Homework 5. Problem 2 (Plischke 2.4) 7. Nov. 2017

The energy (neglecting translation as it does not couple to rotation)

is:

$$H = \frac{1}{2} I \underbrace{\left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta \right)}_{\text{kinetic energy of rotation}} - \mu E \cos\theta$$

simple dipolar interaction with the applied field (along z).

The question is formulated in terms of canonical momenta.

If $\mathcal{L}$ is the Lagrangian $\mathcal{L} = \mathcal{L}(q_i, p_i, t)$, canonically conjugate variables (Q_i, P_i) are introduced by the transformation:

$$q_i \to Q_i$$
$$P_i = \frac{\partial \mathcal{L}}{\partial \dot{Q}_i}$$

In this case, the Jacobian of the transformation is 1:

$$\int d\vec{q}\, d\vec{p} = \int d\vec{Q}\, d\vec{P}$$

In our case, the kinetic energy $\mathcal{L}_K = \frac{1}{2} I \left(\dot{\theta}^2 + \dot{\phi}^2 \sin^2\theta \right)$. The interaction term does not depend on the velocity. Hence: in polar coordinates:

$$P_\theta = \frac{\partial \mathcal{L}_K}{\partial \dot{\theta}} = \frac{1}{\cancel{2}} \cancel{2} I \dot{\theta} = I \dot{\theta}$$

$$P_\varphi = \frac{\partial \mathcal{L}_K}{\partial \dot{\varphi}} = \frac{1}{\cancel{2}} I \sin^2\theta\, \cancel{2} \dot{\phi} = I \sin^2\theta\, \dot{\phi}$$

In terms of the canonically conjugate momenta:

$$H = \frac{1}{2} I \left(\left(\frac{P_\theta}{I} \right)^2 + \left(\frac{P_\varphi}{I \sin^2\theta} \right)^2 \sin^2\theta \right) - \mu E \cos\theta$$

$$= \frac{P_\theta^2}{2I} + \frac{P_\varphi^2}{2I \sin^2\theta} - \mu E \cos\theta$$

The partition function is (single particle), in canonical coordinates:

$$Z = \int \frac{d\theta\, dP_\theta\, d\varphi\, dP_\varphi}{h^2} e^{-\beta H} = \frac{1}{h^2} \int_0^\pi d\theta \int_0^{2\pi} d\varphi \int_{-\infty}^{\infty} dP_\theta \int_{-\infty}^{\infty} dP_\varphi\, e^{-\beta \left[\frac{P_\theta^2}{2I} + \frac{P_\varphi^2}{2I \sin^2\theta} - \mu \right.}$$

The Gaussian integral : $\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}$ 7-Nov-2017

Hence:

$$Z = \cancel{\frac{1}{h^2} 2\pi / 2\pi}\ \frac{1}{h^2} 2\pi \int_0^{\pi} \sqrt{\frac{2\pi I}{\beta}} \sqrt{\frac{2\pi I \sin^2\theta}{\beta}} \oint_0^{\pi} d\theta\, e^{\beta\mu E\cos\theta}$$

$$Z = \frac{4\pi^2 I}{h^2\beta} \int_0^{\pi} d\theta \sin\theta\, e^{\beta\mu E\cos\theta}$$

Call $x = \beta\mu E\cos\theta$

$dx = -\beta\mu E \sin\theta\, d\theta$

$$\rightarrow Z = \frac{4\pi^2 I}{h^2\beta} \int_{\beta\mu E}^{-\beta\mu E} \left(- \frac{dx}{\beta\mu E \cancel{\sin\theta}} \right) \cancel{\sin\theta}\, e^x =$$

$$= \frac{4\pi^2 I}{h^2\beta^2\mu E} \int_{-\beta\mu E}^{\beta\mu E} dx\, e^x = \frac{4\pi^2 I}{h^2\beta^2\mu E} \left(e^{\beta\mu E} - e^{-\beta\mu E} \right) \rightarrow$$

$$\boxed{Z = \frac{8\pi^2 I}{h^2\beta^2\mu E} \sinh(\beta\mu E)} = \boxed{\frac{2I}{\hbar^2\beta^2\mu E} \sinh(\beta\mu E)}$$

b) Polarization is defined.

$$P = \frac{N}{V} \langle \mu\cos\theta \rangle$$

Given that $Z = \int \frac{d\theta\, dp_\theta\, d\varphi\, dp_\varphi}{h^2} e^{-\beta K} e^{\beta\mu E\cos\theta}$

$$= \cancel{\int \frac{d\theta\, dp_\theta\, d\varphi\, dp_\varphi}{h^2} e^{-\beta K}}$$

$$P = \frac{N}{V} \frac{1}{Z h^2} \int d\theta\, dp_\theta\, d\varphi\, dp_\varphi\, (\mu\cos\theta)\, e^{-\beta K} e^{\beta\mu E\cos\theta}$$

$$= \frac{N}{V h^2} \frac{1}{Z} \frac{\partial}{\partial \beta E} \int d\theta\, dp_\theta\, d\varphi\, dp_\varphi\, e^{-\beta K} e^{\beta\mu E\cos Z} = \frac{N}{VZ} \frac{\partial Z}{\partial(\beta E)} = \boxed{\frac{N}{V} \frac{\partial \ln Z}{\partial(\beta E)} = P}$$

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c)
$$P = \frac{N k_B T}{V} \frac{\partial}{\partial E} \ln\left[\frac{2I}{\hbar^2 \beta^2 \mu E} \sinh(\beta\mu E)\right] =$$

$$= \frac{N k_B T}{V} \frac{\partial}{\partial E} \ln\left(\frac{1}{E} \sinh(\beta\mu E)\right) = \frac{N k_B T}{V}\left(-\frac{1}{E} + \frac{\partial}{\partial E} \sinh(\beta\mu E)\right)$$

$$= \frac{N k_B T}{V}\left[-\frac{1}{E} + \frac{\cosh(\beta\mu E)\beta\mu}{\sinh(\beta\mu E)}\right] = \boxed{\frac{N}{V}\left[\mu \coth(\beta\mu E) - \frac{k_B T}{E}\right] = P}$$

d) Now:

$$\epsilon E = \epsilon_0 E + P = \epsilon_0 E + \frac{N}{V}\left[\mu \coth(\beta\mu E) - \frac{k_B T}{E}\right]$$

For small field:

$$\coth x = 1/x + x/3 + \cdots$$

$$\Rightarrow \epsilon E \simeq \epsilon_0 E + \frac{N}{V}\left[\cancel{\mu \frac{1}{\beta\mu E}} + \frac{1}{3}\beta\mu E - \cancel{\frac{k_B T}{E}}\right] =$$

$$= \left(\epsilon_0 + \frac{N}{V}\frac{1}{3}\beta\mu\right) E \quad \Rightarrow \boxed{\epsilon = \epsilon_0 + \frac{N}{V}\frac{1}{3}\beta\mu}$$