Exam Statistical Mechanics
29 November 2021, 2pm

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

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

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

4 points

Velocity distribution in 2d

We consider a classical system in two dimensions.

a) Write $p(v_x, v_y)$ the velocity distribution of a single particle (v_x and v_y are the components of the velocity vector).

b) Obtain from the previous result $g(v)$ the distribution of the speed $v = \sqrt{v_x^2 + v_y^2}$

c) Calculate the root mean squared speed defined as

$$v_{\mathrm{rms}} = \sqrt{\langle v^2 \rangle}$$

d) Find the probability that a particle has speed $v \geq 2v_{\mathrm{rms}}$.

3 points

Mixture of ideal gases

We consider a mixture of two ideal gases enclosed in a volume V at a temperature T. The first gas is composed by N_a particles with mass m_a and the second gas of N_b particles with mass m_b.

Calculate the total energy of the system $\langle E \rangle$ and the variance of the energy $\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2$.

4 points

Chemical Potential of ideal gas

a) Using the thermodynamic relation

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

calculate $\mu(N, V, T)$ the chemical potential of an ideal gas in the canonical ensemble.

b) Compute $\mu(N, V, T)$ for an ideal gas using the grand canonical ensemble and verify that the result matches that obtained in a).

DIFFUSION

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

GENERAL SOLUTION $c(x,t) = \frac{1}{\sqrt{4\pi D(t+t_0)}} e^{-\frac{x^2}{4D(t+t_0)}}$

CHOOSE t_0 SUCH $4Dt_0 = 2a^2$ $\quad t_0 = \frac{a^2}{2D}$

$$c(x,t) = \frac{1}{\sqrt{2\pi a^2 + 4\pi D t}} e^{-\frac{x^2}{2a^2+4Dt}}$$

VELOCITY DISTRIBUTION 2D

a) $p(v_x, v_y) = \frac{\beta m}{2\pi} e^{-\beta \frac{m}{2}(v_x^2+v_y^2)}$

b) $g(v^*) = \int dv_x dv_y \, \delta\left(v^* - \sqrt{v_x^2+v_y^2}\right) p(v_x, v_y) =$

$$= \int dv \, 2\pi v \, \delta(v^* - v) \frac{\beta m}{2\pi} e^{-\frac{\beta m}{2} v^2} = \beta m v^* e^{-\frac{\beta m v^{*2}}{2}}$$

c) EQUIPARTITION $\frac{m}{2}\langle v_x^2 + v_y^2 \rangle = \cancel{2} \frac{k_B T}{\cancel{2}}$ $\quad \langle v^2 \rangle = \frac{2k_BT}{m}$ $\quad v_{rms} = \sqrt{\frac{2k_BT}{m}}$

d) $$p = \int_{2v_{rms}}^{+\infty} g(v)\,dv = \beta m \int_{\sqrt{\frac{8k_BT}{m}}}^{+\infty} v e^{-\frac{\beta m v^2}{2}} dv = \frac{\beta m}{2} \int_{\frac{8k_BT}{m}}^{+\infty} dv^2 \, e^{-\frac{\beta m v^2}{2}}$$

$$= -e^{-\frac{\beta m v^2}{2}} \Big|_{\frac{8k_BT}{m}}^{+\infty} = e^{-\beta \frac{m}{2} \frac{8}{m\beta}} = e^{-4}$$

MIXTURE OF IDEAL GASES

$$Z = \frac{V^{N_1}}{(\lambda_T^{(1)})^{3N_1} N_1!} \frac{V^{N_2}}{(\lambda_T^{(2)})^{3N_2} N_2!}$$

$$E = -\frac{\partial \log Z}{\partial \beta} = \frac{\partial}{\partial \beta}\left(\log \lambda_T^{(1)\,3N_1} + \log \lambda_T^{(2)\,3N_2}\right)$$

$$= \frac{3}{2}(N_1+N_2) k_B T$$

$$\sigma_E^2 = \frac{\partial^2 \log Z}{\partial \beta^2} = \frac{3}{2}(N_1+N_2) k_B^2 T^2$$

6 points

Two dimensional oscillator

We consider a single harmonic oscillator in two dimensions at temperature T with Hamiltonian

$$H = \frac{p_x^2 + p_y^2}{2m} + \frac{k}{2}\left(x^2 + y^2\right) + \gamma xy$$

$(k, \gamma > 0)$. Different from the usual harmonic oscillator this system is characterized by a quadratic cross-term xy. Note that for stability we require that $k > \gamma$ (otherwise the energy is not bounded from below).

a) Calculate the average total energy $E = \langle H \rangle$ and the average potential energy $\langle \phi \rangle$ from the canonical partition function Z. *(Tip: there are several ways to calculate Z. You can for instance use a linear change of variables $(x, y) \to (s, t)$ of the form $x = as + bt$ and $y = cs + dt$ and choose suitable values for the parameters a, b, c, d. Another possibility is to integrate first in dx, with a suitable shift, and then in dy).*

b) Calculate $\langle \phi \rangle$ from the generalized equipartition theorem and show that your result agrees with what obtained in a).

c) Let us suppose that γ is small so that we can expand the Boltzmann factor $\exp(-\beta\phi(x, y))$ in Taylor series in powers of γ. Show that the total partition function to lowest orders in γ can be written as

$$Z \quad \approx \quad Z_0 \left(1 - \beta\gamma\langle xy\rangle_0 + \frac{\beta^2\gamma^2}{2}\langle x^2 y^2\rangle_0 + \dots\right) \tag{2}$$

where $\langle\rangle_0$ is the average with respect to the above Hamiltonian with $\gamma = 0$ and Z_0 is the partition function of the model with $\gamma = 0$. Work out the calculation of the right hand side of (2) and show that the result matches to lowest order in γ that obtained from the expansion of the full partition function calculated in a).

