Examen
Statistical Mechanics
21 November 2016, 2-4pm

3 points

Diffusion

Consider N diffusing particles in one dimension and let D be the diffusion coefficient. Let us suppose that at time $t = 0$ the concentration is

$$c(x, 0) = \frac{N}{\sqrt{2a^2\pi}} e^{-\frac{x^2}{2a^2}} \tag{1}$$

where a is given. Calculate $c(x, t)$ the concentration at later times.

2 points

Ideal Gas in grand canonical ensemble

Calculate the average number of particles $\langle N \rangle$ of an ideal gas as a function of the temperature T, volume V and chemical potential μ.

3 points

Second virial coefficient

We consider a real gas of particles interacting through a purely repulsive long range potential given by

$$\phi(r) = \frac{\varepsilon}{r^n}$$

where $\varepsilon > 0$, $n > 0$. Is the second virial coefficient $b_2(T)$ positive or negative? Give some intuitive physical arguments to explain this result. How does $b_2(T)$ depend on temperature (eg. power-law, exponential...)?

6 points

Diatomic molecule

Consider a classical system of N noninteracting diatomic molecules enclosed in a box of volume V at temperature T. The molecule is considered as composed by two atoms of mass m and charges $+q$ and $-q$, as shown in the Fig. 1. We assume that the two masses are bound by an harmonic spring with spring constant K. In the system there is a constant electric field $\vec{E} = \epsilon\hat{z}$ pointing along the z-direction. The Hamiltonian for a single molecule is then given by

$$\mathcal{H}_1 = \frac{1}{2m}\left(\vec{p}_1^{\,2} + \vec{p}_2^{\,2}\right) + \frac{K}{2}|\vec{r}_1 - \vec{r}_2|^2 + q\varepsilon(z_1 - z_2) \tag{2}$$

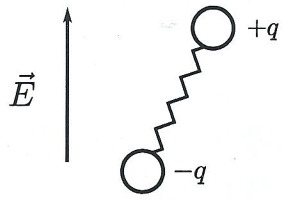

Figure 1: Molecule coomposed by two charged atoms, subject to an electric field $\vec{E}$.

where $\vec{p}_1$, $\vec{p}_2$, $\vec{r}_1$, $\vec{r}_2$ are the momenta and positions of the two atoms in a molecule. z_i is the z-component of the vector $\vec{r}_i$.

a) Compute the canonical partition function for a single molecule and deduce from that the partition function for N molecules. *Hint: whenever necessary use a change of variables to transform the integrals into gaussian ones.*

b) Compute the average internal energy per molecule $\langle \mathcal{H}_1 \rangle$ and the pressure of a gas of N molecules.

c) Compute the mean extension of a molecule in the x, y and z directions, i.e. $\langle x_1 - x_2 \rangle$, $\langle y_1 - y_2 \rangle$ and $\langle z_1 - z_2 \rangle$ and the mean quadratic extensions, i.e. $\langle (x_1 - x_2)^2 \rangle$, $\langle (y_1 - y_2)^2 \rangle$ and $\langle (z_1 - z_2)^2 \rangle$.

6 points

Chain of oscillators

Consider a one dimensional chain of $N-1$ identical coupled oscillators shown in the Fig. 2. The total Hamiltonian of the system is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \frac{K}{2} (x_{i+1} - x_i)^2$$

a) Calculate the average of the total energy $\langle E \rangle$ and the variance $\langle E^2 \rangle - \langle E \rangle^2$ and show that the relative fluctuations of E are small in the thermodynamic limit.

b) Repeat the calculations of a) for anharmonic oscillators described by the following Hamiltonian

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N-1} \frac{K}{4} (x_{i+1} - x_i)^4$$

Figure 2: Linear chain of oscillators

EXAM 21 NOVEMBER 2016

DIFFUSION

$$c(x,t) = \frac{N}{\sqrt{4\pi D(t+t_0)}} e^{-\frac{x^2}{4D(t+t_0)}}$$ is SOLUTION OF DIFFUSION EQUATION

