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Relation between fluctuation of total electric dipole moment and electric susceptibility

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$V = L_x L_y L_z a_0^3$: volume of the supercell

$\mathcal{E}$: external electric field

$\mathbf{p} = \sum_{\mathbf{R}} Z^* \mathbf{u}(\mathbf{R})$: **total** electric dipole moment in the supercell

$\mathbf{p} = (p_x, p_y, p_z)$

$\mathcal{H}(s) = \mathcal{H}_0(s) - \mathcal{E}\cdot\mathbf{p}(s)$: Hamiltonian of the supercell, s is a state

Thermal average (here "average" means average-in-time) of p_α and $p_\alpha p_\gamma$ ($\alpha, \gamma = x, y, z$) can be calculated with partition function $Z(\beta, \mathcal{E}) = \sum_s e^{-\beta\mathcal{H}(s)}$, where $\beta = 1/k_B T$, as

$$\langle p_\alpha \rangle = \frac{1}{Z(\beta,\mathcal{E})} \sum_s e^{-\beta[\mathcal{H}_0(s) - \mathcal{E}\cdot\mathbf{p}(s)]} p_\alpha(s) = \frac{1}{\beta} \frac{\partial \log Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\alpha}$$

$$\langle p_\alpha p_\gamma \rangle = \frac{1}{Z(\beta,\mathcal{E})} \sum_s e^{-\beta[\mathcal{H}_0(s) - \mathcal{E}\cdot\mathbf{p}(s)]} p_\alpha(s) p_\gamma(s) = \frac{1}{\beta^2} \frac{1}{Z(\beta,\mathcal{E})} \frac{\partial^2 Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\gamma}$$

Now, fluctuation can be calculated as

$$\langle p_\alpha - \langle p_\alpha \rangle \rangle \langle p_\gamma - \langle p_\gamma \rangle \rangle = \langle p_\alpha p_\gamma \rangle - \langle p_\alpha \rangle \langle p_\gamma \rangle$$

$$= \frac{1}{\beta^2} \frac{1}{Z(\beta,\mathcal{E})} \frac{\partial^2 Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\gamma} - \frac{1}{\beta^2} \frac{\partial \log Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\alpha} \frac{\partial \log Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\gamma}$$

$$= \frac{1}{\beta^2} \frac{\partial^2 \log Z(\beta,\mathcal{E})}{\partial \mathcal{E}_\alpha \partial \mathcal{E}_\gamma} = \frac{1}{\beta} \frac{\partial \langle p_\alpha \rangle}{\partial \mathcal{E}_\gamma}$$

Here, electric susceptibility per unit volume is,

in $\boxed{\text{CGS}}$

$$\chi_{\alpha\gamma} = \frac{4\pi}{V} \frac{\partial \langle p_\alpha \rangle}{\partial \mathcal{E}_\gamma} = 4\pi \frac{\beta}{V} \left(\langle p_\alpha p_\gamma \rangle - \langle p_\alpha \rangle \langle p_\gamma \rangle \right) = \frac{4\pi}{V k_B T} \left(\langle p_\alpha p_\gamma \rangle - \langle p_\alpha \rangle \langle p_\gamma \rangle \right)$$

in $\boxed{\text{SI}}$

relative susceptibility (no dimension)

$$\chi_{\alpha\gamma} = \frac{1}{\epsilon_0 V k_B T} \left(\langle p_\alpha p_\gamma \rangle - \langle p_\alpha \rangle \langle p_\gamma \rangle \right)$$

ϵ_0: $\frac{F}{m} = \frac{C^2}{J\,m}$; V: m^3; $k_B T$: J; $\left(\langle p_\alpha p_\gamma \rangle - \langle p_\alpha \rangle \langle p_\gamma \rangle \right)$: $(C\,m)^2$