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**Non-interacting particles**

1. *Rotating gas:* Consider a gas of  $N$  identical atoms confined to a spherical harmonic trap in three dimensions, i.e. the particles are subject to the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{p_i^2}{2m} + \frac{K}{2} r_i^2 \right].$$

(a) Show that the angular momentum of each particle  $\vec{L}_i = \vec{r}_i \times \vec{p}_i$  is a conserved quantity, i.e.  $\{\vec{L}_i, \mathcal{H}\} = 0$ . (Note that once interactions between particles are included, individual angular momenta are no longer conserved, while their sum  $\vec{L} = \sum_{i=1}^N \vec{L}_i$  remains a conserved quantity.)

(b) Since angular momentum is conserved, a generalized canonical distribution can be defined with probability

$$p[\mu \equiv \{\vec{p}_i, \vec{r}_i\}] = \frac{1}{Z(\beta, \vec{\Omega})} \exp\left(-\beta\mathcal{H}(\mu) - \beta\vec{\Omega} \cdot \vec{L}(\mu)\right).$$

Compute the classical partition function for this gas of identical particles, assuming  $\vec{\Omega} = \Omega \hat{z}$ , with  $\Omega < \sqrt{K/m}$ .

(c) Find the expectation value of angular momentum  $\langle L_z \rangle$  in the above ensemble.

(d) Write down the probability density of finding a particle at location  $(x, y, z)$ , and hence obtain the expectation values  $\langle x^2 \rangle$ ,  $\langle y^2 \rangle$ , and  $\langle z^2 \rangle$ .

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2. *Molecular adsorption:*  $N$  diatomic molecules are stuck on a metal surface of square symmetry. Each molecule can either lie flat on the surface in which case it must be aligned to one of two directions,  $x$  and  $y$ , or it can stand up along the  $z$  direction. There is an energy cost of  $\varepsilon > 0$  associated with a molecule standing up, and zero energy for molecules lying flat along  $x$  or  $y$  directions.

(a) How many microstates have the smallest value of energy? What is the largest microstate energy?

(b) For *microcanonical* macrostates of energy  $E$ , calculate the number of states  $\Omega(E, N)$ , and the entropy  $S(E, N)$ .

- (c) Calculate the heat capacity  $C(T)$  and sketch it.
- (d) What is the probability that a specific molecule is standing up?
- (e) What is the largest possible value of the internal energy at any positive temperature?

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**3. Curie susceptibility:** Consider  $N$  non-interacting quantized spins in a magnetic field  $\vec{B} = B\hat{z}$ , and at a temperature  $T$ . The work done by the field is given by  $BM_z$ , with a magnetization  $M_z = \mu \sum_{i=1}^N m_i$ . For each spin,  $m_i$  takes only the  $2s + 1$  values  $-s, -s + 1, \dots, s - 1, s$ .

- (a) Calculate the Gibbs partition function  $\mathcal{Z}(T, B)$ . (Note that the ensemble corresponding to the macrostate  $(T, B)$  includes magnetic work.)
- (b) Calculate the Gibbs free energy  $G(T, B)$ , and show that for small  $B$ ,

$$G(B) = G(0) - \frac{N\mu^2 s(s+1)B^2}{6k_B T} + \mathcal{O}(B^4).$$

- (c) Calculate the zero field susceptibility  $\chi = \partial M_z / \partial B|_{B=0}$ , and show that it satisfies *Curie's law*

$$\chi = c/T.$$

- (d) Show that  $C_B - C_M = cB^2/T^2$  where  $C_B$  and  $C_M$  are heat capacities at constant  $B$  and  $M$  respectively.

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**4. Langmuir isotherms:** An ideal gas of particles is in contact with the surface of a catalyst.

- (a) Show that the chemical potential of the gas particles is related to their temperature and pressure via  $\mu = k_B T [\ln(P/T^{5/2}) + A_0]$ , where  $A_0$  is a constant.
- (b) If there are  $\mathcal{N}$  distinct adsorption sites on the surface, and each adsorbed particle gains an energy  $\epsilon$  upon adsorption, calculate the grand partition function for the two dimensional gas with a chemical potential  $\mu$ .
- (c) In equilibrium, the gas and surface particles are at the same temperature and chemical potential. Show that the fraction of occupied surface sites is then given by  $f(T, P) = P/(P + P_0(T))$ . Find  $P_0(T)$ .

(d) In the grand canonical ensemble, the particle number  $N$  is a random variable. Calculate its characteristic function  $\langle \exp(-ikN) \rangle$  in terms of  $\mathcal{Q}(\beta\mu)$ , and hence show that

$$\langle N^m \rangle_c = -(k_B T)^{m-1} \left. \frac{\partial^m \mathcal{G}}{\partial \mu^m} \right|_T,$$

where  $\mathcal{G}$  is the grand potential.

