Ex4016: Polar adsorption of particles to a surface

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The problem:

Consider an M site system in an equilibrium with gas of particles that have mass m. The chemical potential of the gas is μ and its temperature is T. A particle can bind to a site. Each site can absorb at most one atom. The binding energy is ε, and the length of the bonds is a. In such state it behaves as a rotor that has moment of inertia $I = ma^2$, and a dipole moment qa. The polarization can be in any direction away from the surface (2π staradians).

Tip: The kinetic part in a rotor Hamiltonian is

$$\frac{1}{2I}\left[p_\theta^2 + \frac{p_\varphi^2}{\sin^2(\theta)}\right]$$

(1) Calculate the partition function $Z_\perp(\beta, f)$ for an occupied site, assuming electric field f perpendicular to the surface.

(2) Calculate the partition function $Z_\parallel(\beta, f)$ for an occupied site, assuming electric field f parallel to the surface.

(3) Express the M site grand partition function $\mathcal{Z}(\beta, \mu, f)$ in terms of Z. Additionally, write an explicit expression for zero field.

(4) Express the average number N of adsorbed particles in terms of Z. Additionally, write an explicit expression for zero field.

(5) Find a leading order expression for the average polarization D/N for weak perpendicular f.

(6) Find a leading order expression for the average polarization D/N for weak parallel f.

(*) Tip: one can use a shortcut in the calculation of Z, bypassing the integration over the momentum variables.

The solution:

(1) The Hamiltonian is:

$$\mathcal{H} = \frac{1}{2I}\left[p_\theta^2 + \frac{p_\varphi^2}{\sin^2(\theta)}\right] - \varepsilon a \cos\theta \qquad \varepsilon \equiv fq$$

For the Dipole:

$$Z_1 = \iint \frac{d\theta dP_\theta}{2\pi} \iint \frac{d\varphi dP_\varphi}{2\pi} e^{-\beta H} = \iint \sqrt{\frac{2\pi I}{\beta}} \sqrt{\frac{2\pi I \sin^2\theta}{\beta}} e^{\beta\varepsilon a\cos\theta} \frac{d\theta d\varphi}{(2\pi)^2} = \frac{I}{2\pi\beta} \iint \sin\theta e^{\beta\varepsilon a\cos\theta} d\theta d\varphi$$

$$Z_1^\perp = \frac{I}{2\pi\beta} \int_0^{2\pi} d\varphi \int_0^{\frac{\pi}{2}} e^{\beta\varepsilon a\cos\theta} \sin\theta d\theta = \frac{I}{\beta} \cdot \frac{e^{\beta\varepsilon a} - 1}{\beta\varepsilon a}$$

(2) For the parallel electric field:

$$Z_1^{\parallel} = \frac{I}{2\pi\beta}\int_0^{\pi} d\varphi \int_0^{\pi} e^{\beta\varepsilon a\cos\theta} \sin\theta d\theta = \frac{I}{\beta}\cdot\frac{\sinh\beta\varepsilon a}{\beta\varepsilon a}$$

(3) Partition function of M sites in a grand canonical formalism

$$\mathcal{Z}(\beta,\mu,\varepsilon) = [1 + Z_1(\beta,\varepsilon)e^{\beta\mu}]^M$$

With zero field:

$$\mathcal{Z}(\beta,\mu,\varepsilon) = [1 + \frac{I}{\beta}\cdot e^{\beta\mu}]^M$$

(4) Number of particles can be obtained with:

$$N = \frac{1}{\beta}\cdot\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \frac{M}{1+\frac{1}{Z_1}e^{-\beta\mu}}$$

With Zero Field:

$$N = \frac{1}{\beta}\cdot\frac{\partial\ln\mathcal{Z}}{\partial\mu} = \frac{M}{1+\frac{\beta}{I}e^{-\beta\mu}}$$

(5) Polarization can be obtained by

$$D = \frac{1}{\beta}\cdot\frac{\partial\ln\mathcal{Z}}{\partial\varepsilon} = \frac{N}{\beta}\cdot\frac{\partial\ln Z_1}{\partial\varepsilon}$$

For weak perpendicular field $\varepsilon^{\perp} << 1,\ \varepsilon^{\parallel} = 0$:

$$Z_1^{\perp} = \frac{I}{\beta}\cdot\frac{e^{\beta\varepsilon a}-1}{\beta\varepsilon a} \propto 1 + \frac{1}{2}\beta\varepsilon a$$

And the polarisation is:

$$\frac{D(\varepsilon)}{N} = \frac{1}{2}a$$

(6) For weak parallel field $\varepsilon^{\perp} = 0,\ \varepsilon^{\parallel} << 1$:

$$Z_1^{\parallel} = \frac{I}{\beta}\cdot\frac{\sinh\beta\varepsilon a}{\beta\varepsilon a} \propto 1 + \frac{1}{6}(\beta\varepsilon a)^2$$

And the polarisation is:

$$\frac{D(\varepsilon)}{N} = \frac{1}{3}\cdot\frac{a^2}{T}\varepsilon$$