Exercise 1 (3 Points)

Consider a classical gas of N noninteracting diatomic molecules in a volumen V. The Hamiltonian of a single molecule is given by

$$H(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{|\vec{p}_1|^2 + |\vec{p}_2|^2}{2m} + \frac{K}{2}|\vec{r}_1 - \vec{r}_2|^2,$$

where $\vec{p}_1$, $\vec{p}_2$, $\vec{r}_1$, and $\vec{r}_2$ are the momenta and coordinates of the two atoms of the molecule. Obtain

- the Helmholtz potential,
- the specific heat at constant volume (C_V),
- the average $\langle|\vec{r}_1 - \vec{r}_2|^2\rangle$.

You may use that $\int d^3\vec{r}_1\ d^3\vec{r}_2\ f(\vec{r}_1, \vec{r}_2) = \int d^3\vec{R}_{cm}\ d^3\vec{r}\ f(\vec{R}_{cm}, \vec{r})$, where $\vec{R}_{cm} = (\vec{r}_1 + \vec{r}_2)/2$ and $\vec{r} = \vec{r}_1 - \vec{r}_2$.

Exercise 2 (3 Points)

Consider a system of non-interacting particles.

- If $Q_1(T, V)$ is the canonical partition function for one particle, show that the grand-canonical partition function is of the form $\tau(z, T, V) = e^{zQ_1(T,V)}$ (Hint: You will probably need to remember the Taylor series of the exponential function).
- Assume that the energy of the non-interacting particles is an arbitrary function of the velocity of the particle, being independent of the position. Using the theory of the grand-canonical ensemble obtain the equation of state, and compare it to the result obtained for the typical case in which $E = p^2/2m$.

Exercise 3 (4 Points)

Consider a classical system with N particles in a volumen V. The particles interact through a two-body potential $u(r)$, where $r = |\vec{r}|$ is the interparticle distance. Hence, the Hamiltonian function of the system is:

$$H = \sum_{i=1}^{N} \frac{|\vec{p}_i|^2}{2m} + \sum_{i<j} u_{ij},$$

where $u_{ij} = u(|\vec{r}_i - \vec{r}_j|)$, and $\vec{r}_i$ is the position of the ith particle. We define the function $f(r) \equiv e^{-\beta u(r)} - 1$, with $\beta = 1/k_B T$.

1. By using the theory of the canonical ensemble show that

$$\frac{Pv}{k_B T} = 1 + v\frac{\partial}{\partial v}R(v,T),$$

where $v = V/N$ is the specific volumen, and

$$R(v,T) \equiv \frac{1}{N} ln \left\{ \frac{1}{v^N N^N} \int d^{3N}\vec{r} \prod_{i<j}(1+f_{ij}) \right\},$$

where $f_{ij} = f(|\vec{r}_i - \vec{r}_j|)$.

2. If the interactions are very weak, one obtains

$$\frac{Pv}{k_B T} \simeq 1 + \frac{1}{v}a_2(T),$$

where $a_2(T) \equiv -\frac{1}{2}\int_0^\infty dr 4\pi r^2 f(r)$.
Calculate the coefficient $a_2(T)$ assuming that $u(r) = 0$ for $r < \sigma$, $u(r) = -\epsilon$ for $\sigma < r < r_0$, and $u(r) = 0$ for $r > r_0$.