AT TIME $t=0$ $\quad c(x,0) = \frac{N}{\sqrt{4\pi D t_0}} e^{-\frac{x^2}{4Dt_0}}$

CHOOSE $t_0 = \frac{a^2}{2D}$ AND WE HAVE THE SOLUTION

$$c(x,t) = \frac{N}{\sqrt{4\pi D t + 2a^2\pi}} e^{-\frac{x^2}{4Dt+2a^2}}$$

IDEAL GAS

$$Z_N = \frac{V^N}{N!\,\lambda_T^{3N}}$$

$$\Xi = \sum_{N=0}^{+\infty} Z_N e^{\beta\mu N} = \exp\left(\frac{V e^{\beta\mu}}{\lambda_T^3}\right)$$

$$\langle N \rangle = \frac{\partial \log \Xi}{\beta\,\partial\mu} = \frac{V e^{\beta\mu}}{\lambda_T^3}$$

VIRIAL COEFFICIENT

$$b_2(T) = -\frac{1}{2}\int_0^{+\infty} dr\, 4\pi r^2 \left(e^{-\beta\varepsilon/r^m} - 1\right)$$

NOTE $b_2(T) > 0$ AS THE FORCE IS PURELY REPULSIVE

DEFINING $\cancel{r} \equiv \omega(\beta\varepsilon)^{1/m}$ WE GET $b_2(T) = A\left(\frac{\varepsilon}{k_B T}\right)^{3/m}$

WITH $A > 0$

2) DIATOMIC MOLECULE

a) WE USE CENTER OF MASS COORDINATES $\vec{R} = \dfrac{\vec{r}_1+\vec{r}_2}{2}$ $\quad \vec{\rho} = \vec{r}_1-\vec{r}_2$

$$Z_1 = \frac{1}{\lambda_T^6}\int d\vec{R}\int d\rho_x\, d\rho_y\, d\rho_z\; e^{-\frac{\beta k}{2}\left(\rho_x^2+\rho_y^2+\rho_z^2\right)-\beta q \mathcal{E}\rho_z}$$

$$= \frac{V}{\lambda_T^6}\int d\rho_x\, e^{-\frac{\beta k}{2}\rho_x^2}\int d\rho_y\, e^{-\frac{\beta k}{2}\rho_y^2}\int d\rho_z\, e^{-\frac{\beta k}{2}\rho_z^2-\beta q\mathcal{E}\rho_z}$$

IDENTICAL TO 1 D HARMONIC OSCILLATORS

$$= \frac{V}{\lambda_T^6}\,\frac{2\pi}{\beta k}\int_{-\infty}^{+\infty} d\rho_z\, e^{-\beta f(\rho_z)}$$

where $f(\rho_z) = \frac{k}{2}\rho_z^2 + q\mathcal{E}\rho_z$ THIS IS A PARABOLA !

$$= \frac{k}{2}\left[\rho_z^2 + \frac{2q\mathcal{E}}{k}\rho_z\right] = \frac{k}{2}\left[\left(\rho_z+\frac{q\mathcal{E}}{k}\right)^2-\left(\frac{q\mathcal{E}}{k}\right)^2\right]$$

$$= \frac{k}{2}\rho_z'^2 - \frac{q^2\mathcal{E}^2}{2k}$$ WHERE $\rho_z' \equiv \rho_z + \frac{q\mathcal{E}}{k}$

$$Z_1 = \frac{V}{\lambda_T^6}\,\frac{2\pi}{\beta k}\int_{-\infty}^{+\infty} d\rho_z'\, e^{-\beta\frac{k}{2}\rho_z'^2}\; e^{\frac{\beta q^2\mathcal{E}^2}{2k}} = \frac{V}{\lambda_T^6}\left(\frac{2\pi}{\beta k}\right)^{3/2} e^{\beta\frac{q^2\mathcal{E}^2}{2k}}$$

$$Z_N = \frac{Z_1^N}{N!}$$

KINETIC ENERGY

b) $$\langle H_1 \rangle = -\frac{\partial \log Z_1}{\partial \beta} = -\frac{\partial}{\partial \beta}\left[\log \beta^{-3} + \log \beta^{-3/2} + \frac{\beta q^2 \varepsilon^2}{2k} + \dots \right]$$