CHEMICAL POTENTIAL IDEAL GAS

a) CANONICAL $\quad Z = \dfrac{V^N}{\lambda_T^{3N} N!}$

$$F = -k_BT \log Z \overset{\text{STIRLING}}{\approx} -k_BT \log \frac{V^N}{\lambda_T^{3N} N^N e^{-N}}$$

$$= N k_BT \log n\lambda_T^3 - N k_BT \qquad \left(n = \frac{N}{V}\right)$$

$$\mu = \left.\frac{\partial F}{\partial N}\right|_{V,T} = k_BT\left(\log n\lambda_T^3 \cancel{-1}\right) + \cancel{N k_BT}\,\frac{1}{N} = k_BT \log n\lambda_T^3$$

b) GRAND CANONICAL $\quad \Xi = \sum_N e^{\beta\mu N}\dfrac{V^N}{N!\,\lambda_T^{3N}} = \exp\left(\dfrac{e^{\beta\mu} V}{\lambda_T^3}\right)$

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

TWO DIMENSIONAL HARMONIC OSCILLATOR

$$H = \underbrace{\frac{p_x^2+p_y^2}{2m}}_{\text{KIN. EN.}} + \underbrace{\frac{k}{2}(x^2+y^2)+\gamma xy}_{=\phi \ \text{POT. EN.}} \qquad k,\gamma>0 \qquad k>\gamma$$

a) $$Z = \frac{1}{\lambda_T^2}\int dx\,dy\; e^{-\beta\Phi} = \frac{1}{\lambda_T^2}\int dx\; e^{-\beta\frac{k}{2}x^2}\int dy\; e^{-\beta\frac{k}{2}\left[y^2+\frac{2\gamma}{k}xy\right]}$$

$$y^2+\frac{2\gamma}{k}xy = \left(y+\frac{\gamma}{k}x\right)^2 - \frac{\gamma^2}{k^2}x^2, \qquad y+\frac{\gamma}{k}x = y'$$

$$= \frac{1}{\lambda_T^2}\int_{-\infty}^{+\infty} dx\; e^{-\beta\frac{k}{2}\left(1-\frac{\gamma^2}{k^2}\right)x^2}\int_{-\infty}^{+\infty} dy'\; e^{-\beta\frac{k}{2}y'^2}$$

$$= \frac{1}{\lambda_T^2}\sqrt{\frac{2\pi}{\beta k(1-\gamma^2/k^2)}}\sqrt{\frac{2\pi}{\beta k}} = (\dots)\,\underset{\uparrow \text{ KIN. EN.}}{\beta^{-1}}\;\beta^{-1} \leftarrow \text{POT. EN.}$$

$$E = -\frac{\partial \log Z}{\partial\beta} = -\frac{\partial}{\partial\beta}\log\beta^{-2} = 2k_BT$$

b) $$\left\langle x\frac{\partial H}{\partial x}\right\rangle = \langle x(kx+\gamma y)\rangle = k\langle x^2\rangle+\gamma\langle xy\rangle = k_BT$$

$$\left\langle y\frac{\partial H}{\partial y}\right\rangle = \langle y(ky+\gamma x)\rangle = k\langle y^2\rangle+\gamma\langle xy\rangle = k_BT$$

$$\Rightarrow \langle x^2\rangle = \langle y^2\rangle$$

SUM : $$k(\langle x^2\rangle+\langle y^2\rangle)+2\gamma\langle xy\rangle = 2\langle\phi\rangle = 2k_BT \quad\Rightarrow\quad \langle\phi\rangle = k_BT$$

c) $$Z = \frac{1}{\lambda_T^2}\int dx\,dy\; e^{-\beta\frac{k}{2}(x^2+y^2)}\left(1-\beta\gamma xy+\frac{\beta^2\gamma^2}{2}x^2y^2+\dots\right) =$$

$$Z_0 = \frac{1}{\lambda_T^2}\int dx\,dy\; e^{-\beta\frac{k}{2}(x^2+y^2)} = \frac{1}{\lambda_T^2}\frac{2\pi}{\beta k}$$

$$Z = Z_0\frac{\int dx\,dy\; e^{-\beta\frac{k}{2}(x^2+y^2)}\left(1-\beta\gamma xy+\frac{\beta^2\gamma^2}{2}x^2y^2+\dots\right)}{\int dx\,dy\; e^{-\beta\frac{k}{2}(x^2+y^2)}} = Z_0\left(1-\beta\gamma\langle xy\rangle_0+\frac{\beta^2\gamma^2}{2}\langle x^2y^2\rangle_0\right)$$

$$\langle xy\rangle_0 = \langle x\rangle_0\langle y\rangle_0 = 0 \qquad \langle x^2y^2\rangle_0 = \langle x^2\rangle_0\langle y^2\rangle_0 = \left(\frac{k_BT}{k}\right)^2 \qquad \frac{k}{2}\langle x^2\rangle_0 = \frac{k_BT}{2} \quad \text{FROM EQUIPARTITION}$$

$$Z = Z_0\left[1+\frac{\cancel{\beta^2}\gamma^2}{2}\left(\frac{\cancel{k_BT}}{k}\right)^2\right] = Z_0\left(1+\frac{\gamma^2}{2k^2}\right)$$

FROM a) $$Z \simeq \frac{1}{\lambda_T^2}\frac{2\pi}{\beta k}\frac{1}{\sqrt{1-\gamma^2/k^2}} \approx \frac{2\pi}{\lambda_T^2\beta k}\left(1+\frac{\gamma^2}{2k^2}+\dots\right)$$