E2173: Polarization of classical polar molecule

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The problem:

Find the polarization $\tilde{P}(\xi)$ and the electric susceptibility χ for gas of N classical molecules with dipole moment μ, The system's temperature is T.

The solution:

This problem has been approached in different branches of Physics , let's discuss it in the way of Statistical Mechanics .

Suppose, each polar molecule of the cluster having Mass and Moment of Inertia m and I respectively is feeling an external Electric field E.

we can write down the Lagrangian for each molecule in (r, θ, ϕ) co-ordinate

$$L(x, y, z, \theta, \phi) = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) + \frac{1}{2}I(\dot{\theta}^2 + \sin^2\theta\dot{\phi}^2)$$

next comes the Energy consideration :

The conjugate momenta as we know are $p_j = \frac{\partial L}{\partial \dot{q}_j}$ where $j = r, \theta, \phi$

furthar if we notice that we can write the Hamiltonian from Lagrangian with those conjugate momenta as ,

$$H_0 = \Sigma p_j \dot{q}_j - L(r, \theta, \phi)$$

With furthar simplification it yields

$$H_0 = \frac{1}{2m}p_r^2 + \frac{1}{2I}p_\theta^2 + \frac{p_\phi^2}{2I\sin^2\theta}$$

or more specifically

$$H_0 = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I}p_\theta^2 + \frac{p_\phi^2}{2I\sin^2\theta}$$

perturbation on the molecule due to the presence of external electric field

$$H_{perturb} = -\mathcal{E}\mu\cos\theta$$

henceforth the modified Hamiltonian reads

$$H_1 = H_0 + H_{perturb} = \frac{1}{2m}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I}p_\theta^2 + \frac{p_\phi^2}{2Isin^2\theta} - \mathcal{E}\mu\cos\theta$$

we are now ready to write the single molecule Partition Function :

$$Z_1 = \int .. \int \frac{dxdydzdp_xdp_ydp_z}{(2\pi)^3} \int \int \frac{d\theta dp_\theta}{2\pi} \int \int \frac{d\phi dp_\phi}{2\pi} e^{-\beta H_1}$$

now, Writing H_1 explicitly , we 've

$$Z_1 = \int .. \int \frac{dxdydzdp_xdp_ydp_z}{(2\pi)^3} e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)} \int \int \frac{d\theta dp_\theta}{2\pi} e^{-\frac{\beta}{2I}p_\theta^2} e^{\beta \mathcal{E} \mu \cos\theta} \int \int \frac{d\phi dp_\phi}{2\pi} e^{-\beta \frac{p_\phi^2}{2I\sin^2\theta}} = I_1.I_2.I_3$$

the first Integral is as usual

$$I_1 = \int .. \int \frac{dxdydzdp_xdp_ydp_z}{(2\pi)^3} e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)} = V(\frac{m}{2\pi\beta})^{3/2}$$

the second integral gives

$$I_2 = \int \int \frac{d\theta dp_\theta}{2\pi} e^{-\frac{\beta}{2I}p_\theta^2} e^{\beta \mathcal{E} \mu \cos\theta} = (\frac{2\pi I}{\beta})^{1/2} \int \frac{d\theta}{2\pi} e^{\beta \mathcal{E} \mu \cos\theta}$$

and the third integral yields

$$I_3 = \int \int \frac{d\phi dp_\phi}{2\pi} e^{-\beta \frac{p_\phi^2}{2I\sin^2\theta}} = \int dp_\phi e^{-\beta \frac{p_\phi^2}{2I\sin^2\theta}} = (\frac{2\pi I \sin^2\theta}{\beta})^{1/2}$$

hence , the single molecule partition function reads

$$Z_1 = I_1.I_2.I_3 = V(\frac{m}{2\pi\beta})^{3/2} \frac{I}{\beta} \int \sin\theta d\theta e^{\beta \mathcal{E} \mu \cos\theta} = V(\frac{m}{2\pi\beta})^{3/2} \frac{2I}{\beta} \frac{\sinh \beta\mu\mathcal{E}}{\beta\mu\mathcal{E}}$$

now Gibbs Prescription is to be followed , i.e, For N molecules the Partition function is

$$Z_N = \frac{1}{N!} Z_1^N$$

So that

$$Z_N = \frac{1}{N!} V^N (\frac{m}{2\pi\beta})^{3N/2} (\frac{2I}{\beta})^N (\frac{\sinh \beta\mu\mathcal{E}}{\beta\mu E})^N$$

since we've learned Polarisation and Electric fields are conjugate variables , so we can write :

$$\widetilde{P} = \frac{1}{\beta} \frac{\partial ln Z_N}{\partial \mathcal{E}}$$

hence in this particular problem , it becomes :

$$\widetilde{P} = N\mu[\coth(\beta\mu\mathcal{E}) - \frac{1}{\beta\mu\mathcal{E}}]$$

Let's define a function as , $\mathcal{L}(u) = \coth(u) - \frac{1}{u}$

If we expand the function $\mathcal{L}(u)$ in the following Taylor expansion series :

$$\mathcal{L}(u) = \coth(u) - \frac{1}{u} = \frac{e^u + e^{-u}}{e^u - e^{-u}} - \frac{1}{u}$$

$$= \frac{(1 + u + \frac{1}{2}u^2 + \frac{1}{6}u^3 + ...) + (1 - u + \frac{1}{2}u^2 - \frac{1}{6}u^3 + ...)}{(1 + u + \frac{1}{2}u^2 + \frac{1}{6}u^3 + ...) - (1 - u + \frac{1}{2}u^2 - \frac{1}{6}u^3 + ...)} - \frac{1}{u}$$

$$= \frac{1 + \frac{1}{2}u^2 + \frac{1}{24}u^4 + \frac{1}{720}u^6 + ...}{u + \frac{1}{6}u^3 + \frac{1}{120}u^5 + ...} - \frac{1}{u}$$

$$= \frac{\frac{1}{3}u^3 + \frac{1}{30}u^5 + \frac{1}{840}u^7 + ...}{u(u + \frac{1}{6}u^3 + \frac{1}{120}u^5 + ...)}$$

since , $u = \beta\mu\mathcal{E}$ is usually very small , so in this limit $u \to 0$

$$\mathcal{L}(u) = u/3$$

so that it yields , $\widetilde{P} \to \frac{1}{3}N\beta\mu^2\mathcal{E}$ and hence ...

Susceptibility, $\chi = \frac{N}{3V}\beta\mu^2$