FACTORS WHICH DO NOT CONTAIN β

$$= 3 k_B T + \frac{3}{2} k_B T - \frac{q^2 \varepsilon^2}{2k} = \frac{9}{2} k_B T - \frac{q^2 \varepsilon^2}{2k}$$

c) WE WANT TO COMPUTE $\langle \rho_x \rangle, \langle \rho_y \rangle, \langle \rho_z \rangle$

$\langle \rho_x \rangle = \langle \rho_y \rangle = 0$ BY SYMMETRY

NOTE $\langle \rho'_z \rangle = 0$ AS WELL! $\Rightarrow \langle \rho_z \rangle = -\frac{q\varepsilon}{k}$

ρ_x IS DISTRIBUTED AS A 1D HARMONIC OSCILLATOR

$\langle \rho_x^2 \rangle = \frac{k_B T}{k} = \langle \rho_y^2 \rangle$ (FROM EQUIPARTITION)

$\langle {\rho'_z}^2 \rangle = \frac{k_B T}{k}$ AS WELL

$\Downarrow$

$$\left\langle \left(\rho_z + \frac{q\varepsilon}{k} \right)^2 \right\rangle = \langle \rho_z^2 \rangle + \frac{2q\varepsilon}{k} \langle \rho_z \rangle + \frac{q^2 \varepsilon^2}{k^2} =$$

$$= \langle \rho_z^2 \rangle - 2\frac{q^2 \varepsilon^2}{k} + \frac{q^2 \varepsilon^2}{k^2} = \langle \rho_z^2 \rangle - \frac{q^2 \varepsilon^2}{k^2} = \frac{k_B T}{k}$$

$$\Rightarrow \langle \rho_z^2 \rangle = \frac{k_B T}{k} + \frac{q^2 \varepsilon^2}{k^2}$$

4] CHAIN OF OSCILLATORS

a) $$Z_N = \int dp_1 \cdots dp_N \, dx_1 \cdots dx_N \; e^{-\beta H} =$$

$$= \frac{1}{\lambda_T^N} \int dx_1 \int du_1 \cdots du_{N-1} \; e^{-\beta \frac{k}{2}\left(u_1^2 + u_2^2 + \cdots + u_{N-1}^2\right)}$$

where we have defined $\quad u_i \equiv x_{i+1} - x_i$

$$Z_N = \frac{L}{\lambda_T^N} \left(\int_{-\infty}^{+\infty} du \; e^{-\beta \frac{k}{2} u^2} \right)^{N-1}$$

$$\langle E \rangle = \frac{N}{2} k_B T + \frac{N-1}{2} k_B T \qquad \text{(FROM EQUIPARTITION)}$$

$$= \left(N - \frac{1}{2}\right) k_B T$$

$$\sigma_E^2 = \frac{\partial^2 \log Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \langle E \rangle = -\frac{\partial}{\partial \beta}\left(N - \frac{1}{2}\right)\frac{1}{\beta} = \left(N - \frac{1}{2}\right)(k_B T)^2$$

$$\frac{\sigma_E^2}{\langle E \rangle^2} = \frac{1}{N - 1/2} \longrightarrow 0 \quad \text{as} \quad N \to \infty$$

b) $$Z_N = \frac{L}{\lambda_T^N} \left(\int_{-\infty}^{+\infty} du \; e^{-\beta \frac{k}{4} u^4} \right)^{N-1}$$

$$\langle E \rangle = \frac{N}{2} k_B T + \frac{N-1}{4} k_B T = \frac{3N-1}{4} k_B T \qquad \text{(FROM EQUIP.)}$$

$$\sigma_E^2 = \frac{\partial^2 \log Z}{\partial \beta^2} = -\frac{\partial}{\partial \beta} \langle E \rangle = \left(\frac{3N-1}{4}\right)(k_B T)^2$$

$$\frac{\sigma_E^2}{\langle E \rangle^2} = \frac{4}{3N-1} \longrightarrow 0 \quad \text{as} \quad N \to \infty$$