
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 $B_2(T)$.

- The second virial coefficient is obtained from

$$B_2 \equiv -\frac{1}{2} \int d^3r_{12} \{ \exp[-\beta\mathcal{V}(r_{12})] - 1 \},$$

where $r_{12} \equiv |\vec{r}_1 - \vec{r}_2|$, as

$$\begin{aligned} B_2 &= -\frac{1}{2} \left[\int_0^a d^3r_{12}(0) + \int_a^b d^3r_{12} (e^{-\beta u} - 1) + \int_b^\infty d^3r_{12}(0) \right] \\ &= -\frac{1}{2} \{ [V_3(b) - V_3(a)] \cdot [\exp(-\beta u) - 1] \}, \end{aligned}$$

where

$$V_3(r) = \frac{4\pi}{3} r^3,$$

is the volume of a 3-dimensional sphere of radius r . Thus,

$$B_2(T) = -\frac{2\pi}{3} (b^3 - a^3) [e^{-\beta u} - 1].$$

(b) In the low density limit, reorganize the equation of state (including B_2 , into the form $\beta P(V - N\Omega) = nk_B T$, and identify the excluded volume parameter $\Omega(T)$.

- Including the correction introduced by the second virial coefficient, pressure as function of density $n = N/V$ takes the form

$$\frac{P}{k_B T} = 1 + nB_2(T) + \mathcal{O}(n^2) \approx \frac{1}{1 - nB_2(T) + \mathcal{O}(n^2)},$$

which can be reorganized as

$$P(V - NB_2(T)) = Nk_B T,$$

identifying $\Omega(T) = B_2(T)$ as an effective excluded volume parameter.

(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?

- For $u \rightarrow \infty$,

$$\Omega = B_2 = \frac{2\pi}{3}(b^3 - a^3),$$

i.e. the volume of the shell. The correct result should not depend on the volume of the interior of the hollow shell. This is an indication of the breakdown of the assumption of equal probability of all allowed states. Configurations that are not allowed by dynamics in an infinite potential should not be counted as allowed states.

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 partition function is obtained by integrating the Boltzmann weight over phase space, as

$$Z(N, T, A) = \int \frac{\prod_{i=1}^N d^2\vec{p}_i d^2\vec{q}_i}{N! h^{2N}} \exp \left[-\beta \sum_{i=1}^N \frac{p_i^2}{2m} - \beta \sum_{i < j} \mathcal{V}(\vec{q}_i - \vec{q}_j) \right],$$

with $\beta = 1/(k_B T)$. The integrals over momenta are simple Gaussians, yielding

$$Z(N, T, A) = \frac{1}{N!} \frac{1}{\lambda^{2N}} \int \prod_{i=1}^N d^2\vec{q}_i \exp \left[-\beta \sum_{i < j} \mathcal{V}(\vec{q}_i - \vec{q}_j) \right],$$

where as usual $\lambda = h/\sqrt{2\pi m k_B T}$ denotes the thermal wavelength.

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.

- To estimate the joint phase space of particles with excluded areas, add them to the system one by one. The first one can occupy the whole area A , while the second can explore only $A - 2\Omega$, where $\Omega = \pi a^2$. Neglecting three body effects (i.e. in the dilute limit), the area available to the third particle is $(A - 2\Omega)$, and similarly $(A - n\Omega)$ for the n -th particle. Hence the joint excluded volume in this dilute limit is

$$A(A - \Omega)(A - 2\Omega) \cdots (A - (N - 1)\Omega) \approx (A - N\Omega/2)^N,$$

where the last approximation is obtained by pairing terms m and $(N - m)$, and ignoring order of Ω^2 contributions to their product.

(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 .

- Assuming a *uniform density* $n = N/A$, an average attractive potential energy, \bar{U} , is estimated as

$$\begin{aligned} \bar{U} &= \frac{1}{2} \sum_{i,j} \mathcal{V}_{\text{attr.}}(\vec{q}_i - \vec{q}_j) = \frac{1}{2} \int d^2\vec{r}_1 d^2\vec{r}_2 n(\vec{r}_1) n(\vec{r}_2) \mathcal{V}_{\text{attr.}}(\vec{r}_1 - \vec{r}_2) \\ &\approx \frac{n^2}{2} A \int d^2\vec{r} \mathcal{V}_{\text{attr.}}(\vec{r}) \equiv -\frac{N^2}{2A} u_0. \end{aligned}$$

Combining the previous results gives

$$Z(N, T, A) \approx \frac{1}{N!} \frac{1}{\lambda^{2N}} (A - N\Omega/2)^N \exp \left[\frac{\beta u_0 N^2}{2A} \right].$$

(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.

