \epsilon + TS(\epsilon) = E - TS(E) - \epsilon + TS(\epsilon)$

   $= E - \epsilon + T \frac{\partial S(E)}{\partial E} (\epsilon - E) + \frac{1}{2} T \frac{\partial S(E)}{\partial E} (\epsilon - E)^2$

   $= -\frac{1}{2T} \frac{\partial T}{\partial E} (\epsilon - E)^2$

   $P(\epsilon) \approx \exp \frac{(\epsilon - E)^2}{2k_B T^2 C_V}$

2. (35 %) The Hamiltonian for $N$ independent particles harmonically bound to fixed lattice points $\{r_{i0}\}$ is
\[ H = \sum_{i=1}^{N} \left( \frac{p_i^2}{2m} + \frac{1}{2}k \| \mathbf{r}_i - \mathbf{r}_{0} \|^2 \right) . \]

a) Calculate the grand partition function \( Z_{gc}(T, \mu, V) \) for this system.

\[ Z_{gc} = \sum_{N} \frac{e^{\beta \mu N}}{h^{3N} N!} \int d\Gamma e^{-\beta H} = \sum_{N} \frac{x^{N}}{N!} = e^x \]

\[ x = \frac{e^{\beta \mu}}{h^3} \int dp \int dr e^{-\beta \frac{1}{2m} p^2} \int dr e^{-\beta \frac{1}{2}kr^2} = \frac{e^{\beta \mu}}{h^3} \beta^{-3} \int dp \int dr e^{-\beta \frac{1}{2m} p^2} \int dr e^{-\beta \frac{1}{2}kr^2} \]

b) Calculate the internal energy as function of \((T, <N>, V)\).

\[ E = \left( -\frac{\partial \ln Z_{gc}}{\partial \beta} \right)_{\beta \mu} = \frac{3}{\beta} \]

\[ <N> = \left( \frac{\partial \ln Z_{gc}}{\partial \beta} \right)_{\beta \mu} = x \]

so

\[ E = \frac{3}{\beta} <N> \]

b) Calculate the pressure and interpret your result.

\[ \beta pV = x = <N> . \]

Ideal gas since particles do not interact with each other.

3. (30 %)

a) Define a Legendre transformation.

Consider a function \( f(x, y) \) with the definition

\[ f(x, y), \quad z = \frac{\partial f}{\partial x} \]

The Legendre transformation from \((x, y)\) to \((z, y)\) is

\[ g(z, y) = f(x, y) - xz \]

b) Give the Legendre transformation from \( E(S, V, N) \) to an appropriate thermodynamic function of the variables \((T, p, N)\).

\[ X(T, p, N) = E - TS + pV \]

\[ dX = \left( \frac{\partial E}{\partial S} \right)_{V,N} dS + \left( \frac{\partial E}{\partial V} \right)_{S,N} dV + \left( \frac{\partial E}{\partial N} \right)_{S,V} dN - TdS - SdT + pdV + Vdp \]

\[ = -SdT + Vdp + \left( \frac{\partial E}{\partial N} \right)_{S,V} dN \]
c) Prove the Maxwell relation

\[
\left( \frac{\partial S}{\partial p} \right)_{T,N} = - \left( \frac{\partial V}{\partial T} \right)_{p,N}.
\]

From above

\[
-S = \left( \frac{\partial X}{\partial T} \right)_{T,N} \quad V = \left( \frac{\partial X}{\partial p} \right)_{p,N}
\]

so

\[
\left( \frac{\partial S}{\partial p} \right)_{T,N} = - \frac{\partial^2 X}{\partial p \partial T} = - \frac{\partial^2 X}{\partial T \partial p} = - \left( \frac{\partial V}{\partial T} \right)_{p,N}.
\]