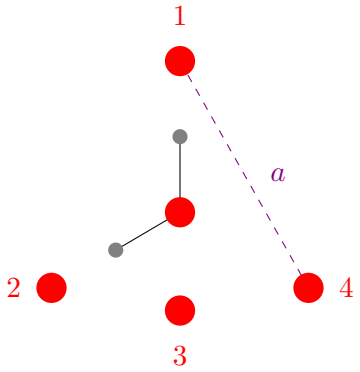
Oil-Water Interface

Oil(s) are **hydrophobic** liquids, meaning that they do not dissolve (well) in water (H_2O). The origin of hydrophobic behavior is molecular, and has to do with the fact that the presence of a nonpolar molecule means that, roughly speaking, water molecules do not have as many favorable orientations in which they can form hydrogen bonds. In this problem, we will consider a simple model for this effect.



Roughly speaking, we can imagine that water molecules in the liquid phase form a loose "lattice" as follows: consider a water molecule at the center of a tetrahedron with side lengths approximately $a \approx 1$ nm. There is also a water molecule at each corner of the tetrahedron. This model was first considered by Linus Pauling as a way to model the structure of ice.

(a) Argue that length scale of the lattice is reasonable. Note that water (and ice) has a density about 10^3 kg/m^3 at reasonable temperatures, and that the mass of the proton/neutron is about 2×10^{-27} kg.

Now, water will like to hydrogen bond with the other molecules. Crudely, we can model this as follows. In the above picture, we showed the hydrogens on the water are facing the water molecules at the corners of the tetrahedron. Let W be the number of configurations of the water molecule, assuming that a configuration of the central molecule corresponds to a way of assigning the hydrogens of this central molecule to a neighboring water molecule, which they may hydrogen bond with. For example, we could say that we hydrogen bond with neighbors 1 and 2, as depicted in the above figure.

When we add a hydrophobic molecule, we approximate that what that does to the central water molecule is remove the possibility for hydrogen bonding with a neighboring atom: e.g., hydrogen bonding with molecule 4 is no longer possible. Let W' be the number of ways to hydrogen bond, i.e. configurations of the water molecule, in this case.

(b) In terms of W, W', and $k_B T$, what is the free energy cost of adding the hydrophobic molecule, assuming that only our central water molecule is affected by its presence? Find the numerical values for W and W', and then plug in for $k_B T \approx 4 \times 10^{-21}$ J: what is your final answer?

Now, let us suppose that we have a solid interface between oil and water of area A, which is very large compared to molecular scales, which is hydrophobic for the reasons described above. The **surface tension** γ of the interface is defined by

$$\gamma \equiv \frac{F}{A},$$

where F Is the free energy cost, to the water molecules, of losing the ability to hydrogen bond.

(c) Typical surface tensions are about $\gamma \approx 0.05$ N/m, for such an interface. Explain why this scale makes sense.

Now, is this interface stable? To answer this, let us ask how many oil molecules we expect to dissolve into the water. Suppose that the volume of the water is V. You can estimate that each oil molecule is approximately a sphere of radius $r \approx 5$ nm, and make any other reasonable approximations.

(d) Estimate the probability for a *single oil molecule* to break free. First find a theoretical expression in terms of V, r, γ and $k_{\mathrm{B}}T$ (you may neglect O(1) factors so long as they are negligible!), and then examine it (you won't know the value V, but be reasonable!). Comment on what you find, and discuss the stability of the oil-water interface.

(e) How does your answer to the previous part depend on the size of the molecule? What does this suggest about hydrophobicity?

(f) If you pour some olive oil in water and stir it around, it will quickly form into many small droplets on the surface of the water. However, once you stop, the large droplets will settle to the surface and sit there. Argue that it is incredibly favorable for the olive oil to condense into a single layer on the surface. Compare these two thoughts: are they contradictory?