- Since the work done is changing the surface area is $dW = \sigma dA$, we have $dF = -TdS + \sigma dA + \mu dN$, where $F = -k_B T \ln Z$ is the free energy. Hence, the contribution of the surfactants to the surface tension of the film is

$$\sigma_s = - \left. \frac{\partial \ln Z}{\partial A} \right|_{T, N} = - \frac{N k_B T}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2},$$

which is a two-dimensional variant of the familiar van der Waals equation. Adding the (constant) contribution in the absence of surfactants gives

$$\sigma(n, T) = \sigma_0 - \left. \frac{\partial \ln Z}{\partial A} \right|_{T, N} = \sigma_0 - \frac{Nk_B T}{A - N\Omega/2} + \frac{u_0 N^2}{2A^2}.$$

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

- Thermodynamic stability requires $\delta\sigma\delta A \geq 0$, i.e. σ must be a monotonically increasing function of A at any temperature. This is the case at high temperatures where the first term in the equation for σ_s dominates, but breaks down at low temperatures when the term from the attractive interactions becomes significant. The critical temperature is obtained by the usual conditions of $\partial\sigma_s/\partial A = \partial^2\sigma_s/\partial A^2 = 0$, i.e. from

$$\left\{ \begin{array}{l} \left. \frac{\partial\sigma_s}{\partial A} \right|_T = \frac{Nk_B T}{(A - N\Omega/2)^2} - \frac{u_0 N^2}{A^3} = 0 \\ \left. \frac{\partial^2\sigma_s}{\partial A^2} \right|_T = -\frac{2Nk_B T}{(A - N\Omega/2)^3} + \frac{3u_0 N^2}{A^4} = 0 \end{array} \right.,$$

The two equations are simultaneously satisfied for $A_c = 3N\Omega/2$, at a temperature

$$T_c = \frac{8u_0}{27k_B\Omega}.$$

As in the van der Waals gas, at temperatures below T_c , the surfactants separate into a high density (liquid) and a low density (gas) phase.

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

- The contribution of the surfactants to the energy of the film is given by

$$E_s = -\frac{\partial \ln Z}{\partial \beta} = 2N \times \frac{k_B T}{2} - \frac{u_0 N^2}{2A}.$$

The first term is due to the kinetic energy of the surfactants, while the second arises from their (mean-field) attraction. The heat capacities are then calculated as

$$C_A = \left. \frac{dQ}{dT} \right|_A = \left. \frac{\partial E}{\partial T} \right|_A = Nk_B,$$

and

$$C_\sigma = \left. \frac{dQ}{dT} \right|_\sigma = \left. \frac{\partial E}{\partial T} \right|_\sigma - \sigma \left. \frac{\partial A}{\partial T} \right|_\sigma.$$

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 $n = N/V$.

- Since the ideal gas partition function is proportional to V^N , we have

$$\ln Z = N \ln V + \frac{\beta b N^2}{2V} - \frac{\beta c N^3}{6V^2} + (V - \text{independent terms}).$$

The pressure is obtained from

$$\beta P = \frac{\partial \ln Z}{\partial V} = \frac{N}{V} - \frac{\beta b N^2}{2V^2} + \frac{\beta c N^3}{3V^3}, \quad \implies \quad P = nk_B T - \frac{bn^2}{2} + \frac{cn^3}{3}.$$

(b) Locate the critical temperature T_c below which this equation must be invalid, and the corresponding density n_c .

- Mechanical stability of the gas requires that any spontaneous change in volume should be opposed by a compensating change in pressure. This corresponds to $\delta P \delta V < 0$, and since $\delta n = -(N/V^2)\delta V$, any equation of state must have a pressure that is an increasing function of density. The transition point between pressure isotherms that are monotonically increasing functions of n , and those that are not (hence manifestly incorrect) is obtained by the usual conditions of $dP/dn = 0$ and $d^2P/dn^2 = 0$. Starting from the cubic equation of state, we thus obtain

$$\begin{aligned} \frac{dP}{dn} &= k_B T_c - bn_c + cn_c^2 = 0 \\ \frac{d^2P}{dn^2} &= -b + 2cn_c = 0 \end{aligned}.$$

From the second equation we obtain $n_c = b/(2c)$, which substituted in the first equation gives $k_B T_c = b^2/(4c)$.

