Gibbs Distribution

Test 2

Stat Physics

(Dated: 02-26-2008)

1. N diatomic molecules are stuck to the metal surface of cubic crystal symmetry (square on the surface). Each molecule can either lie flat on the surface, in which case it will be aligned to one of two directions, x and y, or it can stand up along z direction. The energy cost of standing up is $\varepsilon > 0$, while there is no energy cost associated with lying flat on the surface. The temperature of the system is T. Find the following quantities and investigate their behavior in the limits of low and high temperatures:

   (a) The probabilities for a molecule to be standing up and to be laying flat;

   (b) Entropy;

   (c) Internal Energy;.

   (d) Specific Heat.

   Magnetic field is now applied perpendicular to the surface (along z). Assuming that the molecules have magnetic moments $\mathbf{m}$, whose (Zeeman) energy in the field is $\mathbf{m} \cdot \mathbf{H}$, recalculate the probabilities of standing up and laying flat in the limits $mH >> \varepsilon$ and investigate the limits of high and low temperature.

   (Bonus question) Consider now the "zero-field limit," $mH << \varepsilon, T$. Calculate the magnetic correction to the free energy F and the magnetic susceptibility, $\chi = -\left(\partial^2 F/\partial H^2\right)_{H=0}$ and investigate the latter at high and low temperatures.

Solution

The following is per molecule.

(a) Partition function

$$Z = 2 + \exp\left(-\varepsilon/T\right)$$

Probabilities

$$p_d = \frac{2}{2 + \exp\left(-\varepsilon/T\right)} \rightarrow \begin{array}{c} 2/3\left[1 + \varepsilon/3T\right], \quad T >> \varepsilon \\ 1 - \exp\left(-\varepsilon/T\right)/2, \ T << \varepsilon \end{array}$$

$$p_u = \frac{\exp\left(-\varepsilon/T\right)}{2 + \exp\left(-\varepsilon/T\right)} \rightarrow \begin{array}{c} 1/3\left[1 - 2\varepsilon/3T\right], \ T >> \varepsilon \\ \exp\left(-\varepsilon/T\right)/2, \quad T << \varepsilon \end{array}$$

With magnetic field

$$Z = 4 + \exp\left[\left(mH - \varepsilon\right)/T\right] + \exp\left[\left(-mH - \varepsilon\right)/T\right]$$
$$= 4 + \exp\left(-\varepsilon/T\right)\left[\exp\left(mH/T\right) + \exp\left(-mH/T\right)\right]$$

For $mH >> \varepsilon$

$$Z \approx 4 + \exp\left(mH/T\right) + \exp\left(-mH/T\right)$$

$$p_d = \frac{4}{4 + \exp\left(mH/T\right) + \exp\left(-mH/T\right)} \to \begin{array}{c} 2/3 + O\left(H^2/T^2\right), \ T >> H \\ 4\exp\left(-mH/T\right), \ T << H \end{array}$$
$$p_u = \frac{\exp\left(mH/T\right) + \exp\left(-mH/T\right)}{4 + \exp\left(mH/T\right) + \exp\left(-mH/T\right)} \to \begin{array}{c} 1/3 + O\left(H^2/T^2\right), \quad T >> H \\ 1 - 4\exp\left(-mH/T\right), \ T << H \end{array}$$

In the zero-field limit

$$Z = 2\left[2 + \exp\left(-\varepsilon/T\right)\right]\left[1 + \frac{\exp\left(-\varepsilon/T\right)\left(mH/T\right)^2}{2\left[2 + \exp\left(-\varepsilon/T\right)\right]}\right]$$

(b) Free energy

$$F = -T\log Z = -T\log\left[2 + \exp\left(-\varepsilon/T\right)\right]$$

Entropy

$$S = -\partial F/\partial T = \log\left[2 + \exp\left(-\varepsilon/T\right)\right] + \frac{\varepsilon\exp\left(-\varepsilon/T\right)}{T\left[2 + \exp\left(-\varepsilon/T\right)\right]}$$
$$\to \begin{array}{cc} \log 3 + O\left(\varepsilon^2/T^2\right), & T >> \varepsilon \\ \log 2 + \left(\varepsilon/2T\right)\exp\left(-\varepsilon/T\right), & T << \varepsilon \end{array}$$

Notice that the ground state is doubly degenerate, along x and y, resulting in $\log 2$.

(c) Energy

$$E = F + TS = \frac{\varepsilon\exp\left(-\varepsilon/T\right)}{2 + \exp\left(-\varepsilon/T\right)} \to \begin{array}{c} \left(\varepsilon/3\right)\left(1 - 4\varepsilon/3T\right), \ T >> \varepsilon \\ \left(\varepsilon/2\right)\exp\left(-\varepsilon/T\right), \ T << \varepsilon \end{array}$$

(d) Specific heat

$$C = \frac{\partial E}{\partial T} = \frac{2\varepsilon^2}{T^2}\frac{\exp\left(-\varepsilon/T\right)}{\left[2 + \exp\left(-\varepsilon/T\right)\right]^2} \to \begin{array}{cc} 2\varepsilon^2/9T^2, & T >> \varepsilon \\ \left(\varepsilon^2/2T^2\right)\exp\left(-\varepsilon/T\right), & T << \varepsilon \end{array}$$

Magnetic correction to the free energy

$$\triangle F = -T\log\left[1 + \frac{\exp\left(-\varepsilon/T\right)\left(mH/T\right)^2}{2\left[2 + \exp\left(-\varepsilon/T\right)\right]}\right] \approx -T\frac{\exp\left(-\varepsilon/T\right)\left(mH/T\right)^2}{2\left[2 + \exp\left(-\varepsilon/T\right)\right]}$$

and magnetic susceptibility

$$\chi = -\frac{\partial^2 \triangle F}{\partial H^2} = \frac{\exp\left(-\varepsilon/T\right)m^2}{T\left[2 + \exp\left(-\varepsilon/T\right)\right]} \to \begin{array}{cc} m^2/3T\left(1 - \varepsilon/3T\right), & T >> \varepsilon \\ \left(m^2/2T\right)\exp\left(-\varepsilon/T\right), & T << \varepsilon \end{array}$$