Problem 1.

Consider a classical ideal gas of molecules that have an electric dipole moment d. Let there be N such molecules in a volume V in a uniform electric field $\vec{E}$ and let the temperature of the gas be T. Neglect rotational and vibrational modes of molecules.

(a) What is the probability that the direction of $\vec{d}$ forms an angle θ with the direction of $\vec{E}$?

(b) Find the average polarization $\vec{P}$ ($\equiv$ dipole moment per unit volume of the gas). Express your result in terms of N, V, d, E and T.

Reminder: the potential energy of a dipole $\vec{d}$ in the external electric field $\vec{E}$ is $U = -\vec{d}\cdot\vec{E}$.

Solution

(a)

The probability density is given by Eq. (2.64) from the lecture notes

$$\rho(q_i, p_i) = \frac{1}{\mathcal{Z}}\, e^{-\beta H(q_i,p_i)} \ ,$$

where the factor $\mathcal{Z}$,

$$\mathcal{Z} = \int \prod_{i=1}^{n} dq_i\, dp_i\, e^{-\beta H(q_i,p_i)} \ ,$$

In our case

$$H \;=\; \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} - \vec{d}_i\cdot\vec{E}\right) \;=\; \sum_{i=1}^{N}\left(\frac{p_i^2}{2m} - dE\cos\theta_i\right)$$

so the probability of a certain molecule to have an angle θ is

$$\rho(\theta) \;=\; \frac{1}{\mathcal{Z}}\int d^3p \int_0^{2\pi} d\phi\ e^{-\beta\frac{p^2}{2m} + \beta dE\cos\theta} \prod_{i=1}^{N-1} dq_i\, dp_i\, e^{-\beta H(q_i,p_i)} \tag{1}$$

Since molecules do not interact, the contribution of all other $N-1$ molecules cancels between the numerator and the denominator of Eq. 1 so we get

$$\rho(\theta) \;=\; \frac{1}{z}\int d^3p \int_0^{2\pi} d\phi\ e^{-\beta\frac{p^2}{2m} + \beta dE\cos\theta} \tag{2}$$

where z is the one-particle partition function

$$z \;=\; \int d^3p \int_0^{2\pi} d\phi \int_0^{\pi} \sin\theta d\theta\ e^{-\beta\frac{p^2}{2m} + \beta dE\cos\theta}$$

Moreover, the integral over momenta and over the azimuthal angle ϕ in Eq. 2 also cancels and we get

$$\rho(\theta) \;=\; \frac{e^{\beta dE\cos\theta}}{\int_0^{\pi}\sin\theta' d\theta'\ e^{\beta dE\cos\theta'}} \;=\; \frac{\beta dE e^{\beta dE\cos\theta}}{e^{\beta dE} - e^{-\beta dE}}$$

$$\langle P\rangle = \frac{\int \sin\theta d\theta\ dE\cos\theta\ e^{\beta dE\cos\theta}}{\int d\cos\theta\ e^{\beta dE\cos\theta}} = \frac{\partial}{\partial\beta}\int \sin\theta d\theta\ e^{\beta dE\cos\theta} = \frac{\partial}{\partial\beta}\ln\left(e^{\beta dE} - e^{-\beta dE}\right)$$

(b)

By symmetry, the direction of the mean dipole moment is collinear to the direction of the electric field. The mean value of the dipole moment for one molecule is given by Eq. (2.8) from the lecture notes which for our case yields

$$\begin{aligned}\bar{d} &= \int_0^\pi \sin\theta d\theta\ d\cos\theta\ \rho(\theta) = \int_0^\pi \sin\theta d\theta\ d\cos\theta \frac{\beta dE e^{\beta dE\cos\theta}}{e^{\beta dE} - e^{-\beta dE}} \\ &= \frac{\beta d}{e^{\beta dE} - e^{-\beta dE}}\frac{\partial}{\partial\beta}\int_0^\pi \sin\theta d\theta\ e^{\beta dE\cos\theta} = \frac{\beta d}{e^{\beta dE} - e^{-\beta dE}}\frac{\partial}{\partial\beta}\frac{1}{\beta dE}(e^{\beta dE} - e^{-\beta dE}) \\ &= d\Big(\frac{1}{\tanh(\beta dE)} - \frac{1}{\beta dE}\Big)\end{aligned}$$