(c) Find the pressure P_c at the critical point, and hence obtain the ratio $k_B T_c n_c / P_c$.

- From the equation of state we then find $P_c = b^3/(24c^2)$, and the dimensionless ratio of

$$\frac{k_B T_c n_c}{P_c} = 3.$$

(d) Calculate the isothermal compressibility $\kappa_T = -\frac{1}{V} \frac{\partial V}{\partial P}|_T$, and sketch its behavior as a function of T for $n = n_c$.

- Using $V = N/n$, we get

$$\kappa_T(n) = -\frac{1}{V} \frac{\partial V}{\partial P}\bigg|_T = \frac{1}{n} \frac{\partial P}{\partial n}\bigg|_T^{-1} = [n(k_B T - bn + cn^2)]^{-1}.$$

For $n = n_c$, $\kappa_T(n_c) \propto (T - T_c)^{-1}$, and diverges at T_c .

(e) On the critical isotherm give an expression for $(P - P_c)$ as a function of $(n - n_c)$.

- Using the coordinates of the critical point computed above, we find

$$\begin{aligned} P - P_c &= -\frac{b^3}{24c^2} + \frac{b^2}{4c}n - \frac{b}{2}n^2 + \frac{c}{3}n^3 \\ &= \frac{c}{3} \left(n^3 - \frac{3b}{2c}n^2 + \frac{3b^2}{4c^2}n - \frac{b^3}{8c^3} \right) \\ &= \frac{c}{3} (n - n_c)^3. \end{aligned}$$

(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 $d\mu = dP/n$.)

- According to the Gibbs–Duhem relation, the variations of the intensive variables are related by $SdT - VdP + Nd\mu = 0$, and thus along an isotherm ($dT = 0$) $d\mu = dP/n = \partial P / \partial n|_T dn/n$. Since the liquid and gas states are in coexistence they should have the same chemical potential. Integrating the above expression for $d\mu$ from n_- to n_+ leads to the so-called Maxwell construction, which reads

$$0 = \mu(n_+) - \mu(n_-) = \int_{n_-}^{n_+} \frac{dP}{n} = \int_{n_c(1-\delta)}^{n_c(1+\delta)} dn \left(\frac{k_B T - bn + cn^2}{n} \right).$$

Performing the integrals gives the equation

$$0 = k_B T \ln \left(\frac{1+\delta}{1-\delta} \right) - b n_c (2\delta) + \frac{c}{2} n_c^2 [(1+\delta)^2 - (1-\delta)^2] = k_B T \ln \left(\frac{1+\delta}{1-\delta} \right) - 2k_B T_c \delta,$$

where for the find expression, we have used $n_c = b/(2c)$ and $k_B T_c = b^2/(4c)$. The implicit equation for δ is thus

$$\delta = \frac{T}{2T_c} \ln \left(\frac{1+\delta}{1-\delta} \right) \approx \frac{T}{T_c} \left(\delta + \frac{1}{3} \delta^3 + \dots \right).$$

The leading behavior as $(T_c - T) \rightarrow 0$ is obtained by keeping up to the cubic term, and given by

$$\delta \approx \sqrt{3 \left(\frac{T_c}{T} - 1 \right)}.$$

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.

- The partition function is

$$Z = \text{tr} \left[e^{-\beta \mathcal{H}} \right] = \text{tr} \left[\exp \left(-\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right) \right] \approx \text{tr} \left[\exp \left(-\beta \frac{p^2}{2m} \right) \exp(-\beta U(\vec{q})) \right],$$

where the last approximation follows from the BCH formula, and is valid to order of β^2 . We can evaluate the trace using a complete set of either coordinate ($|\vec{q}\rangle$) or momentum ($|\vec{p}\rangle$) basis, e.g. as

$$Z \approx \sum_{\vec{q}} \left[\langle \vec{q} | \exp \left(-\beta \frac{p^2}{2m} \right) \exp(-\beta U(\vec{q})) | \vec{q} \rangle \right].$$

