Statistical Mechanics Core Proficiency Exam, August 19, 2017

You can use a textbook of your choice and no other notes

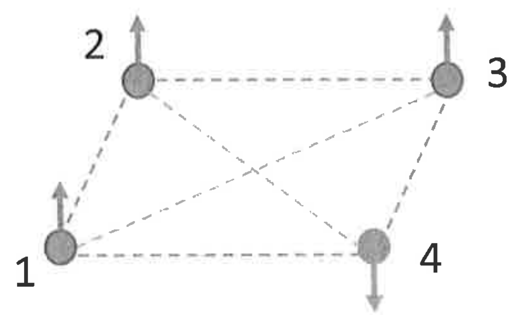
Short problems: solve 2 out of 3

S1. Helium gas is heated in a process for which the molar heat capacity (neither c_V nor c_P) is 2R. During the process, the volume of the gas quadruples.

(a) How does the absolute temperature of the gas change?

(b) How does the pressure of the gas change?

S2. Four distinguishable spin-1/2 particles are placed on the corners of a square as shown in the figure, in a heat bath in thermal equilibrium at an absolute temperature T. Each pair of particles interacts via spin-spin exchanges. The system's Hamiltonian is given by



$$\mathcal{H} = -\sum_{i=1}^{4}\sum_{j=i+1}^{4} J_{ij}\, s_i s_j$$

in terms of particle's spin quantum numbers $s_i = \pm 1/2$ and a symmetric matrix J_{ij} . Assume $J_{13} = J_{24} = 4\ \mu eV$ for non-adjacent particles (across a diagonal) and $J_{ij} = 8\ \mu eV$ for all adjacent ones (on the same square's side).

a) Which energy values can the system have?
b) In the limit $T \to 0$, what is the most probable energy value, and what is the associated probability? Explain.
c) In the limit $T \to \infty$, compare the probabilities of the most probable and the least probable energy states. Explain.
d) Bonus: write down the probability for having energy E at arbitrary T.

S3. Derive a Maxwell-like relation to write $\left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ as another partial derivative of different variables. Be sure to specify which variables are held fixed (like T and N above).

What is $\left(\frac{\partial \mu}{\partial p}\right)_{T,N}$ for an ideal gas?

Long problems: solve 2 out of 3

L1. In this problem, you will explore entropic damping. A horizontal cylinder of cross-sectional area A encloses an ideal monatomic gas with a massless frictionless piston. The surrounding atmospheric pressure P_0 keeps the piston from flying out of the cylinder. The gas is not thermally insulated from the room which is at absolute temperature T_R. The piston is held in place at $x = x_0$ with a pin. The pressure in the gas is adjusted to P_0 while the temperature in the gas is set to T_0 which is slightly hotter than T_R. At time $t = 0$, the pin is removed.

(a) What is the final position of the piston x_f?

(b) Use Newton's 2nd law for the massless piston to derive a relation between T and x valid at any time.

(c) What is dU in terms of dT?

(d) What is the work done on the gas in terms of T and x?

(e) For the rate of heat transfer from the hotter gas to the cooler room, use Newton's law of cooling, that it is linearly proportional to the temperature difference $T - T_R$.

(f) What is the equation for the first law of thermodynamics for this problem?

(g) Write this as a differential equation for x and solve for $x(t)$.

L2. A sealed container contains hydrogen chloride gas (HCl) in thermal equilibrium at absolute temperature T.

a) Write down, but do not evaluate, the total canonical partition function Z for N molecules of HCl, assuming that they are identical and non-interacting. What categories of the degrees of freedom generally contribute to the internal energy of the HCl canonical state?

b) Focusing on the quantum-mechanical angular momentum J of the molecules, derive the average thermal rotational energy $\langle E_{rot} \rangle$ and the average squared angular momentum $\langle J^2 \rangle$ of this system in the limit of high absolute temperature T. Remember to account for degenerate quantum states, neglect the internal angular momenta (spins). You may need to replace an infinite series by an integral. The moment of inertia of the molecule is I.

d) Calculate $\langle E_{rot} \rangle$ and $\langle J^2 \rangle$ of 1 mole of HCl at room temperature, given $B_{HCl} \equiv \frac{\hbar}{4\pi c I} = 10.6\ cm^{-1}$.

L3. Find the difference in heat capacities $C_P - C_V$ in terms of two other experimentally measurable quantities: the isothermal compressibility $K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$ and and the isobaric thermal expansion coefficient $\beta_P = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. Hint: Find an expression for $\left(\frac{\partial S}{\partial T}\right)_P$ from the differentials $dS(T, V)$ and $dV(T, P)$. Using this and Maxwell's relation, express $C_P - C_V$ in terms of T, $\left(\frac{\partial V}{\partial T}\right)_P$, and $\left(\frac{\partial P}{\partial T}\right)_V$.

Set the differential $dV = 0$ to obtain $\left(\frac{\partial P}{\partial T}\right)_V$. Finally, relate $C_P - C_V$ to T, V, K_T, and β_P.