1. Show that the following relations for state functions hold:
   a. In analogy to \( -\partial (\ln Z/\partial \beta)_{N,V}=U \) and \( \partial (\partial (\ln Z/\partial \beta)_{N,V})/\partial \beta,U_{N,V} \) proved in class, what are \( \partial (\ln Z/\partial \beta)_{N,V} \) and \( \partial^2 (\ln Z/\partial \beta \mu)_{N,V} \) where \( Z=e^{\beta PV} \) is the grand canonical partition function? Work in the Grand ensemble to derive this most easily by analogy of corresponding variables in the canonical ensemble!
   b. For the ideal gas \( PV=nRT=N/\beta \) show that: i) \( \ln Z=N \); ii) \( \ln Z=e^{\beta \mu} \) [Hint: use the derivative \( \partial (\ln Z/\partial \beta \mu)_{N,V} \) from above, and remember that if \( \partial y/\partial x=y \), then \( y=e^x \).]; iii) \( N=\delta^2 N \) [Hint: the second derivative \( \partial^2 y/\partial x^2=y \) also if \( y=e^x \).]
   c. Based on your answer in c-iii), what happens to the fluctuation of particle numbers \( \sqrt{\delta^2 N} \) when a system becomes macroscopic, i.e. \( N>>1 \)?

2. Using the van der Waals equation of state, at what temperature \( T_c(a,b) \) is the critical point, where the two roots of \( P(V) \) disappear?

3. \( |a> \) and \( |b> \) are one-particle states, \( 1 \) and \( 2 \) serve as labels for indistinguishable particles.
   a. Show that \( |a_1> |b_2> \) is not an eigenfunction of the permutation operator \( \mathcal{P} \).
   b. Show that \( (1/\sqrt{2}) \{ |a_1> |b_2> \pm |b_1> |a_2> \} \) are eigenfunctions of \( \mathcal{P} \) with eigenvalue \( \pm 1 \).
   c. Show that two identical fermions cannot occupy the state \( |a> \) with non-zero probability.

4. If you have an unlimited supply of $1, $2 and $5 bills, how many ways are there to make change for $10? How many ways are there to make change for $10 with exactly 6 bills?

5. Let us derive the heat capacity for phonons. Like photons discussed in lecture, phonons can be annihilated and created in any number by anharmonic couplings in the potential energy, therefore \( \mu=0 \).
   a. The dispersion relation for phonons for the above chain of atoms is \( \lambda v=\omega' k=\alpha(\gamma/m)^{1/2} \) at low frequencies (obtained by normal mode analysis, which you learn about in Chem 542). What is the velocity \( v \) of phonons? Plug in reasonable rough values for \( a, \gamma \) and \( m \) to estimate the velocity. (For example, \( m=12 \) amu = \( 12 \times 1.66 \times 10^{-27} \) kg for a carbon.)
   b. Using a and making the analogy to photons, write down \( u(T,\omega) \), the energy per unit frequency and unit volume at temperature \( T \) for a chain of atoms, in terms of \( \omega, T, \) and \( v \). For the 3-D case, assume for simplicity that the velocity \( v \) is the same for all types of modes in all directions, and note that phonons have 3 polarizations (2 transverse polarizations like photons, and 1 longitudinal polarization):
c. The lowest possible phonon frequency is close to 0, when the left half of atoms in the macroscopic crystal move left, and right half move right. To approximate the highest possible phonon frequency, what is the vibrational frequency $\omega_{\text{max}}$ of a single atom moving back and forth between two walls of fixed atoms?

d. Using d, write down $u(T)$, the energy per unit volume integrated from the lowest ($\approx 0$) to the highest frequency of the crystal lattice.

e. By Taylor-expanding the exponential in the denominator in d, show that at high temperature, $u(T) \sim T$. Therefore, what happens to the heat capacity $c_v$ at high $T$? Note that to get the correct constant value $c_v=3k_B T$ per atom in the lattice, the maximum frequency for a cubical crystal that goes into the integration limit would have to be determined accurately, instead of your rough estimate in c.