To simultaneously evaluate both operators, we can insert additional momentum/coordinate sums, such as

$$Z \approx \sum_{\vec{q}, \vec{q}', \vec{p}, \vec{p}'} \left[\langle \vec{q} | \vec{p} \rangle \langle \vec{p} | \exp \left(-\beta \frac{p^2}{2m} \right) \vec{p}' \rangle \langle \vec{p}' | \vec{q}' \rangle \langle \vec{q}' | \exp (-\beta U(\vec{q})) | \vec{q} \rangle \right].$$

The needed matrix elements are now diagonal, leading to

$$Z \approx \sum_{\vec{q}, \vec{p}} \left[\langle \vec{q} | \vec{p} \rangle \langle \vec{p} | \exp \left(-\beta \frac{p^2}{2m} \right) \vec{p} \rangle \langle \vec{p} | \vec{q} \rangle \langle \vec{q} | \exp (-\beta U(\vec{q})) | \vec{q} \rangle \right].$$

For the relevant normalizations, note that in one dimensions

$$\langle x' | x \rangle = \delta(x' - x) = \int \frac{dk}{2\pi} e^{ik(x' - x)} = \int \frac{dp}{2\pi\hbar} e^{ip(x - x')/\hbar} = \sum_p \langle x' | p \rangle \langle p | x \rangle,$$

with appropriate generalization to higher dimensions. Thus with the choice of $\langle \vec{q} | \vec{p} \rangle = \exp(-i\vec{p} \cdot \vec{q}/\hbar)$, we get $\sum_{\vec{p}} \rightarrow \int d^3\vec{p}/h^3$, and

$$Z \approx \int \frac{d^3\vec{q} d^3\vec{p}}{h^3} \exp \left(-\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right),$$

which is the classical partition function, made dimensionless by division with h^3 .

(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

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

• In this special case of a general potential, the integration over coordinate \vec{q} simply yields the volume of the box. Evaluating the classical partition function starting from the classical perspective yields:

$$Z = \int \frac{d^3\vec{q} d^3\vec{p}}{h^3} \exp \left(-\beta \frac{p^2}{2m} - \beta U(\vec{q}) \right) = V \int \frac{d^3\vec{p}}{h^3} \exp \left(-\beta \frac{p^2}{2m} \right) = V \int \frac{d^3\vec{k}}{(2\pi)^3} e^{-\beta \frac{\hbar^2 k^2}{2m}}.$$

The quantum formula gives

$$Z = \text{tr} e^{-\beta \mathcal{H}} = \sum_{\vec{k}} e^{-\beta \hbar^2 k^2 / 2m}.$$

Matching the two formulae yields the required result.

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 $(\beta\hbar\omega)^2$.

- The partition function of a harmonic oscillator is

$$Z_{\text{vib.}}(\beta) = \sum_{n=0}^{\infty} \exp \left[-\beta\hbar\omega \left(n + \frac{1}{2} \right) \right] = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}.$$

Expanding $\ln Z_{\text{vib.}}$ in powers of $\beta\hbar\omega \equiv u$ yields

$$\begin{aligned} \ln Z_{\text{vib.}} &= -\frac{u}{2} - \ln(1 - e^{-u}) = -\frac{u}{2} - \ln \left(u - \frac{u^2}{2} + \frac{u^3}{6} - \dots \right) \\ &= -\frac{u}{2} - \ln u - \ln \left(1 - \frac{u}{2} + \frac{u^2}{6} + \dots \right) = -\frac{u}{2} - \ln u + \frac{u}{2} - \frac{u^2}{6} + \frac{u^2}{8} + \dots \\ &= -\ln u - \frac{u^2}{24} + \dots \end{aligned}$$

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

- The energy of the oscillator is obtained from

$$E_{\text{vib.}} = -\frac{\partial \ln Z_{\text{vib.}}}{\partial \beta} = -\hbar\omega \frac{\partial \ln Z_{\text{vib.}}}{\partial u} = \hbar\omega \left(\frac{1}{u} + \frac{u}{12} + \dots \right) = k_B T + \frac{(\hbar\omega)^2}{12k_B T} + \dots$$

The heat capacity is obtained from the temperature derivative as

$$C_{\text{vib.}} = \frac{dE_{\text{vib.}}}{dT} = k_B \left[1 - \frac{1}{12} \left(\frac{\hbar\omega}{k_B T} \right)^2 + \dots \right].$$

Quantum corrections reduce the heat capacity at high temperatures.

