1. An approximate partition function for a dense gas is of the form

\[
Q(N,V,T) = \frac{1}{N!} \left( \frac{2\pi nkT}{h^2} \right)^{3N/2} \frac{(V - Nb)^N}{(V - Nb)^{N!}} \exp \left( \frac{aN^2}{VkT} \right)
\]

where \(a\) and \(b\) are constants related to the intermolecular forces in the gas. Calculate the equation of state from this partition function. What equation of state is this? Calculate the thermodynamic energy, \(U\), and the heat capacity at constant volume for this gas. \(\{$McQuarrie, 2-17\}\)

2. The probability of observing a closed, thermally equilibrated system with a given energy \(U\) is 
\[
P(U) \propto \Omega(U) \exp(-\beta U) = \exp[\ln\Omega(U) - \beta U].
\]
Both \(\ln\Omega(U)\) and \(-\beta U\) are of the order of \(N\), which suggests that \(P(U)\) is a very narrow distribution centered on the most probable value of \(U\). Verify this suggestion by performing a steepest descent calculation with \(P(U)\). That is, expand \(\ln P(U)\) in powers of \(\delta U = U - <U>\) and truncate the expansion after the quadratic term. Use this expansion to estimate for 0.001 moles of an ideal monoatomic gas the probability of observing a spontaneous fluctuation in \(U\) of the size of \(10^{-6}<U>\). Data: \(k_B = 1.38 \times 10^{-23} J/K\); for ideal monoatomic gases, \(C_V = 3/2Nk_B\) and \(U = 3/2Nk_BT\). \(\{$Chandler, 3.8\}\)

3. The constant-pressure (NPT) ensemble is often used in computer simulations.
   a. What is the probability of a given microstate \(v\) (with known \(U_v\) and \(V_v\)) in this ensemble?
   b. What is the corresponding partition function, \(\Xi\)? Obtain an expression for the average volume of a system, \(<V>\) in terms of the partition function \(\Xi\).
   c. Obtain an expression for the fluctuation in enthalpy \(<(H - <H>)^2>\) in this ensemble in terms of thermodynamic derivatives (analogous to the expression for \(<(U - <U>)^2>\) in the canonical ensemble). What is the behavior of this derivatives as the limit of stability of a pure component is approached? Repeat for \(<(V - <V>)^2>\).

4. Consider a solution containing a solute species at a low concentration. The solute molecules undergo conformational transitions between two isomers, \(A\) and \(B\). Let \(N_A\) and \(N_B\) denote the numbers of \(A\) and \(B\) isomers, respectively. While the total number of solute molecules \(N = N_A + N_B\) remain constant, at any instant the values of \(N_A\) and \(N_B\) differ from their mean values of \(<N_A>\) and \(<N_B>\). Show that mean square fluctuations are given by

\[
<(N_A - <N_A>)^2> = x_A x_B N,
\]

where \(x_A\) and \(x_B\) are the average mole fractions of \(A\) and \(B\) species. You will need to assume that the solutes are at such a low concentration that each solute molecule is uncorrelated from every other solute molecule. \(\{$Chandler 3.23\}\)

5. We discussed in class the possibility of systems with negative temperatures. You are asked to explain (a) which direction heat flows when a system at negative temperature contacts a system at positive temperature and (b) whether the efficiency of a Carnot engine operating between reservoirs of \(T_H > 0\) and \(T_C < 0\) is still \(\eta = (T_H - T_C)/T_H\). Since \(T_C < 0\), is \(\eta > 1\) for power generation in this case? Does this violate the 2nd Law?