1 Thermodynamics

1.1 Problem 2

Since the gas is dilute and non-interacting, we can say it's ideal.

(a) The polarization density $\boldsymbol{P}$ is the dipole moment per unit volume. We know that the energy of interaction of a dipole with an external electric field is:

$$U = -\boldsymbol{\mu} \cdot \boldsymbol{E} = -\mu E cos\theta$$

where θ is the angle between $\boldsymbol{E}$ and $\boldsymbol{\mu}$. We need to write the total energy, which will be the sum of this and the usual ideal gas energy (for each particle):

$$U = U_{ideal}(n) - \mu E cos\theta$$

where n somehow numbers the ideal gas states. We need to write the partition function:

$$Z_1 = \sum_n \int_0^{2\pi} \int_0^{\pi} e^{(\mu E cos\theta - U_{ideal}(n))/kT} sin\theta \, d\theta d\phi$$

$$Z_1 = \sum_n \int_0^{2\pi} \int_0^{\pi} e^{\mu E cos\theta/kT} e^{-U_{ideal}(n)/kT} sin\theta \, d\theta d\phi$$

The complete expression for U_{ideal} is not given in the problem. It's a little tricky to derive it because of the need to find to perpendicular components of angular momentum to write. M06T.2 gives the Hamiltonian, so I don't bother deriving it (it seems easy enough to remember or bullshit):

$$H = \frac{1}{2M}(p_x^2 + p_y^2 + p_z^2) + \frac{1}{2I}p_\theta^2 + \frac{1}{2I sin^2\theta} p_\phi^2 - \mu E cos\theta$$

All the variables are continuous, so we need to convert the sum into an integral:

$$Z_1 = \int_0^{2\pi} \int_0^{\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{allphasespace} e^{-H/kT} \frac{1}{(2\pi\hbar)^3} \, dx dy dz dp_x dp_y dp_z \frac{1}{(2\pi\hbar)^2 sin\theta} \, dp_\theta dp_\phi sin\theta \, d\theta d\phi$$

The $sin\theta$'s accompanying the momenta and coordinates of the rotation are because of the spherical coordinates choice. The numerator $sin\theta$ is well known. The one in the denominator comes about because if you were to write the integral in Cartesian coordinates and then convert to spherical ones, the phase space volume should remain invariant. The integral over coordinate variables just gives the volume, V. The integral over ϕ gives just 2π because there is no dependence on this parameter. And the five momentum integrals are simple Gaussian integrals. After putting all this together, we get:

$$Z_1 = \frac{(2\pi kT)^{5/2} M^{3/2} I 2\pi V}{(2\pi\hbar)^5} \int_0^{\pi} sin\theta e^{\mu E cos\theta/kT} \, d\theta$$

After changing coordinates to $x = cos\theta$, you can compute this integral very easily and obtain:

$$Z_1 = \frac{(kT)^{7/2} M^{3/2} I V}{(2\pi)^{3/2} \hbar^5 \mu E} 2 sinh(\mu E/kT)$$

This gives the free energy of each particle, and since the particles are distinguishable, we can get the total free energy by multiplying by the total number of particles:

$$F_N = -NkTln[\frac{2(kT)^{7/2}M^{3/2}IV}{(2\pi)^{3/2}\hbar^5\mu E}sinh(\mu E/kT)]$$

You might be bothered by the fact that N and V are not given in the problem, but we are not asked for Z_1 and F_N, so we won't bother about that.

(a) Note that, for each particle, the average dipole moment in the direction perpendicular to $\boldsymbol{E}$ should be 0, because there is no preferred direction in that plane. So we just want the average dipole moment in the direction parallel to the field. For that, we need to average $cos\theta$. But then we can use a famous trick:

$$< cos\theta >= \frac{1}{Z_1}\frac{kT}{E}\frac{\partial Z_1}{\partial \mu} = \frac{kT}{E}\frac{\partial lnZ_1}{\partial \mu}$$

$$< cos\theta >= coth(\frac{\mu E}{kT}) - \frac{kT}{\mu E}$$

$$< \boldsymbol{P} >= \mu n[coth(\frac{\mu E}{kT}) - \frac{kT}{\mu E}]\hat{E} \quad (1)$$

(b)

$$\epsilon\epsilon_0\boldsymbol{E} = \epsilon_0\boldsymbol{E} + \boldsymbol{P}$$

Here, since the average polarization is in the direction of $\boldsymbol{E}$, we can replace all vectors by their norms, and divide through by $\epsilon_0 E$. Then,

$$\epsilon = 1 + \frac{P}{\epsilon_0 E}$$

$$\epsilon = 1 + \frac{\mu n}{\epsilon_0 E}[coth(\frac{\mu E}{kT}) - \frac{kT}{\mu E}] \quad (2)$$

In the low-temperature limit, we can make the approximation of small angle to second order and obtain:

$$\epsilon \approx 1 + \frac{\mu^2 n}{2\epsilon_0 kT}$$