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 .

- According to the Abel–Plana formula

$$\begin{aligned} S_{\text{vib.}} &\equiv \sum_{n=0}^{\infty} e^{-nu} = \int_0^{\infty} dx e^{-ux} + \frac{1}{2} + i \int_0^{\infty} dt \frac{e^{-iut} - e^{iut}}{e^{2\pi t} - 1} \\ &= \frac{1}{u} + \frac{1}{2} + 2 \int_0^{\infty} dt \frac{1}{e^{2\pi t} - 1} \sin(ut). \end{aligned}$$

Expanding the cosine in powers of u yields

$$\begin{aligned} S_{\text{vib.}} &= \frac{1}{u} + \frac{1}{2} - 2 \int_0^{\infty} dt \frac{1}{e^{2\pi t} - 1} \sum_{p=1}^{\infty} \frac{(-1)^p}{(2p-1)!} (ut)^{2p-1} \\ &= \frac{1}{u} + \frac{1}{2} - 2 \sum_{p=1}^{\infty} \frac{(-1)^p u^{2p-1}}{(2p-1)!(2\pi)^{2p}} \int_0^{\infty} \frac{x^{2p-1} dx}{e^x - 1} \\ &= \frac{1}{u} + \frac{1}{2} - 2 \sum_{p=1}^{\infty} \frac{(-1)^p u^{2p-1}}{(2\pi)^{2p}} \zeta_{2p} = \frac{1}{u} + \frac{1}{2} + \frac{u}{12} + \dots, \end{aligned}$$

where we have used $n! \zeta_{n+1} = \int_0^{\infty} dx x^n / (e^x - 1)$, and $\zeta_2 = \pi^2/6$. It can be checked that the same result is obtained from first summing the geometric series to $S_{\text{vib.}} = 1/(1 - e^{-u})$ and expanding the latter in powers of u .

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

- For the rotation partition sum we need

$$\begin{aligned} S_{\text{rot.}} &\equiv \sum_{\ell=0}^{\infty} (2\ell+1) e^{-u\ell(\ell+1)} \\ &= \int_0^{\infty} dx (2x+1) e^{-ux(x+1)} + \frac{1}{2} + i \int_0^{\infty} dt \frac{(2it+1)e^{-iut(it+1)} - (-2it+1)e^{iut(-iut+1)}}{e^{2\pi t} - 1} \\ &= \frac{1}{u} + \frac{1}{2} - 4 \int_0^{\infty} dt \frac{t}{e^{2\pi t} - 1} + 2u \int_0^{\infty} dt \frac{t - 2t^3}{e^{2\pi t} - 1} + \mathcal{O}(u^2) \\ &= \frac{1}{u} + \frac{1}{2} - \frac{4}{(2\pi)^2} \zeta_2 + 2u \left(\frac{\zeta_2}{(2\pi)^2} - 2 \frac{3! \zeta_4}{(2\pi)^4} \right) + \mathcal{O}(u^2) \\ &= \frac{1}{u} + \frac{1}{3} + \frac{u}{15} + \mathcal{O}(u^2), \end{aligned}$$

using $\zeta_2 = \pi^2/6$ and $\zeta_4 = \pi^4/90$.

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

- Allowed energies of a Harmonic oscillator are $\hbar^2 \ell(\ell+1)/2I$ for integer ℓ , with degeneracy $(2\ell+1)$. Using the above result, the corresponding partition function is

$$Z_{\text{rot.}} = \sum_{\ell=0}^{\infty} (2\ell+1) e^{-u\ell(\ell+1)} = \frac{1}{u} + \frac{1}{3} + \frac{u}{15} + \mathcal{O}(u^2), \quad \text{for } u = \frac{\beta \hbar^2}{2I},$$

and

$$\ln Z_{\text{rot.}} = -\ln u + \ln \left(1 + \frac{u}{3} + \frac{u^2}{15} + \cdots \right) = -\ln u + \frac{u}{3} + \frac{u^2}{15} - \frac{u^3}{18} + \cdots$$

