Dipole-Dipole Interactions

If a material consists of polar molecules that are not rigidly bound in a crystal lattice, often the strongest intermolecular forces come from a dipole-dipole interaction between the electric dipoles present in the molecules themselves. Suppose the material we are working with has n molecules per unit volume, with permanent electric dipoles of strength p, has permittivity ϵ and is at temperature T.

Consider two such molecules in the material a distance r apart. Assume that the molecules (i.e., dipoles) are perfectly free to rotate. As you will find shortly, the partition function does not have an elegant exact expression. Since we often come across systems we'd like to study that have this problem, we can use a high temperature perturbation technique to roughly compute the partition function about $T = \infty$, by writing Z as a Taylor series:

$$Z = \sum_{k=0}^{\infty} Z_k \beta^k.$$

(a) Show that, if a system has Hamiltonian H,

$$Z_k = \frac{1}{k!} \int \mathrm{d}\Gamma \; H^k.$$

(b) Apply this perturbation theory technique to the problem of the interacting dipoles, and show that, to lowest non-trivial order, the interaction energy between the two dipoles is given by

$$U_{\mathrm{dd}}(r) = -\frac{p^2}{48\pi^2\epsilon^2 k_{\mathrm{B}} T r^6}.$$

Now, suppose we have very large slabs of this material, separated by a distance d, which is much smaller than the thickness of either slab in any direction. We know that the total interaction energy of this system is given by integrating over the interactions between each point in the materials (in the continuum limit)

$$U = \frac{1}{2} \int n^2 U_{\mathrm{dd}}(|\mathbf{r}_1 - \mathbf{r}_2|) \mathrm{d}^3\mathbf{r}_1 \mathrm{d}^3\mathbf{r}_2.$$

(c) Show that there is an attractive pressure between the two plates, given approximately by

$$P = \frac{n^2 p^2}{576\pi^2\epsilon^2 k_{\mathrm{B}} T d^3}.$$

Since P decays only as d^{-3}, we see that for bulk materials these interactions can be quite a bit stronger. Indeed, intermolecular forces such as these are strong enough to allow insects to walk on walls and other objects.