
Interacting particles & Quantum ensembles

1. Repulsive shell potential: Consider a gas of particles in three dimensions interacting through a pair-wise central potential, $\mathcal{V}(r)$, where

$$\mathcal{V}(r) = \begin{cases} 0 & \text{for } 0 < r < a, \\ +u & \text{for } a < r < b, \\ 0 & \text{for } b < r < \infty. \end{cases}$$

- (a) Calculate the second virial coefficient $B_2(T)$.
- (b) In the low density limit, reorganize the equation of state (including B_2 , into the form $P(V - N\Omega) = Nk_B T$, and identify the excluded volume parameter $\Omega(T)$.
- (c) Consider the $B_2(T)$ in the limit of $u \rightarrow \infty$ (hard shell). Does the dependence of the answer on a make sense?

2. 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 kinetic 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.

3. Critical point behavior: Consider a system of N classical point particles of mass m at temperature T , and volume V . An unspecified form of interaction between the particles modifies the energy of any configuration by an amount $-bN^2/(2V) + cN^3/(6V^2)$ with $b, c > 0$, such that the partition function is

$$Z(T, N, V) = Z_{\text{ideal gas}}(T, N, V) \times \exp\left(\frac{\beta b N^2}{2V} - \frac{\beta c N^3}{6V^2}\right),$$

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 the pressure $P(n, T)$, as a function of the density $n = N/V$.
- (b) Locate the critical temperature T_c below which this equation must be invalid, and the corresponding density n_c .
- (c) Find the pressure P_c at the critical point, and hence obtain the ratio $k_B T_c n_c / P_c$.
- (d) 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 $n = n_c$.
- (e) On the critical isotherm give an expression for $(P - P_c)$ as a function of $(n - n_c)$.
- (f) 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 $(T_c - T) \rightarrow 0$. (Hint: Along an isotherm, variations of chemical potential obey $d\mu = dP/n$.)

4. Quantum-Classical correspondence: The Hamiltonian for a single particle is given by

$$\mathcal{H} = \frac{p^2}{2m} + U(\vec{q}) .$$

(a) Use the Baker–Campbell–Hausdorff expansion

$$\exp(\beta A) \exp(\beta B) = \exp \left[\beta(A + B) + \beta^2[A, B]/2 + \mathcal{O}(\beta^3) \right],$$

to show that the quantum partition function reduces to its classical form in the high temperature limit.

(b) For a particle in a box (with $U(\vec{q}) = 0$ inside the box, and infinite otherwise), the single particle states have energies $\epsilon(\vec{k}) = \hbar^2 k^2 / 2m$, with (quantized) allowed values of \vec{k} determined by the shape of the box. Use the above result to show that in the limit of a large box of volume V

$$\sum_{\vec{k}} \rightarrow V \int \frac{d^3 \vec{k}}{(2\pi)^3} \quad .$$

5. 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.

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

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

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} .

7. (Optional) *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

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

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 $\beta \rightarrow 0$, including the leading two terms. By matching to $E_{\text{cl}}(\beta)$ find the parameter x .

8. (Optional) *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 $S(t) = -\text{tr} [\rho(t) \ln \rho(t)]$.

(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 ρ_{max} which maximizes the functional $S[\rho]$, subject to the constraint of fixed average energy $\langle \mathcal{H} \rangle = \text{tr}(\rho \mathcal{H}) = E$.

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

9. (Optional) *Electron spin:* The Hamiltonian for an electron in a magnetic field \vec{B} is

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

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.

† Reviewing the problems and solutions provided on the course web-page for preparation for *Test 3* should help you with the above problems.