Notes

Notes on the Units for Polarizability

Bilin Zhuang*
Harvey Mudd College
(Dated: February 20, 2025)

This notes explore the units and the magnitudes of numerical quantities used in the polarizability calculation.

I. WATER

Let us first take a look at water's polarizability and its corresponding index of refraction. This would help us to get a sense of the magnitudes of the quantities in the different units.

A. CGS unit

Water polarizability is $\alpha = 1.45$ Å$^3 = 1.45 \times 10^{-24}$ cm^3 expressed in the cgs unit.

To calculate the index of refraction, we can use the Lorentz-Lorenz relation in cgs unit given by

$$\alpha = \frac{3}{4\pi n}\left(\frac{\eta^2 - 1}{\eta^2 + 2}\right) \tag{1}$$

where η is the index of refraction and n is the number density of the water molecule. Rearranging the equation gives

$$\begin{aligned} \frac{4\pi n\alpha}{3} &= \left(\frac{\eta^2 - 1}{\eta^2 + 2}\right) \\ \gamma &= \left(\frac{\eta^2 - 1}{\eta^2 + 2}\right) \\ \gamma\eta^2 + 2\gamma &= \eta^2 - 1 \\ 2\gamma + 1 &= (1-\gamma)\eta^2 \\ \eta &= \sqrt{\frac{1+2\gamma}{1-\gamma}} \end{aligned} \tag{2}$$

where we have set $\gamma = \frac{4\pi n\alpha}{3}$ in the second equality.

Water's density at room temperature is 0.997 g/cm^3 and its molar mass is 18.01528 g/mol. The number density can be worked out as

$$n = \frac{(0.997\ \text{g/cm}^3)\left(\frac{1\ \text{cm}^3}{10^{24}\ \text{Å}^3}\right)}{(18.01528\ \text{g/mol})\left(\frac{1\ \text{mol}}{6.02\ \times 10^{23}\ \text{molecules}}\right)}$$

* bzhuang@hmc.edu

$$= 0.03332 \text{ Å}^{-3} \tag{3}$$

Substituting the various values into Eq. (2), we have the following value for refractive index of water

$$\begin{aligned} \gamma &= \frac{4\pi n\alpha}{3} = \frac{4\pi(0.03332 \text{ Å}^{-3})(1.45 \text{ Å}^{3})}{3} = 0.2024 \\ \eta &= \sqrt{\frac{1+2\times 0.2024}{1-0.2024}} = 1.327 \end{aligned} \tag{4}$$

which is consistent with water's measured refractive index at 1.33 at 20°C.

Note that the optical dielectric constant (the part of the dielectric constant due to polarizability) is given by $\varepsilon = n^2$.

II. LAMMPS CALCULATION UNIT

We run the simulations in Lennard-Jones Units in LAMMPS. The Lennard-Jones Units is defined by Lennard-Jones length σ and Lennard-Jones energy ϵ.

There is no other length unit in the LAMMPS calculation. So the polarizability must have been in units of σ^3.

Currently, we have $n = \frac{900}{11^3\sigma^3}$ and $\alpha = 1.5\sigma^3$. That would make $\gamma > 1$, possibly this is too large. (Is it because of this that our Drude electrons are flying away?)

III. REASONABLE VALUE TO USE FOR WATER?

Let's try to come up with a set of parameters to use for water based on the SWM4-NDP model of water. In that model, $\sigma = 3.18395 \text{ Å}^3$. Therefore, the polarizability is $\alpha = 1.45 \text{ Å}^3 = 0.0449\sigma^3$. Water's density is 0.03332 Å^{-3}, that is a density of $n = 1.0755\sigma^{-3}$ in Lennard Jones Units.

In the SWM4-NDP model, we also have the energy unit $\epsilon = 0.21094$ kcal/mol $= 1.466 \times 10^{-21}$ J/molecule, so the temperature unit is $\epsilon/k_B = 106.2$ K. That is to say, if we want to simulate a temperature at 300 K, it is 2.823 ϵ/k_B as temperature in Lennard-Jones units. Similarly, for the Drude oscillator at 1 K, it is 0.009413 ϵ/k_B as temperature in Lennard-Jones units.