For N molecules in a volume V we get

$$P(E) = \frac{N}{V}d\Big(\frac{1}{\tanh(\beta dE)} - \frac{1}{\beta dE}\Big) = \frac{N}{V}d\Big(\frac{1}{\tanh\left(\frac{dE}{k_BT}\right)} - \frac{k_BT}{dE}\Big)$$

A quick check: as $E \to 0$ polarization is proportional to E

$$P(E) = \frac{N}{V}d\Big(\frac{1}{\tanh(\beta dE)} - \frac{1}{\beta dE}\Big) \simeq \frac{Nd^2}{3Vk_BT}E$$

Problem 2.

(a) For a classical harmonic oscillator with Hamiltonian $H = \frac{p^2}{2m} + \frac{m\omega^2x^2}{2}$ find the average $\overline{x^2}$ at temperature T.

(b) Same problem in quantum statistics: for a harmonic oscillator with Hamiltonian $\hat{H} = \frac{\hat{p}^2}{2m} + \frac{m\omega^2\hat{x}^2}{2}$ find the average $\langle\hat{x}^2\rangle$ at temperature T and show that at $k_BT \gg \hbar\omega$ the quantum result agrees with the one obtained in part (a).

Solution

(a)

By definition,

$$\overline{x^2} = \frac{\int dpdx\ x^2 e^{-\beta\left(\frac{p^2}{2m}+\frac{m\omega^2x^2}{2}\right)}}{\int dpdx\ e^{-\beta\left(\frac{p^2}{2m}+\frac{m\omega^2x^2}{2}\right)}} = \frac{\int dx\ x^2 e^{-\beta\frac{m\omega^2x^2}{2}}}{\int dx\ e^{-\beta\frac{m\omega^2x^2}{2}}} = \frac{k_BT}{m\omega^2} \tag{3}$$

(b)

In quantum statistics

$$\langle\hat{x}^2\rangle = \frac{\mathrm{Tr}\ \hat{x}^2 e^{-\beta\left(\frac{\hat{p}^2}{2m}+\frac{m\omega^2\hat{x}^2}{2}\right)}}{\mathrm{Tr}\ e^{-\beta\left(\frac{\hat{p}^2}{2m}+\frac{m\omega^2\hat{x}^2}{2}\right)}} = \frac{1}{m\omega\beta}\frac{\partial}{\partial\omega}\ln\Big(\mathrm{Tr}\ e^{-\beta\left(\frac{\hat{p}^2}{2m}+\frac{m\omega^2\hat{x}^2}{2}\right)}\Big) = -\frac{1}{m\omega\beta}\frac{\partial}{\partial\omega}\ln z$$

where

$$\ln z = -\frac{\beta\hbar\omega}{2} - \ln(1 - e^{-\beta\hbar\omega})$$

for a harmonic oscillator (see Eq. (7.40) from the lecture notes). We get

$$\langle \hat{x}^2 \rangle = -\frac{1}{m\omega\beta}\frac{\partial}{\partial\omega}\ln z = \frac{\hbar}{m\omega}\Big(\frac{1}{2} + \frac{e^{-\beta\hbar\omega}}{1 - e^{-\beta\hbar\omega}}\Big) = \frac{\hbar}{m\omega}\Big(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\Big)$$

As $T \to \infty$

$$\langle \hat{x}^2 \rangle = \frac{\hbar}{m\omega}\Big(\frac{1}{2} + \frac{1}{e^{\frac{\hbar\omega}{k_B T}} - 1}\Big) \stackrel{T\to\infty}{\to} \frac{k_B T}{m\omega^2} + \frac{\hbar}{2m\omega} \simeq \frac{k_B T}{m\omega^2}$$

which is the classical result (3).

