

PROBLEM SET 6

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

$$Q(N, \underline{V}, T) = \frac{1}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2} (\underline{V} - Nb)^N \exp(aN^2/\underline{V}kT)$$

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, \underline{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 \underline{U} is $P(\underline{U}) \propto \Omega(\underline{U}) \exp(-\beta\underline{U}) = \exp[\ln\Omega(\underline{U}) - \beta\underline{U}]$. Both $\ln\Omega(\underline{U})$ and $-\beta\underline{U}$ are of the order of N , which suggests that $P(\underline{U})$ is a very narrow distribution centered on the most probable value of \underline{U} . Verify this suggestion by performing a steepest descent calculation with $P(\underline{U})$. That is, expand $\ln P(\underline{U})$ in powers of $\delta\underline{U} = \underline{U} - \langle \underline{U} \rangle$ 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 \underline{U} of the size of $10^{-6} \langle \underline{U} \rangle$. Data: $k_B = 1.38 \times 10^{-23}$ J/K; for ideal monoatomic gases, $C_V = 3/2 Nk_B$ and $\underline{U} = 3/2 Nk_B T$. {Chandler, 3.8}
3. The constant-pressure (NPT) ensemble is often used in computer simulations.
- What is the probability of a given microstate v (with known \underline{U}_v and \underline{V}_v) in this ensemble?
 - What is the corresponding partition function, \mathcal{E} ? Obtain an expression for the average volume of a system, $\langle \underline{V} \rangle$ in terms of the partition function \mathcal{E} .
 - Obtain an expression for the fluctuation in enthalpy $\langle (\underline{H} - \langle \underline{H} \rangle)^2 \rangle$ in this ensemble in terms of thermodynamic derivatives (analogous to the expression for $\langle (\underline{U} - \langle \underline{U} \rangle)^2 \rangle$ in the canonical ensemble). What is the behavior of this derivatives as the limit of stability of a pure component is approached? Repeat for $\langle (\underline{V} - \langle \underline{V} \rangle)^2 \rangle$.
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 $\langle N_A \rangle$ and $\langle N_B \rangle$. Show that mean square fluctuations are given by
- $$\langle (N_A - \langle N_A \rangle)^2 \rangle = x_A x_B N,$$
- 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?