The energy is then obtained from

$$\begin{aligned} E_{\text{rot.}} &= -\frac{\partial \ln Z_{\text{rot.}}}{\partial \beta} = -\frac{\hbar^2}{2I} \frac{\partial \ln Z_{\text{rot.}}}{\partial u} \\ &= \frac{\hbar^2}{2I} \left(\frac{1}{u} - \frac{1}{3} - \frac{u}{45} + \cdots \right) = k_B T - \frac{\hbar^2}{6I} - \frac{\hbar^4}{180 I^2 k_B T} + \cdots \end{aligned}$$

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

- The heat capacity is obtained from the temperature derivative of the energy as

$$C_{\text{rot.}} = \frac{dE_{\text{rot.}}}{dT} = k_B \left[1 + \frac{1}{180} \left(\frac{\hbar^2}{2I k_B T} \right)^2 + \cdots \right].$$

Unlike the case of vibrations, quantum corrections increase the 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} .

- Ignoring quantum effects and taking the coarse graining scale to be h ,

$$Z = \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \int \prod_{n=1}^N \frac{d^3 \vec{p}_n d^3 \vec{q}_n}{h^3} e^{-\beta [\sum_{i=1}^N \frac{\vec{p}_i^2}{2m} + U(\vec{q}_1, \dots, \vec{q}_N)]}.$$

Now with a magnetic field,

$$\begin{aligned} Z(\vec{B}) &= \sum_{\mu_s} e^{-\beta \mathcal{H}(\mu_s)} = \int \prod_{n=1}^N \frac{d^3 \vec{p}_n d^3 \vec{q}_n}{h^3} e^{-\beta [\sum_{i=1}^N \frac{(\vec{p}_i - e\vec{A})^2}{2m} + U(\vec{q}_1, \dots, \vec{q}_N)]} \\ &= \int \prod_{n=1}^N \frac{d^3 \vec{p}'_n d^3 \vec{q}_n}{h^3} e^{-\beta [\sum_{i=1}^N \frac{\vec{p}'_i{}^2}{2m} + U(\vec{q}_1, \dots, \vec{q}_N)]}, \end{aligned}$$

for $\vec{B} = \vec{\nabla} \times \vec{A}$, where we have defined $\vec{p}' = \vec{p} - e\vec{A}$. Hence we see that classically,

$$Z(\vec{B}) = Z(\vec{0}),$$

so 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.

- The classical partition function is

$$Z_{\text{cl}}(\beta) = \int \frac{dq dp}{h} e^{-\frac{\beta p^2}{2m} - \frac{\beta m \omega^2 q^2}{2}} = \frac{2\pi}{h\beta\omega},$$

and the energy is

$$E_{\text{cl}}(\beta) = -\frac{\partial \ln Z_{\text{cl}}}{\partial \beta} = \frac{1}{\beta} = k_B T.$$

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

- The partition function with the postulated quantized energies is

$$Z_{\text{qm}}(\beta) = \sum_{n=0}^{\infty} e^{-\beta(x+yn)} = \frac{e^{-\beta x}}{1 - e^{-\beta y}}, \quad \implies \quad \lim_{\beta \rightarrow 0} Z_{\text{qm}}(\beta) = \frac{1}{\beta y}.$$

Matching the latter to the classical result yields

$$y = \frac{\hbar\omega}{2\pi} = \hbar\omega.$$

(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 .

- The energy of the quantized oscillator is given by

$$E_{\text{qm}}(\beta) = -\frac{\partial \ln Z_{\text{qm}}}{\beta} = x + \frac{y}{e^{\beta y} - 1}.$$

Expanding the above result in β gives

$$\lim_{\beta \rightarrow 0} E_{\text{qm}}(\beta) = x + \frac{y}{\beta y(1 + \beta y/2 + \dots)} = \frac{1}{\beta} + \left(x - \frac{y}{2}\right) + \mathcal{O}(\beta).$$

Demanding agreement with the classical energy at this order, then yields

$$x = \frac{y}{2} = \frac{1}{2}\hbar\omega \quad !$$

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 .

- The time evolution of the density operator is given by the Heisenberg equation

$$\frac{\partial \rho}{\partial t} = i\hbar [\rho, \mathcal{H}],$$

leading to

$$\frac{dS}{dt} = i\hbar \text{tr} \{ (1 + \ln \rho) [\rho, \mathcal{H}] \} = i\hbar \{ \text{tr}(\rho \mathcal{H}) - \text{tr}(\mathcal{H} \rho) + \text{tr}(\rho \ln \rho \mathcal{H}) - \text{tr}(\rho \mathcal{H} \ln \rho) \} = 0,$$

since the trace of a product is invariant under cyclic permutations, and $[\rho, \ln \rho] = 0$.