Problem 3.

A particle in thermal equilibrium with the reservoir at temperature T can be only in two states: ground state with energy $E_0 = 0$ and excited state with energy E_1. The ground state is non-degenerate and the degeneracy of the excited state is 2. Find the probability that the particle has energy E_0, probability that the particle has energy E_1, and find the mean energy.

$$P(E_0) = \frac{1}{1 + 2e^{-\beta E_1}}, \quad P(E_1) = \frac{2e^{-\beta E_1}}{1 + 2e^{-\beta E_1}}, \quad \overline{E} = \frac{2E_1 e^{-\beta E_1}}{1 + 2e^{-\beta E_1}}$$

Solution

First, the partition function has the form

$$\mathcal{Z} = \mathrm{Tr}(e^{-\beta\hat{H}}) = \langle 0|e^{-\beta\hat{H}}|0\rangle + \langle 1a|e^{-\beta\hat{H}}|1a\rangle + \langle 1b|e^{-\beta\hat{H}}|1b\rangle = e^{-\beta E_0} + 2e^{-\beta E_1}$$

where $|1a\rangle$ and $|1b\rangle$ are the two degenerate excited states. The density operator is

$$\hat{\rho} = \frac{1}{\mathcal{Z}}e^{-\beta\hat{H}} = \frac{1}{e^{-\beta E_0} + 2e^{-\beta E_1}}e^{-\beta\hat{H}}$$

A general formula for the probability of the particle to be in a state $|s\rangle$ is $\langle s|\hat{\rho}|s\rangle$ so in our case

$$P(0) = \langle 0|\hat{\rho}|0\rangle = \frac{1}{\mathcal{Z}}e^{-\beta E_0}, \quad P(1a) = \langle 1a|\hat{\rho}|1a\rangle = \frac{1}{\mathcal{Z}}e^{-\beta E_1}, \quad P(1b) = \langle 1b|\hat{\rho}|1b\rangle = \frac{1}{\mathcal{Z}}e^{-\beta E_1}$$

and therefore

$$P(E_0) = \frac{e^{-\beta E_0}}{e^{-\beta E_0} + 2e^{-\beta E_1}} \quad \text{and} \quad P(E_1) = \frac{2e^{-\beta E_1}}{e^{-\beta E_0} + 2e^{-\beta E_1}}$$

The mean energy is (see Eq. (6.78) from the lecture notes)

$$\overline{E} \;=\; \mathrm{Tr}(\hat{H}\hat{\rho}) \;=\; \frac{1}{\mathcal{Z}}\mathrm{Tr}\hat{H}e^{-\beta H} \;=\; E_0P(E_0) + E_1P(E_1) \;=\; \frac{E_0e^{-\beta E_0} + 2E_1e^{-\beta E_1}}{e^{-\beta E_0} + 2e^{-\beta E_1}}$$

Check (see Eq. (6.93) from lecture notes):

$$\overline{E} \;=\; -\frac{\partial}{\partial\beta}\ln\mathcal{Z} \;=\; -\frac{\partial}{\partial\beta}\ln\left(e^{-\beta E_0} + 2e^{-\beta E_1}\right) \;=\; \frac{E_0e^{-\beta E_0} + 2E_1e^{-\beta E_1}}{e^{-\beta E_0} + 2e^{-\beta E_1}}$$

Finally, the heat capacity for N_A particles is

$$c_V \;=\; \frac{\partial}{\partial T}N_A\overline{E} \;=\; -N_Ak_B\beta^2\frac{\partial}{\partial\beta}\overline{E} \;=\; 2R(\frac{E_1 - E_0}{k_BT})^2\frac{e^{-\frac{E_0+E_1}{k_BT}}}{\left(e^{-\beta E_0} + 2e^{-\beta E_1}\right)^2}$$