Exam
Statistical Mechanics
20 November 2017, 2-4pm

The total score is 20 points!

5 points

Energy fluctuations of anharmonic oscillators

We consider a set of N one-dimensional anharmonic oscillators. Each oscillator is described by the following Hamiltonian

$$\mathcal{H}_1 = \frac{p^2}{2m} + \frac{Kq^4}{4}$$

Calculate the average total energy $\langle E \rangle$ of the N oscillators and its variance $\sigma_E^2 \equiv \langle E^2 \rangle - \langle E \rangle^2$.

What can you conclude about the relative fluctuations of the energy for this system $\sigma_E / \langle E \rangle$ in the limit $N \to \infty$?

3 points

Two gases

Two gases, each containing N molecules, are placed at the two sides of a container with total volume V. The two sides are separated by a sliding piston (see Fig 1). The gases are at temperature T and their densities are sufficiently low such that one can use just the second virial coefficient for their equation of state.

We assume that one gas has a positive virial coefficient $b > 0$, while the other has a negative virial coefficient $-a$ (with $a > 0$).

Find the equilibrium values of the volumes V_1 and V_2 occupied by the two gases. Throughout the calculation you can assume that the densities on both sides are small, so that only the lowest order term in the density needs to be considered.

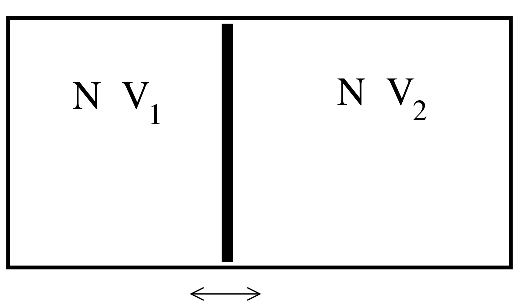

Figure 1:

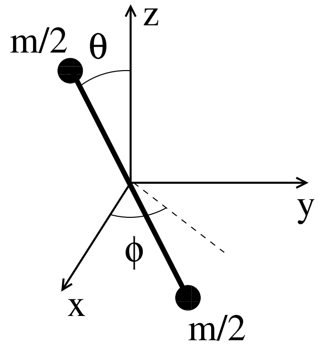

Figure 2:

5 points

Two dimensional Lennard-Jones fluid

Consider a Lennard-Jones fluid in two dimensions. The fluid is composed of particles of mass m, in a volume V and at a temperature T. Write down and plot the probability distribution of the speed $v = |\vec{v}| = \sqrt{v_x^2 + v_y^2}$ of a particle. Calculate the averages $\langle v \rangle$ and $\langle v^2 \rangle$. Do some of these follow also from the equipartition theorem? Explain!

7 points

Rigid Rotor

We consider a simple model of a gas of N molecules in equilibrium at temperature T and volume V. A molecule consists of two equal masses $m/2$ separated by a fixed distance R. A configuration of the molecule is given by the center of mass position $\vec{Q}$ and the two polar angles θ and ϕ which identify the orientation of the molecule with respect to the cartesian axes (see Fig. 2). The conjugated momenta are $\vec{P}$, p_θ and p_ϕ.

The Hamiltonian for one molecule is given by:

$$\mathcal{H}_1 = \frac{\vec{P}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\phi^2}{2I \sin^2 \theta}$$

where $I = mR^2/4$ is the moment of inertia.

To obtain the canonical single molecule partition function $Z_1(V, T)$ one needs to integrate over the center of mass position and momentum and also over $dp_\theta d\theta dp_\phi d\phi$.

a) Obtain the average internal energy E of the system from the calculation of $Z_1(V, T)$

b) Obtain E via the equipartition theorem and show that the result matches that of a).

c) Calculate the pressure of the gas of molecules.

CORRECTION EXAM 20/11/2017

ANHARMONIC OSCILLATORS

$$Z_1 = \int dp \int dq \; e^{-\beta\left(\frac{p^2}{2m} + \frac{kq^4}{4}\right)} \underset{\substack{\uparrow \\ \text{CHANGE OF} \\ \text{VARIABLES}}}{=} \beta^{-1/2}\, \beta^{-1/4} \underbrace{(\text{-----})}_{\text{independent on } \beta}$$

$$= \beta^{-3/4} (\text{---})$$

$$Z_N = (Z_1)^N = \beta^{-\frac{3N}{4}} (\text{---})$$

$$\langle E \rangle = -\frac{\partial \log Z_N}{\partial \beta} = \frac{3N}{4\beta} = \frac{3N}{4} k_B T$$

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = \frac{\partial^2 \log Z_N}{\partial \beta} = -\frac{\partial}{\partial \beta} \langle E \rangle = \frac{3N}{4\beta^2} = \frac{3N}{4} (k_B T)^2$$

$$\frac{\sigma_E}{\langle E \rangle} = \frac{\sqrt{\frac{3N}{4}}\, \cancel{k_B T}}{\frac{3N}{4}\, \cancel{k_B T}} = \frac{2}{\sqrt{3N}} \to 0 \quad \text{as } N \to \infty$$

