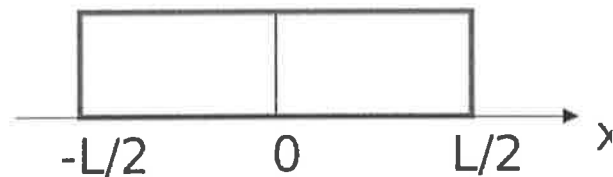


Short problems: solve 2 out of 3

S1. You have two urns and a small bag. One urn contains 100 balls, numbered 1 to 100. The other urn is empty. 100 small slips of paper with numbers 1 to 100 written in sequence are put into the bag. Each second, a paper slip is drawn randomly from the bag, the number is noted, and the slip is returned to the bag. The ball bearing that number is moved from its current urn to the other urn. After a while, we would expect that the system settles into an equilibrium state in which there are about 50 balls in each urn. The ball counts in the urns will fluctuate about the 50-50 distribution, however, it would appear highly unlikely that the system would ever return to the state in which all 100 balls are back in the first urn. Nevertheless, the Poincare' Recurrence Theorem that such situation will surely reoccur. But after how long?

- 1) Estimate the likely difference of the numbers of balls in two urns that may result because of a fluctuation from the 50-50 equilibrium.
- 2) What is the Poincare' recurrence time in years for the urns to return to the state with 100 balls in one and zero in the other? Explain.
- 3) What is the Poincare' recurrence time for one liter of helium at STP to be found in half of its container? Explain.

S2. An insulated container of mass M and length L is at rest on a horizontal frictionless surface. The container is filled with an ideal gas of unknown mass m and temperature T . The container is divided in half by a light movable insulated piston.

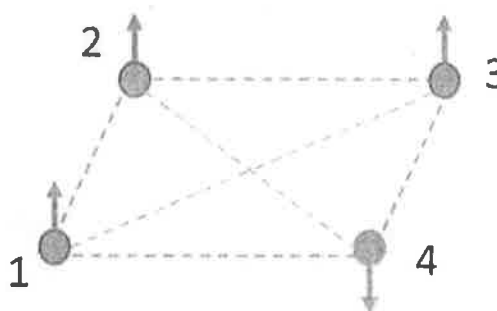


A heater is turned on inside the left part of the container, bringing the temperature of gas there to $2T$. The temperature of the gas inside the right part of the container remains unchanged. As a result, the container moves a distance x along the surface. Find the mass m of the gas.

S3. The molecules of an imaginary ideal gas have internal energy that are equally spaced so that the n -th energy eigenvalue is $E_n = n\epsilon$, where $n = 0, 1, 2, \dots$. The degeneracy of the n -th energy level is $n+1$. Calculate the contribution to the thermal energy of the internal energy states. **Hint:** $\sum_{n=0}^{\infty} x^n = 1/(1-x)$ for $x = e^{-\beta\epsilon}$.

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 $T \rightarrow 0$, what is the most probable energy value, and what is the associated probability? Explain.
- c) In the limit $T \rightarrow \infty$, 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 .

Long problems: solve 2 out of 3

L1. a) Prove that, if $y(x)$ is a smooth function of a random variable x with average \bar{x} and a small uncertainty Δx (so that $\Delta x/|\bar{x}| \ll 1$), then

$$\bar{y} \approx y(\bar{x}) \text{ and } \Delta y \approx |y'(\bar{x})| \Delta x.$$



b) A rectangular array of resistors shown in the figure has K parallel resistors in series. The resistors are drawn from a lot with an average r and an uncertainty of 10%. Assuming that K and L are large in the relations from part a), calculate the average of, and the uncertainty resistance of the array.

L2. A system is composed of K one-dimensional classical oscillators. Assume that the potential for the oscillators contains a small quartic "anharmonic term":

$$V(x) = \frac{k_0}{2} x^2 + \alpha x^4,$$

where $\alpha \langle x^4 \rangle \ll kT$. To the first order in the parameter α , derive the anharmonic correction to the Dulong—Petit law. **Hint:** You may need to find an approximate expression for the partition function of a single oscillator by expanding the $\exp(-\alpha x^4)$ term as the Taylor series.

L3. A system is composed of a large number N of one-dimensional quantum harmonic oscillators whose angular frequencies are distributed over the range $\omega_a \leq \omega \leq \omega_b$ with a frequency distribution function $D(\omega) = A/\omega$.

- What is the value of A , given that there are N oscillators?
- What is the partition function of a single harmonic oscillator?
- Find the energy E of N oscillators in the thermodynamic equilibrium at temperature T .
- Calculate the specific heat C per oscillator.
- Evaluate the specific heat in the limits of high and low T .

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.

- What is the final position of the piston x_f ?
- Use Newton's 2nd law for the massless piston to derive a relation between T and x valid at any time.
- What is dU in terms of dT ?
- What is the work done on the gas in terms of T and x ?
- 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 $T - T_R$.
- What is the equation for the first law of thermodynamics for this problem?
- 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 $B_{HCl} \equiv \frac{\hbar}{4\pi c I} = 10.6 \text{ cm}^{-1}$.

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 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 .