(e) Using the characteristic function, show that

$$\langle N^2 \rangle_c = k_B T \left. \frac{\partial \langle N \rangle}{\partial \mu} \right|_T.$$

(f) Show that fluctuations in the number of adsorbed particles satisfy

$$\frac{\langle N^2 \rangle_c}{\langle N \rangle_c^2} = \frac{1-f}{\mathcal{N}f}.$$

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**5. Molecular oxygen** has a net magnetic spin,  $\vec{S}$ , of unity, i.e.  $S^z$  is quantized to -1, 0, or +1. The Hamiltonian for an ideal gas of  $N$  such molecules in a magnetic field  $\vec{B} \parallel \hat{z}$  is

$$\mathcal{H} = \sum_{i=1}^N \left[ \frac{\vec{p}_i^2}{2m} - \mu B S_i^z \right],$$

where  $\{\vec{p}_i\}$  are the center of mass momenta of the molecules. The corresponding coordinates  $\{\vec{q}_i\}$  are confined to a volume  $V$ . (Ignore all other degrees of freedom.)

(a) Treating  $\{\vec{p}_i, \vec{q}_i\}$  classically, but the spin degrees of freedom as quantized, calculate the Gibbs partition function,  $\mathcal{Z}(T, N, V, B)$ .

(b) What are the probabilities for  $S_i^z$  of a specific molecule to take on values of -1, 0, +1 at a temperature  $T$ ?

(c) Find the average magnetic dipole moment,  $\langle M \rangle / V$ , where  $M = \mu \sum_{i=1}^N S_i^z$ .

(d) Calculate the zero field susceptibility  $\chi = \partial \langle M \rangle / \partial B|_{B=0}$ .

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**6. One dimensional polymer:** Consider a polymer formed by connecting  $N$  disc shaped molecules into a one dimensional chain. Each molecule can align either along its long axis

(of length  $2a$ ) or short axis (length  $a$ ). The energy of the monomer aligned along its shorter axis is higher by  $\varepsilon$ , i.e. the total energy is  $\mathcal{H} = \varepsilon U$ , where  $U$  is the number of monomers standing up.

- (a) Calculate the partition function,  $Z(T, N)$ , of the polymer.
- (b) Find the relative probabilities for a monomer to be aligned along its short or long axis.
- (c) Calculate the average length,  $\langle L(T, N) \rangle$ , of the polymer.
- (d) Obtain the variance,  $\langle L(T, N)^2 \rangle_c$ .
- (e) What does the central limit theorem say about the probability distribution for the length  $L(T, N)$ ?

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**7. Polar rods:** Consider rod shaped molecules with moment of inertia  $I$ , and a dipole moment  $\mu$ . The contribution of the rotational degrees of freedom to the Hamiltonian is given by

$$\mathcal{H}_{\text{rot.}} = \frac{1}{2I} \left( p_\theta^2 + \frac{p_\phi^2}{\sin^2 \theta} \right) - \mu E \cos \theta \quad ,$$

where  $E$  is an external electric field. ( $\phi \in [0, 2\pi]$ ,  $\theta \in [0, \pi]$  are the azimuthal and polar angles, and  $p_\phi$ ,  $p_\theta$  are their conjugate momenta.)

- (a) Calculate the contribution of the rotational degrees of freedom of each dipole to the *classical* partition function.
- (b) Obtain the mean polarization  $P = \langle \mu \cos \theta \rangle$ , of each dipole.
- (c) Find the *zero-field* polarizability

$$\chi_T = \left. \frac{\partial P}{\partial E} \right|_{E=0} \quad .$$

- (d) Calculate the rotational energy per particle (at finite  $E$ ), and comment on its high and low temperature limits.
- (e) Sketch the rotational heat capacity per dipole.

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**8. (Optional) Disordered glass:** The heat capacity of many disordered materials vanishes linearly at low temperatures. A commonly used model such glassy materials materials is

a collection of  $N$  non-interacting defects in thermal equilibrium at temperature  $T$ . Each defect is assumed to have two possible energies  $\epsilon_i$  and  $\epsilon_i + \delta_i$ , with different values of  $\epsilon_i$  and  $\delta_i$  for each defect.

(a) Compute the partition function  $Z(T)$ , the average energy  $E(T)$ , and the contribution to heat capacity  $C(T)$  from these independent defects.

(b) The number of defects with excitation energies between  $\delta$  and  $\delta + d\delta$  is given by  $\rho(\delta)d\delta$ , where  $\rho(\delta)$  is the density of states of defects as a function of excitation energy. Assuming that  $\rho(\delta)$  is uniformly distributed between energies of 0 and  $\Delta$ , find the defect heat capacity  $C(T)$ , and comment on its behavior at low and high temperatures.

(c) A uniform density of states may not be realistic. What feature of  $\rho(\delta)$  will ensure  $C \propto T$  at low temperatures?

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**9. (Optional)** *Classical virial theorem:* Let  $\bar{X} = \{\vec{q}_i, \vec{p}_i\}$  denote any of the  $6N$  coordinates in phase space, and consider any function  $f(\bar{X})$ .

(a) Show that in a canonical ensemble governed by a Hamiltonian  $\mathcal{H}(\bar{X})$

$$\left\langle \frac{\partial f}{\partial X_i} \right\rangle = \beta \left\langle f \frac{\partial \mathcal{H}}{\partial X_i} \right\rangle,$$

where  $\beta = 1/(k_B T)$ .

(b) Find the forms of the virial theorem obtained by substituting  $f = q_i$  and  $f = p_i$  in the general expression.

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