Interacting particles & Quantum ensembles

1. *Surfactant condensation:* N surfactant molecules are added to the surface of water over an area A. They are subject to a Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\ 2}}{2m} + \frac{1}{2} \sum_{i,j} \mathcal{V}(\vec{q}_i - \vec{q}_j),$$

where $\vec{q}_i$ and $\vec{p}_i$ are two dimensional vectors indicating the position and momentum of particle i. (This simple form ignores the couplings to the fluid itself. The actual kientic and potential energies are more complicated.)

(a) Write down the expression for the partition function $Z(N, T, A)$ in terms of integrals over $\vec{q}_i$ and $\vec{p}_i$, and perform the integrals over the momenta.

   The inter–particle potential $\mathcal{V}(\vec{r})$ is infinite for separations $|\vec{r}| < a$, and attractive for $|\vec{r}| > a$ such that $\int_a^\infty 2\pi r dr \mathcal{V}(r) = -u_0$.

(b) Estimate the total non–excluded area available in the positional phase space of the system of N particles.

(c) Estimate the total *potential* energy of the system, within a *uniform density approximation* $n = N/A$. Using this potential energy for all configurations allowed in the previous part, write down an approximation for Z.

(d) The surface tension of water without surfactants is σ_0, approximately independent of temperature. Calculate the surface tension $\sigma(n, T)$ in the presence of surfactants.

(e) Show that below a certain temperature, T_c, the expression for σ is manifestly incorrect. What do you think happens at low temperatures?

(f) Compute the heat capacities, C_A and write down an expression for C_σ without explicit evaluation, due to the surfactants.

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2. *Critical point behavior:*   The pressure P of a gas is related to its density $n = N/V$, and temperature T by the truncated expansion

$$P = k_B Tn - \frac{b}{2}n^2 + \frac{c}{6}n^3 \quad ,$$

where b and c are assumed to be *positive* temperature independent constants.

(a) Locate the critical temperature T_c below which this equation must be invalid, and the corresponding density n_c and pressure P_c of the critical point. Hence find the ratio $k_B T_c n_c / P_c$.

(b) Calculate the isothermal compressibility $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}\big|_T$, and sketch its behavior as a function of T for $n = n_c$.
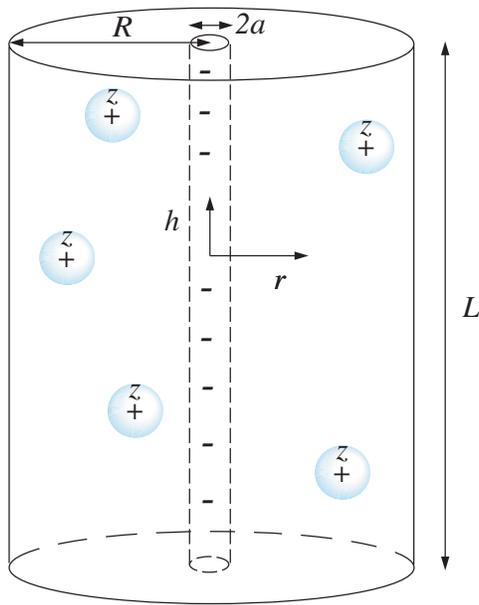
(c) On the critical isotherm give an expression for $(P - P_c)$ as a function of $(n - n_c)$.

(d) The instability in the isotherms for $T < T_c$ is avoided by phase separation into a liquid of density n_+ and gas of density n_-. For temperatures close to T_c, these densities behave as $n_\pm \approx n_c (1 \pm \delta)$. Using a Maxwell construction, or otherwise, find an implicit equation for $\delta(T)$, and indicate its behavior for $(T_c - T) \to 0$. (Hint: Along an isotherm, variations of chemical potential obey $d\mu = dP/n$.)

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3. (Optional) *The Manning transition:* When ionic polymers (polyelectrolytes) such as DNA are immersed in water, the negatively charged *counter-ions* go into solution, leaving behind a positively charged polymer. Because of the electrostatic repulsion of the charges left behind, the polymer stretches out into a cylinder of radius a, as in the figure below. While thermal fluctuations favor ions wandering in the solvent, electrostatic attractions prefer their return and condensation on the polymer. If the number of counter-ions is N, they interact with the N positive charges left behind on the rod through the potential $\phi(r) = -2(Ne/L)\ln(r/R)$, where r is the radial coordinate in a cylindrical geometry. If we ignore the Coulomb repulsion between counter-ions, they can be described by the classical Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + 2e^2 n \ln\left(\frac{r}{R}\right) \right],$$

where $n = N/L$.

(a) For a cylindrical container of radius R, calculate the canonical partition function Z in terms of temperature T, density n, and radii R and a.

(b) Calculate the probability distribution function $p(r)$ for the radial position of a counter-ion, and its first moment $\langle r \rangle$, the average radial position of a counter-ion.

(c) The behavior of the results calculated above in the limit $R \gg a$ is very different at high and low temperatures. Identify the transition temperature, and characterize the nature of the two phases. In particular, how does $\langle r \rangle$ depend on R and a in each case?

