Examen
Statistical Mechanics
16 November 2015, 16:00

The total score is 20 points!

8 points

Diffusion with reflecting boundaries

We consider the diffusion of particles in a one dimensional interval $-a/2 \le x \le a/2$ with reflecting boundary conditions at $x = \pm a/2$. The diffusion coefficient is equal to D. At time $t = 0$ we place $3N/4$ particles at $x = a/4$ and $N/4$ particles at $x = -a/4$.

a) Plot schematically (no calculations!) the concentration $c(x,t)$ as a function of x for a few successive times $t_1 < t_2 < t_3 \ldots$ and explain the behavior of $c(x,t)$ at the boundaries.

b) To which limiting behavior does the concentration evolve after long times $\lim_{t\to\infty} c(x,t)$?

c) One can think to this problem as that of drift-diffusion in a square-well potential

$$V(x) = \begin{cases} 0 & \text{for } |x| \le a/2 \\ +\infty & \text{for } |x| > a/2 \end{cases}$$

Does the result of point b) matches the equilibrium distribution expected for this potential? Explain!

We consider now a different initial condition. At time $t = 0$ all particles are at the origin, hence $c(x,0) = N\delta(x)$. The general solution of the diffusion equation with this initial condition can be written as an infinite sum of gaussians $g_n(x,t)$ as follows

$$c(x,t) = \sum_{n=-\infty}^{+\infty} g_n(x,t)$$

d) Explain how this solution can be obtained and find the gaussians $g_n(x,t)$.

2 points

Specific heat and fluctuations

Show that in the canonical ensemble the specific heat at constant volume

$$c_V = \left.\frac{\partial E}{\partial T}\right|_{V,N}$$

is related to the fluctuations in the energy as follows:

$$c_V = \frac{\langle E^2\rangle - \langle E\rangle^2}{k_B T^2}$$

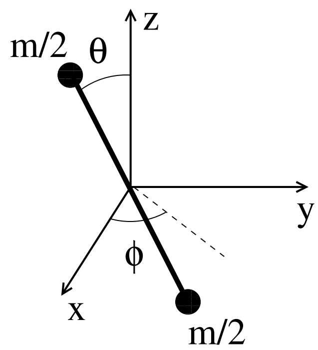

Figure 1:

6 points

Rigid Rotor

We consider a simple model of a gas of N molecules in equilibrium at a temperature T and in a 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 angles θ and ϕ which identify the orientation of the molecule with respect to the cartesian axes (see Fig. 1). 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 $Z_1(V,T)$ the canonical single molecule partition function one needs to integrate over position and momenta of the center of massa and also on $dp_\theta d\theta dp_\phi d\phi$.

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 an show that the result matches that of a).

c) Calculate the pressure of the gas of molecules.

2 points

Van der Waals model

In rescaled units the van der Waals equation of state is

$$\tilde{p} = \frac{8\tilde{T}}{3\tilde{v}-1} - \frac{3}{\tilde{v}^2}$$

so that the critical point corresponds to $\tilde{p} = \tilde{T} = \tilde{v} = 1$. Calculate form the above equation of state the exponent δ describing the variation of p with respect of v along the critical isotherm $T = T_c$.

2 points

Radial distribution function

Draw schematically the radial distribution function $g(r)$ for a Lennard-Jones fluid at low and high particle densities. Discuss in both cases the behavior at small r. At high densities $g(r)$ has some damped oscillations. Explain their origin.