(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 $\langle \mathcal{H} \rangle = \text{tr}(\rho \mathcal{H}) = E$.

- In order to satisfy the two constraints, normalization and constant average energy, written respectively as

$$\text{tr}\rho = 1, \quad \text{and} \quad \langle \mathcal{H} \rangle = \text{tr}\rho\mathcal{H} = E,$$

we construct the functional

$$S(t) = \text{tr}\rho [-\ln\rho - \alpha - \beta\mathcal{H}] + \alpha + \beta E,$$

where α and β are Lagrange multipliers. Extremizing the above expression with respect to ρ results in

$$\left. \frac{\partial S}{\partial \rho} \right|_{\rho=\rho_{\max}} = -\ln\rho_{\max} - \alpha - \beta\mathcal{H} - 1 = 0.$$

The solution to this equation is

$$\ln\rho_{\max} = -(\alpha + 1) - \beta\mathcal{H},$$

which can be rewritten as

$$\rho_{\max} = C \exp(-\beta\mathcal{H}), \quad \text{where} \quad C = e^{-(\alpha+1)}.$$

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

- The density obtained in part (b) is stationary, as the commutator of \mathcal{H} with any function of \mathcal{H} vanishes, implying, in particular,

$$\frac{\partial\rho_{\max}}{\partial t} = 0.$$

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.

- By definition,

$$\rho = \frac{\exp(-\beta\mathcal{H})}{\text{tr} \exp(-\beta\mathcal{H})}.$$

Noting that for any $i = 1, 2, 3$, $\sigma_i^2 = I$, we get,

$$\exp(a\sigma_i) = (1 + \frac{1}{2!}a^2 + \frac{1}{4!}a^4 + \dots)I + (a + \frac{1}{3!}a^3 + \frac{1}{5!}a^5 + \dots)\sigma_i = \cosh aI + \sinh a\sigma_i,$$

and thus

$$\text{tr} \exp(a\sigma_i) = \text{tr}(\cosh aI + \sinh a\sigma_i) = 2 \cosh a,$$

as the Pauli matrices are traceless. Hence in the case $\vec{B} = B\hat{z}$,

$$\begin{aligned} \rho &= \frac{\exp(\beta\mu_B\sigma_z B)}{2 \cosh(\beta\mu_B B)} \\ &= \frac{\cosh(\beta\mu_B B)I + \sinh(\beta\mu_B B)\sigma_z}{2 \cosh(\beta\mu_B B)} = \frac{1}{2 \cosh(\beta\mu_B B)} \begin{pmatrix} e^{\beta\mu_B B} & 0 \\ 0 & e^{-\beta\mu_B B} \end{pmatrix}. \end{aligned}$$

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

- For $\vec{B} = B\hat{x}$,

$$\begin{aligned} \rho &= \frac{\exp(-\beta\mathcal{H})}{\text{tr} \exp(-\beta\mathcal{H})} = \frac{\exp(\beta\mu_B\sigma_x B)}{2 \cosh(\beta\mu_B B)} \\ &= \frac{\cosh(\beta\mu_B B)I + \sinh(\beta\mu_B B)\sigma_x}{2 \cosh(\beta\mu_B B)} = \begin{pmatrix} 1/2 & \tanh(\beta\mu_B B)/2 \\ \tanh(\beta\mu_B B)/2 & 1/2 \end{pmatrix}. \end{aligned}$$

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

- Note that

$$\text{tr} \sigma_i \exp(a\sigma_i) = \text{tr}(\cosh a\sigma_i + \sinh aI) = 2 \sinh a,$$

so that for $\mathcal{H} = -\mu_B B\sigma_i$,

$$\begin{aligned} \frac{\text{tr} \mathcal{H} \rho}{\text{tr} \rho} &= \frac{\text{tr}[-\mu_B B\sigma_i \exp(\beta\mu_B\sigma_i B)]}{\text{tr}[\exp(\beta\mu_B\sigma_i B)]} \\ &= \frac{-2\mu_B B \sinh(\beta\mu_B B)}{2 \cosh(\beta\mu_B B)} = -\mu_B B \tanh(\beta\mu_B B), \end{aligned}$$

independent of the direction of \vec{B} .