(d) Calculate the pressure exerted by the counter-ions on the wall of the container, at $r = R$, in the limit $R \gg a$, at all temperatures.

(e) The character of the transition examined in part (d) is modified if the Coulomb interactions between counter-ions are taken into account. An approximate approach to the interacting problem is to allow a fraction N_1 of counter-ions to condense along the polymer rod, while the remaining $N_2 = N - N_1$ fluctuate in the solvent. The free counter-ions are again treated as non-interacting particles, governed by the Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + 2e^2 n_2 \ln \left(\frac{r}{R} \right) \right],$$

where $n_2 = N_2/L$. *Guess* the equilibrium number of non-interacting ions, N_2^*, and justify your guess by discussing the response of the system to slight deviations from N_2^*. (This is a qualitative question for which no new calculations are needed.)
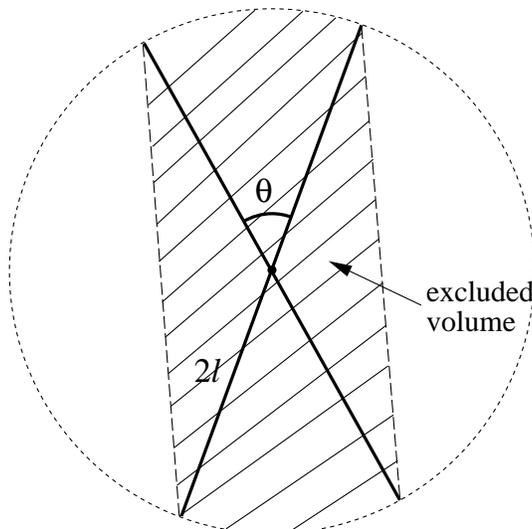
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4. *Point particle condensation:* Consider a system of N classical point particles of mass m at temperature T, and volume V. An unspecified form of attraction between the particles reduces the energy of any configuration by an amount $-uN^2/(2V)$ with $u > 0$, such that the partition function is

$$Z(T, N, V) = Z_{\text{ideal gas}}(T, N, V) \times \exp\left(\frac{\beta u N^2}{2V}\right),$$

where $Z_{\text{ideal gas}}(T, N, V)$ is the partition function of a classical gas, and $\beta = (k_B T)^{-1}$.

(a) Using the partition function, or otherwise, compute all cumulants, $\langle \mathcal{H}^p \rangle_c$, of the energy.

(b) Using the partition function, or otherwise, compute the pressure $P(n, T)$, as a function of the density $n = N/V$.

(c) Compute the isothermal compressibility $\kappa_T(n) = -\frac{1}{V}\frac{\partial V}{\partial P}\big|_T$.

(d) Find the condensation line $P_c(T)$.

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5. (Optional problem) *Hard rods:* A collection of N asymmetric molecules in two dimensions may be modeled as a gas of rods, each of length $2l$ and lying in a plane. A rod can move by translation of its center of mass and rotation about latter, as long as it does not encounter another rod. Without treating the hard-core interaction exactly, we can incorporate it approximately by assuming that the rotational motion of each rod is restricted (by the other rods) to an angle θ, which in turn introduces an excluded volume $\Omega(\theta)$ (associated with each rod). The value of θ is then calculated self consistently by maximizing the entropy at a given density $n = N/V$, where V is the total accessible area.

(a) Write down the entropy of such a collection of rods in terms of N, n, Ω, and $A(\theta)$, the phase space volume associated to the rotational freedom of a *single* rod. (You may ignore the momentum contributions throughout, and consider the large N limit.)

(b) Extremizing the entropy as a function of θ, relate the density to Ω, A, and their derivatives Ω', A'; express your result in the form $n = f(\Omega, A, \Omega', A')$.

(c) Express the excluded volume Ω in terms of θ and sketch f as a function of $\theta \in [0, \pi]$, assuming $A \propto \theta$.

(d) Describe the equilibrium state at high densities. Can you identify a phase transition as the density is decreased? Draw the corresponding critical density n_c on your sketch. What is the critical angle θ_c at the transition? You don't need to calculate θ_c explicitly, but give an (implicit) relation defining it. What value does θ adopt at $n < n_c$?

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6. *Electron spin:* The Hamiltonian for an electron in a magnetic field $\vec{B}$ is

$$\mathcal{H} = -\mu_B \vec{\sigma}.\vec{B}, \quad \text{where} \quad \sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix},$$

are the Pauli spin operators, and μ_B is the Bohr magneton.

(a) In the quantum canonical ensemble evaluate the density matrix if $\vec{B}$ is along the z direction.

(b) Repeat the calculation assuming that $\vec{B}$ points along the x-direction.

(c) Calculate the average energy in each of the above cases.

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7. (Optional problem) *Quantum rotor:* Consider a rotor in two dimensions with

$$\mathcal{H} = -\frac{\hbar^2}{2I}\frac{d^2}{d\theta^2}, \quad \text{and} \quad 0 \le \theta < 2\pi.$$

(a) Find the eigenstates and energy levels of the system.

(b) Write the expression for the density matrix $\langle \theta' | \rho | \theta \rangle$ in a canonical ensemble of temperature T, and evaluate its low and high temperature limits.