TWO GASES

$$P_1 = P_2 \qquad \frac{\cancel{N k_B T}}{V_1}\left(1 + \frac{bN}{V_1}\right) = \frac{\cancel{N k_B T}}{V_2}\left(1 - \frac{aN}{V_2}\right)$$

$$\frac{V_1}{1 + \frac{bN}{V_1}} = \frac{V_2}{1 - \frac{aN}{V_2}} \implies V_1\left(1 - \frac{bN}{V_1} + \dots\right) = V_2\left(1 + \frac{aN}{V_2} + \dots\right)$$

$$\begin{cases} V_1 - V_2 = (a+b) N \\ V_1 + V_2 = V \end{cases} \implies \begin{cases} V_1 = \frac{V}{2} + \frac{a+b}{2} N \\ V_2 = \frac{V}{2} - \frac{a+b}{2} N \end{cases}$$

TWO DIMENSIONAL LENNARD-JONES FLUID

THE DISTRIBUTION OF VELOCITIES IS INDEPENDENT ON THE POTENTIAL.

THE SPEED IS DISTRIBUTED AS $\rho(v) = A v\, e^{-\beta \frac{m v^2}{2}}$

$$1 = \int_0^{+\infty} \rho(v)\,dv = A \int_0^{+\infty} e^{-\beta\frac{m v^2}{2}} \frac{dv^2}{2} = \frac{A}{\beta m} \implies \boxed{A = \beta m}$$

$$\langle v \rangle = \beta m \int_0^{+\infty} v^2 e^{-\beta\frac{m v^2}{2}}\,dv = -\cancel{\beta m}\,\frac{2}{\cancel{m}}\frac{\partial}{\partial\beta}\int_0^{+\infty} e^{-\beta\frac{m v^2}{2}}\,dv$$

$$= -\cancel{2}\beta\,\frac{\sqrt{\pi}}{\cancel{2}}\,\frac{\partial}{\partial\beta}\sqrt{\frac{2}{m\beta}} = \frac{\sqrt{2\pi}\,\beta}{\sqrt{m}}\,\frac{1}{2\beta^{3/2}} = \sqrt{\frac{\pi}{2m\beta}} = \sqrt{\frac{\pi k_B T}{2m}}$$

$$\langle v^2 \rangle = \beta m \int_0^{+\infty} e^{-\beta\frac{m v^2}{2}} v^3\,dv = \frac{\beta m}{2}\int_0^{+\infty} e^{-\beta\frac{m v^2}{2}} v^2\,dv^2$$

$$x \equiv \beta\frac{m}{2} v^2$$

$$= \frac{\cancel{\beta m}}{\cancel{2}}\left(\frac{2}{\beta m}\right)^{\cancel{2}} \int_0^{+\infty} e^{-x} x\,dx =$$

$$= \frac{2}{\beta m} = \frac{2 k_B T}{m}$$

EQUIPARTITION $\left\langle \frac{p_x^2}{2m} \right\rangle + \left\langle \frac{p_y^2}{2m} \right\rangle = \cancel{2}\cdot\frac{k_B T}{\cancel{2}} = k_B T$

$$\frac{m}{2}\langle v_x^2 + v_y^2 \rangle = k_B T \implies \langle v^2 \rangle = \frac{2 k_B T}{m}$$

RIGID ROTOR

$$Z_1 = \int \frac{d\vec{P}\, d\vec{Q}}{h^5}\, dp_\theta\, d\theta\, dp_\varphi\, d\varphi \; e^{-\beta\left(\frac{\vec{P}^2}{2m} + \frac{p_\theta^2}{2I} + \frac{p_\varphi^2}{2I\sin^2\theta}\right)}$$

$$= \frac{V}{h^2 \lambda_T^3} \sqrt{\frac{2\pi I}{\beta}}\; 2\pi \sqrt{\frac{2\pi I}{\beta}} \int_0^\pi d\theta \sin\theta$$

$\vec{P},\vec{Q}$ $\qquad p_\theta \qquad \varphi$

$$= \frac{V}{\lambda_T^3} \frac{8\pi^2 I}{h^2 \beta} \qquad \lambda_T \sim \beta^{-1/2}$$

$$Z_1 \sim \beta^{-5/2} (\text{----}) \qquad E = -\frac{\partial \log Z_1}{\partial \beta} = \frac{5}{2\beta} = \frac{5 k_B T}{2}$$

EQUIPARTITION

$$\left\langle \frac{\vec{P}^2}{2m} \right\rangle = \frac{3 k_B T}{2} \qquad \left\langle \frac{p_\theta^2}{2I} \right\rangle = \frac{k_B T}{2}$$

$$\left\langle p_\varphi \frac{\partial H}{\partial p_\varphi} \right\rangle = k_B T \qquad \left\langle \frac{p_\varphi^2}{I \sin^2\theta} \right\rangle = k_B T \implies \left\langle \frac{p_\varphi^2}{2I\sin^2\theta} \right\rangle = \frac{k_B T}{2}$$

HENCE $\quad E = \dfrac{5 k_B T}{2}$

PRESSURE

$$P = -\left.\frac{\partial F}{\partial V}\right|_{N,T} = + k_B T N \left.\frac{\partial}{\partial V} \log Z_1 \right|_{N,T}$$

$$Z_1 \sim V(\text{---}) \qquad \boxed{P = \frac{N k_B T}{V}} \qquad \text{IDEAL GAS}$$