# Suspensions and polymer solutions

## Solution of Exercise 2

1. When the molecule's dipole $\vec{\mu}$ makes an angle $\theta$ with the external field $\vec{E}$, its energy of interaction with the field is $H = -\vec{\mu}\cdot\vec{E} = -\mu E\cos\theta$. The partition function of the molecule is obtained by integrating $e^{-\beta H}$ over all possible solid angles $\Omega = (\theta, \varphi)$ between $\vec{\mu}$ and $\vec{E}$,

   $$Z = \int d\Omega e^{-\beta H} = \int_0^{2\pi} d\varphi \int_{-1}^{1} d(\cos\theta) e^{\beta\mu E\cos\theta} = 4\pi\frac{\sinh(\beta\mu E)}{\beta\mu E}. \tag{1}$$

   We can continue using this exact expression or, since we are only after the linear response, examine just the leading terms in $\beta\mu E$,

   $$Z \simeq 4\pi\left[1 + \frac{1}{6}(\beta\mu E)^2\right]. \tag{2}$$

   The free energy of the molecule is

   $$F = -k_{\mathrm{B}}T\ln Z \simeq -k_{\mathrm{B}}T\left[\ln(4\pi) + \frac{1}{6}(\beta\mu E)^2\right] = -\frac{\mu^2}{6k_{\mathrm{B}}T}E^2 + \mathrm{const.} \tag{3}$$

   By definition, the induced dipole satisfies $dF = -\vec{\mu}^{\mathrm{ind}}\cdot d\vec{E}$. Therefore, $\vec{\mu}^{\mathrm{ind}} = -(\partial F/\partial E)\hat{E}$, from which we find $\vec{\mu}^{\mathrm{ind}} = \alpha\vec{E}$, with

   $$\alpha = \frac{\mu^2}{3k_{\mathrm{B}}T}. \tag{4}$$

   Alternatively, since we know that in this simple case the induced dipole is parallel to $\vec{E}$, we could find it by averaging, $\mu^{\mathrm{ind}} = \langle\vec{\mu}\cdot\hat{E}\rangle = \mu\langle\cos\theta\rangle$.

2. (a) As we did in the class, assuming pairwise additivity, the interaction between the molecule and the bulk is calculated by integrating the van der Waals pair potential over layers of the bulk and over concentric rings within each layer:

   $$F(h) = \int_h^\infty dx \int_0^\infty dR 2\pi Rc\left[-\frac{C}{(x^2+R^2)^3}\right] = -\frac{\pi Cc}{6}\frac{1}{h^3}, \tag{5}$$

   where $c$ is the concentration (number density) of water molecules, $c = (1/18)6.0\times10^{23} = 3.3\times10^{22}$ molecules/cm$^3$.

   (b) From Eq. (5) we get

   $$h = \left(\frac{\pi Cc}{6k_{\mathrm{B}}T}\right)^{1/3}. \tag{6}$$

   Substituting all the values gives $h \simeq 4\times10^{-8}$ cm = 4 Å. This is the typical height to which water molecules will be "kicked" by thermal noise, i.e., the typical width of the water-air interface. We obtain, therefore, that this interfacial width is of a molecular scale (a few Å).