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8. *Quantum mechanical entropy:* A quantum mechanical system (defined by a Hamiltonian $\mathcal{H}$), is described by a density matrix $\rho(t)$, which has an associated entropy $S(t) = -\operatorname{tr}\left[\rho(t)\ln\rho(t)\right]$.

(a) Write down the time evolution equation for the density matrix, and calculate dS/dt.

(b) Using the method of Lagrange multipliers, find the density operator $\rho_{\max}$ which maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy $\langle\mathcal{H}\rangle = \operatorname{tr}(\rho\mathcal{H}) = E$.

(c) Show that the solution to part (b) is stationary, i.e. $\partial\rho_{\max}/\partial t = 0$.

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9. *Zero point energy:* The classical Hamiltonian for a harmonic oscillator of frequency ω is

$$\mathcal{H}_{\text{cl}} = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}.$$

We will assume that in quantum mechanics the energy levels are quantized as

$$\mathcal{H}_{\text{qm}} = x + yn, \qquad \text{for} \quad n = 0, 1, 2, \cdots,$$

and aim to find the parameters x and y by matching to classical counterparts.

(a) Compute the classical partition function $Z_{\text{cl}}(\beta)$, and energy $E_{\text{cl}}(\beta)$ at temperature $T = (k_B\beta)^{-1}$, using $(dp\, dq)/h$ as dimensionless measure of phase space.

(b) Compute the quantum partition function $Z_{\text{qm}}(\beta)$, and obtain y by matching to $Z_{\text{cl}}(\beta)$ at high temperatures.

(c) Compute the energy $E_{\text{qm}}(\beta)$, and expand the result for $\beta \to 0$, including the leading two terms. By matching to $E_{\text{cl}}(\beta)$ find the parameter x.

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10. *Vibrational and rotational heat capacities at high temperatures:*

(a) Calculate the partition function $Z_{\text{vib.}}$ of a (quantum) harmonic oscillator of frequency ω, and expand the resulting $\ln Z_{\text{vib.}}$ at high temperatures to order of $(\beta\hbar\omega)^2$.

(b) Use the above expansion to find the first correction to vibrational heat capacity at high temperatures due to quantization.

The *Abel–Plana* formula provides a systematic way of replacing sums with integrals, as

$$\sum_{n=0}^{\infty} f(n) = \int_0^{\infty} dx\, f(x) + \frac{1}{2} f(0) + i \int_0^{\infty} dt \frac{f(it) - f(-it)}{e^{2\pi t} - 1}.$$

(c) Check the above formula to confirm that it provides the correct expansion for the geometric series $\sum_n e^{-nu}$ for small u.

(d) Use the Abel-Plana formula to show that $\sum_{\ell=0}^{\infty} (2\ell+1) e^{-u\ell(\ell+1)} = \frac{1}{u} + \frac{1}{3} + \frac{u}{15} + \mathcal{O}(u^2)$.

(e) Use the result above to calculate the energy of a quantum rotor with moment of inertia I at high temperatures.

(f) Find the first quantum correction to rotational heat capacity at high temperatures.

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11. (Optional) *Ortho/para–hydrogen:* Hydrogen molecules can exist in ortho and para states.

(a) The two nuclei (protons) of H_2 in para-hydrogen form a singlet (antisymmetric) state. The orbital angular momentum can thus only take even values; i.e.

$$\mathcal{H}_p = \frac{\hbar^2}{2I} \ell(\ell+1),$$

where $\ell = 0, 2, 4, \cdots$. Calculate the rotational partition function of para-hydrogen, and evaluate its low and high temperature limits.

(b) In ortho-hydrogen the protons are in a triply degenerate symmetric state, hence

$$\mathcal{H}_o = \frac{\hbar^2}{2I} \ell(\ell+1),$$

with $\ell = 1, 3, 5, \cdots$. Calculate the rotational partition function of ortho-hydrogen, and evaluate its low and high temperature limits.

(c) For an equilibrium gas of N hydrogen molecules calculate the partition function.

(Hint: Sum over contributions from mixtures of N_p para- and $N_o = N - N_p$ ortho-hydrogen particles. Ignore vibrational degrees of freedom.)

(d) Write down the expression for the rotational contribution to the internal energy $\langle E_{\text{rot.}} \rangle$, and comment on its low and high temperature limits.

Actually, due to small transition rates between ortho- and para-hydrogen, in most circumstances the mixture is not in equilibrium.

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12. *van Leeuwen's theorem:* Consider a gas of charged particles subject to a general Hamiltonian of the form

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\vec{p}_i^{\,2}}{2m} + U(\vec{q}_1, \cdots, \vec{q}_N).$$

In an external magnetic field, $\vec{B}$, the canonical momenta, $\vec{p}_n$, are replaced with $\vec{p}_n - e\vec{A}$, where $\vec{A}$ is the vector potential, $\vec{B} = \vec{\nabla} \times \vec{A}$. Show that if quantum effects are ignored, the thermodynamics of the problem is independent of $\vec{B}$.

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8.333 Statistical Mechanics I: Statistical Mechanics of Particles
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