Notes

Notes on the Units for Polarizability

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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

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

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

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

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$$= 0.03332 \text{ Å}^{-3} \tag{3}$$

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?

A. Length and density

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, $\sigma = 3.18395$ Å. 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.

B. Energy and temperature

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 $2.823\ \epsilon/k_B$ as temperature in Lennard-Jones units. Similarly, for the Drude oscillator at 1 K, it is $0.009413\ \epsilon/k_B$ as temperature in Lennard-Jones units.

C. Time

The dimension of energy is

$$[\text{energy}] = [\text{mass}][\text{length}]^2[\text{time}]^{-2} \tag{5}$$

so the unit of time (let us denote it by τ) in LAMMPS is given by

$$\tau = \left(\frac{m\sigma^2}{\epsilon}\right)^{\frac{1}{2}} \tag{6}$$

where the mass m is the mass of the particle.

If we convert this to the SI unit, this is

$$\begin{aligned}
\tau &= \left(\frac{m\sigma^2}{\epsilon}\right)^{\frac{1}{2}} \\
&= \left(\frac{(18 \times 1.66 \times 10^{-27}\ \text{kg/molecule})(3.18395\ \times 10^{-10}\text{m})^2}{1.466 \times 10^{-21}\ \text{J/molecule}}\right)^{\frac{1}{2}} \\
&= 1.437 \times 10^{-12}\ \text{s}
\end{aligned} \tag{7}$$

In the Langevin integrator, the damping coefficient is approximately $1/(10\ \text{ps}^{-1})$. We can convert that to the LJ unit as follows:

$$\frac{1}{(10\ \text{ps}^{-1})} = \frac{1}{(10\ \text{ps}^{-1})}\frac{1\ \text{s}}{10^{12}\text{ps}}\frac{\tau}{1.437 \times 10^{-12}\ \text{s}} \approx 0.1\tau \tag{8}$$